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Configuration Partition Functions for Vinyl Polymers Containing Articulated Side Chains with Threefold Rotational Potentials

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ABSTRACT: The configuration partition function, Z, for vinyl polymers containing articulated side chains with threefold rotational potentials has been evaluated using rotational isomeric state theory in the form appropriate for branched molecules. Of particular interest is the form adopted by Z when it is to be utilized for the computation of an average property of the main chain, such as its mean-square unperturbed end-to-end distance, $\langle r^2\rangle_0$, or the average end-to-end vector, $\langle \mathbf{r}\rangle$. The second and succeeding atoms of the articulated side chain then give rise to five factors which appear in seven of the nine elements in statistical weight matrices for alternate bonds of the main chain. Precise definitions of these factors are presented for articulated side chains containing two or three bonds, threefold rotational potentials being assumed. Their effect on the conformations adopted by bonds in the main chain, on $\langle r^2\rangle_0$, and on d ln $\langle r^2\rangle_0/dT$ is evaluated.

Configuration-dependent properties for a variety of linear chain molecules can be successfully treated using matrix methods.[1,2] Among such properties is the mean-square unperturbed end-to-end distance, $\langle r^2\rangle_0$. The presence of unarticulated side chains in a polymer affects the computation of $\langle r^2\rangle_0$ through straightforward modifications of the statistical weight matrices associated with bonds in the main chain. A more complex situation arises if the side chains are articulated, since their interaction with the main chain will now depend on the conformations which they and the main chain adopt. For example, it becomes difficult to accommodate an articulated side chain if the main chain bonds flanking its point of attachment to the backbone both occupy trans states.[1,3] Recognition of this effect prompted Flory and co-workers[1,3] to incorporate a factor τ^* in the statistical weight for the tt sequence, with the expectation that $\tau^* < 1$. In general, each element in the statistical weight matrix for the main chain bond following the point of side chain attachment should be multiplied by a factor which arises from the configuration partition function for the side chain.[4]

The present approach to polymers containing articulated side chains is to view them as combs, in which comparatively short branches are attached to a main chain at regular intervals. The configuration partition function, Z, for any branched molecule can be rigorously evaluated in the rotational isomeric state approximation through the definition of a rectangular statistical weight matrix for use at each branch point and application of the direct product.[5] Branching may be of virtually any desired complexity. Exact expressions for the computation of a variety of configuration-dependent properties can be formulated.[6] In the case of the mean-square unperturbed radius of gyration, such expressions have been applied to molecules containing one[7] or two[8,9] trifunctional branch points. The necessary expressions for a comb containing the number of branch points currently of interest would be prohibitively cumbersome. The complexity of the calculation can be reduced remarkably if the objective is to simply compute $\langle r^2\rangle_0$ for the main chain. Simplifications in the expression for Z can now be achieved with absolutely no sacrifice in rigor. The final expressions reduce exactly to those developed by Flory and co-workers[3,10] under special circumstances. Equivalence for the two treatments in all cases can be achieved by the introduction of four factors into the statistical weight matrices used by Flory et al.[3] and an appropriate definition for their τ^*. The present treatment resembles that developed by Abe[4] in the introduction of such factors, but their number and general definition differs. Circumstances under which the four factors and the definition for τ^* may become important are explored.

Side Chains Containing Two Bonds. Treatment as Meso and Racemic Dyads

The main chain and articulated side chains for a polymer prepared from x molecules of a vinyl derivative are shown in Figure 1. This molecule contains $x - 1$ trifunctional branch points and $2x - 1$ branches. Branches are numbered so that the main chain consists of the odd-numbered branches. Even-numbered branches contain two bonds and have the configuration which yields an isotactic polymer. Application of the procedures described for branched molecules[5] permits the configuration partition function to be written as

$$Z = {}_1\mathbf{U}_1({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1)({}_2\mathbf{U}_2 \otimes {}_3\mathbf{U}_2)({}_4\mathbf{U}_1 \ominus {}_5\mathbf{U}_1)({}_4\mathbf{U}_2 \otimes {}_5\mathbf{U}_2)\ldots$$
$$({}_{2x-2}\mathbf{U}_1 \ominus {}_{2x-1}\mathbf{U}_1)({}_{2x-2}\mathbf{U}_2 \otimes {}_{2x-1}\mathbf{U}_2)({}_{2x-1}\mathbf{U}_3)({}_{2x-1}\mathbf{U}_4) \quad (1)$$

where ${}_j\mathbf{U}_i$ is the statistical weight matrix for the ith bond in branch j, $\otimes$ denotes the direct product, and ${}_j\mathbf{U}_1 \ominus {}_{j+1}\mathbf{U}_1$ is the rectangular matrix assembled according to the procedures defined in ref 5.

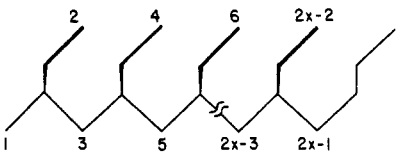

Figure 1. Diagrammatic representation of an isotactic vinyl polymer in which the side chains contain two bonds. The main chain consists of the odd-numbered branches and contains no unsaturated bonds as drawn.

Specification of the composition of the statistical weight matrices for a vinyl polymer of any conceivable tacticity may be accomplished either in terms of meso and racemic dyads or in terms of *d* and *l* centers. Present development utilizes the meso and racemic dyads. The pertinent rotational states for the bonds in the main chain are denoted by t, g, and $\bar{g}$.[10] They have been defined previously.[10] Corresponding matrices for a treatment as *d* and *l* centers will be given following the present development.

First-order interactions arising from rotation about the bonds in branches 3, 5, . . ., $2x - 3$ and the first bond in branch $2x - 1$ are given by diag $(\eta, 1, \tau)$.[3,10] Order of presentation is for states t, g, and $\bar{g}$. Here η compares the first-order interaction between the first atom in a side chain and a main chain atom with the first-order interaction between two main chain atoms. The factor τ arises when a main chain atom participates in simultaneous first-order interactions with another main chain atom and the first atom in a side chain. First-order interactions arising from threefold rotation about the first bond in a side chain are given by diag $(1, 1, \tau_1)$. The order of presentation is for states t, g, and $\bar{g}$, with $\bar{g}$ being the state which causes the final atom in the side chain to participate in simultaneous first-order interactions with two main chain atoms. Atom ${}_{j-1}A_2$ and the atoms in side chain *j* are planar trans when the first bond in branch *j* is in state t.

Second-order interactions are denoted by ω. At times we shall make distinctions between five different ω. Location of the atoms which participate in these interactions are: ω, both atoms in main chain; ω_1, atom in the main chain and first atom in a side chain (ω' of Flory et al.[10]); ω_2, first atoms in adjacent side chains (ω'' of Flory et al.[10]); ω_3, atom in main chain and second atom in a side chain; ω_4, atom in main chain and third atom in a side chain.

Statistical weight matrices can now be assembled in a straightforward manner. Columns are indexed by t, g, $\bar{g}$ when there are three and tt, tg, t$\bar{g}$, gt, gg, g$\bar{g}$, $\bar{g}$t, $\bar{g}$g, $\bar{g}\bar{g}$ when there are nine. Rows correspond to t, g, $\bar{g}$ for the preceeding bond.

$$ {}_1\mathbf{U}_1 = [1] \tag{2} $$

$$ {}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1 = [\eta\omega_3 \quad 1 \quad \tau \quad \eta \quad 1 \quad \tau \quad \eta\tau_1 \quad \tau_1 \quad \tau\tau_1\omega_3] \tag{3} $$

$$ ({}_3\mathbf{U}_2)_m = ({}_5\mathbf{U}_2)_m = \ldots = ({}_{2x-3}\mathbf{U}_2)_m = \begin{bmatrix} \eta\omega_2 & 1 & \tau\omega_1 \\ \eta & \omega & \tau\omega_1 \\ \eta\omega_1 & \omega_1 & \tau\omega\omega_2 \end{bmatrix} \tag{4} $$

$$ ({}_3\mathbf{U}_2)_r = ({}_5\mathbf{U}_2)_r = \ldots = ({}_{2x-3}\mathbf{U}_2)_r = \begin{bmatrix} \eta & \omega_1 & \tau\omega_2 \\ \eta\omega_1 & 1 & \tau\omega \\ \eta\omega_2 & \sigma & \tau\omega_1{}^2 \end{bmatrix} \tag{5} $$

$$ {}_4\mathbf{U}_1 \ominus {}_5\mathbf{U}_1 = {}_6\mathbf{U}_1 \ominus {}_7\mathbf{U}_1 = \ldots = {}_{2x-2}\mathbf{U}_1 \ominus {}_{2x-1}\mathbf{U}_1 $$

$$ = \begin{bmatrix} \eta\omega_3 & 1 & \tau & \eta\omega_3 & \omega_3 & \tau\omega_3 & \eta\tau_1 & \tau_1 & \tau\tau_1\omega_3 \\ \eta\omega_3 & \omega & \tau & \eta & \omega & \tau & \eta\tau_1 & \tau_1 & \tau\tau_1\omega_3 \\ \eta\omega_3 & 1 & \tau\omega & \eta & 1 & \tau\omega & \eta\tau_1\omega & \tau_1\omega_3 & \tau\tau_1\omega\omega_3{}^2 \end{bmatrix} \tag{6} $$

$$ {}_2\mathbf{U}_2 = {}_4\mathbf{U}_2 = \ldots = {}_{2x-2}\mathbf{U}_2 = {}_{2x-1}\mathbf{U}_4 = \text{col}\,(1, 1, 1) \tag{7} $$

$$ {}_{2x-1}\mathbf{U}_2 = \begin{bmatrix} 1 & \sigma & \sigma\omega_1 \\ 1 & \sigma\omega & \sigma \\ 1 & \sigma\omega_1 & \sigma\omega \end{bmatrix} \tag{8} $$

$$ {}_{2x-1}\mathbf{U}_3 = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma\omega & \sigma \\ 1 & \sigma & \sigma\omega \end{bmatrix} \tag{9} $$

The expression in eq 2 denotes a matrix whose sole element is unity. Subscripts *m* and *r* in eq 4 and 5 refer to meso and racemic dyads. These statistical weight matrices are identical with $\mathbf{U}''_m$ and $\mathbf{U}''_r$ respectively of Flory and co-workers.[10] States for the second and third bonds in branch $2x - 1$ are defined by an imaginary meso side chain attached to atom ${}_{2x-1}A_2$.

It is of interest to consider the products ${}_j\mathbf{U}'_m$ and ${}_j\mathbf{U}'_r$, defined as

$$ {}_j\mathbf{U}'_m = ({}_j\mathbf{U}_1 \ominus {}_{j+1}\mathbf{U}_1)({}_j\mathbf{U}_2 \otimes {}_{j+1}\mathbf{U}_2)_m \qquad j = 4, 6, \ldots, 2x - 4 \tag{10} $$

and

$$ {}_j\mathbf{U}'_r = ({}_j\mathbf{U}_1 \ominus {}_{j+1}\mathbf{U}_1)({}_j\mathbf{U}_2 \otimes {}_{j+1}\mathbf{U}_2)_r \qquad j = 4, 6, \ldots, 2x - 4 \tag{11} $$

Dimensions for the two matrices on the right-hand side of eq 10 and 11 are 3×9 and 9×3, causing ${}_j\mathbf{U}'_m$ and ${}_j\mathbf{U}'_r$ to each be 3×3. For a vinyl polymer with a high degree of polymerization, the dominant contribution to *Z* will arise from ${}_j\mathbf{U}'_m$ and ${}_j\mathbf{U}'_r$. For ${}_j\mathbf{U}'_m$ we obtain eq 12,

$$ {}_j\mathbf{U}'_m{}^{\mathrm{C}} = \begin{bmatrix} \eta[\eta\omega_2(\tau_1 + 2\omega_3) + 1 + \tau_1 + \omega_3 + \tau\omega_1 \times (1 + \omega_3 + \tau_1\omega_3)] \\ \eta(\tau_1 + 2\omega_3) + \omega(1 + \tau_1 + \omega_3) + \tau\omega_1 \times (1 + \omega_3 + \tau_1\omega_3) \\ \tau[\eta\omega_1(\tau_1 + 2\omega_3) + \omega_1(1 + \tau_1 + \omega_3) + \tau\omega\omega_2(1 + \omega_3 + \tau_1\omega_3)] \\ \eta[\eta\omega_2(1 + \tau_1 + \omega_3) + \omega(2 + \tau_1) + \tau\omega_1 \times (2 + \tau_1\omega_3)] \\ \eta(1 + \tau_1 + \omega_3) + \omega^2(2 + \tau_1) + \tau\omega_1 \times (2 + \tau_1\omega_3) \\ \tau[\eta\omega_1(1 + \tau_1 + \omega_3) + \omega\omega_1(2 + \tau_1) + \tau\omega\omega_2(2 + \tau_1\omega_3)] \\ \eta[\eta\omega_2(1 + \omega_3 + \tau_1\omega_3) + 2 + \tau_1\omega_3 + \tau\omega\omega_1(2 + \tau_1\omega_3{}^2)] \\ \eta(1 + \omega_3 + \tau_1\omega_3) + \omega(2 + \tau_1\omega_3) + \tau\omega\omega_1 \times (2 + \tau_1\omega_3{}^2) \\ \tau[\eta\omega_1(1 + \omega_3 + \tau_1\omega_3) + \omega_1(2 + \tau_1\omega_3) + \tau\omega^2\omega_2(2 + \tau_1\omega_3{}^2)] \end{bmatrix} \tag{12} $$

where the presentation is as a column composed of the elements of ${}_j\mathbf{U}'_m$ arranged in "reading order".

Notation is simplified through multiplication of this column by $(1 + \tau_1 + \omega_3)^{-1}$ and resort to the following definitions:

$$ \tau^* = (\tau_1 + 2\omega_3)(1 + \tau_1 + \omega_3)^{-1} \tag{13} $$

$$ f_1 = (1 + \omega_3 + \tau_1\omega_3)(1 + \tau_1 + \omega_3)^{-1} \tag{14} $$

$$ f_2 = (2 + \tau_1\omega_3)(1 + \tau_1 + \omega_3)^{-1} \tag{15} $$

$$ f_3 = (2 + \tau_1)(1 + \tau_1 + \omega_3)^{-1} = 2 - \tau^* \tag{16} $$

Table I
Range for τ^* and the f_i

Factor	Range $0 < \tau_1, 0 < \omega_3$	Range $0 < \tau_1 < 1$, $0 < \omega_3 < 1$	Limit $\tau_1 \to 0$	Limit $\omega_3 \to 0$	Limit $\tau_1 \to 0, \omega_3 \to 0$
τ^*	$0 < \tau^* < 2$	$0 < \tau^* < 1$	$2\omega_3(1+\omega_3)^{-1}$	$\tau_1(1+\tau_1)^{-1}$	0
f_1	$0 < f_1$	$\frac{1}{2} < f_1 < 1$	1	$(1+\tau_1)^{-1}$	1
f_2	$0 < f_2$	$1 < f_2 < 2$	$2(1+\omega_3)^{-1}$	$2(1+\tau_1)^{-1}$	2
f_3	$0 < f_3 < 2$	$1 < f_3 < 2$	$2(1+\omega_3)^{-1}$	$(2+\tau_1)(1+\tau_1)^{-1}$	2
f_4	$0 < f_4$	$1 < f_4 < 2$	$2(1+\omega_3)^{-1}$	$2(1+\tau_1)^{-1}$	2

$$f_4 = (2 + \tau_1\omega_3^2)(1 + \tau_1 + \omega_3)^{-1} \quad (17)$$

Numerical values for τ^* and the f_i so defined are determined solely by the interaction of the second atom in the side chain with atoms in the main chain. The f_i and τ^* are unity if $\omega_3 = 1$, i.e., if the second-order interaction between the main chain and the second atom in the side chain is negligible. The column in eq 12 can now be written as eq 18.

$$ {}_j\mathbf{U}'_m{}^{\mathrm{C}} = \begin{bmatrix} \eta(\eta\tau^*\omega_2 + 1 + \tau\omega_1 f_1) \\ \eta\tau^* + \omega + \tau\omega_1 f_1 \\ \tau(\eta\tau^*\omega_1 + \omega_1 + \tau\omega\omega_2 f_1) \\ \eta[\eta\omega_2 + \omega(2-\tau^*) + \tau\omega_1 f_2] \\ \eta + \omega^2(2-\tau^*) + \tau\omega_1 f_2 \\ \tau[\eta\omega_1 + \omega\omega_1(2-\tau^*) + \tau\omega\omega_2 f_2] \\ \eta(\eta\omega_2 f_1 + f_2 + \tau\omega\omega_1 f_4) \\ \eta f_1 + \omega f_2 + \tau\omega\omega_1 f_4 \\ \tau(\eta\omega_1 f_1 + \omega_1 f_2 + \tau\omega^2\omega_2 f_4) \end{bmatrix} \quad (18)$$

The matrix represented as a column in eq 18 can be generated identically as

$$ {}_j\mathbf{U}'_m = \begin{bmatrix} \eta\tau^* & 1 & \tau f_1 \\ \eta & \omega(2-\tau^*) & \tau f_2 \\ \eta f_1 & f_2 & \tau\omega f_4 \end{bmatrix} \begin{bmatrix} \eta\omega_2 & 1 & \tau\omega_1 \\ \eta & \omega & \tau\omega_1 \\ \eta\omega_1 & \omega_1 & \tau\omega\omega_2 \end{bmatrix} \quad (19)$$

where the terminal statistical weight matrix is identical with the $\mathbf{U}''_m$ of Flory et al.[10] Its predecessor in eq 19 differs from their $\mathbf{U}'$ in the appearance of $\tau^*, f_1, f_2, f_3 = 2 - \tau^*$, and f_4. An additional trivial difference is the appearance of ω in the 2,2 and 3,3 elements, which arises simply because Flory et al.[10] confined their attention to cases where these conformations for the bond pair occur to a negligible extent.

Equivalent treatment of ${}_j\mathbf{U}'_r$ yields

$$ {}_j\mathbf{U}'_r = \begin{bmatrix} \eta\tau^* & 1 & \tau f_1 \\ \eta & \omega(2-\tau^*) & \tau f_2 \\ \eta f_1 & f_2 & \tau\omega f_4 \end{bmatrix} \begin{bmatrix} \eta & \omega_1 & \tau\omega_2 \\ \eta\omega_1 & 1 & \tau\omega \\ \eta\omega_2 & \omega & \tau\omega_1{}^2 \end{bmatrix} \quad (20)$$

where the terminal statistical weight matrix is identical with Flory's $\mathbf{U}''_r$. It is preceeded by the same statistical weight matrix used before $\mathbf{U}''_m$ to generate ${}_j\mathbf{U}'_m$.

Clearly the present treatment of vinyl polymers containing articulated side chains with threefold rotational potentials reduces to that proposed by Flory and co-workers[10] when τ^* and the f_i are unity. A value of 1 for the statistical weight ω_3 is the necessary condition. For most polymers containing articulated side chains we anticipate that $\omega_3 \neq 1$ and $\tau^* \neq 1$. Under such circumstances the leading statistical weight matrix in eq 19 and 20 is different from $\mathbf{U}'$.

Third-order interactions are inevitable whenever the main chain bond pair flanking the point of side chain attachment occupies the gg or $\bar{g}\bar{g}$ states.[10] Such states are suppressed by assigning null values to the 2,2 and 3,3 elements in the leading statistical weight matrix used to generate ${}_j\mathbf{U}'_m$ and ${}_j\mathbf{U}'_r$.[10] This assignment would eliminate $f_3 = 2 - \tau^*$ and f_4 from the expression for Z. The factors τ^*, f_1, and f_2 would remain.

Side Chains Containing Two Bonds. Treatment as *d* and *l* Centers

An equivalent development is possible using t, g^+, and g^- rotational states and considering the point of side chain attachment to constitute a *d* or *l* center. Final expressions are eq 21–24.

$$ {}_j\mathbf{U}'_{dd} = \begin{bmatrix} \eta\tau^* & 1 & \tau f_1 \\ \eta f_1 & f_2 & \tau\omega f_4 \\ \eta & \omega(2-\tau^*) & \tau f_2 \end{bmatrix} \begin{bmatrix} \eta\omega_2 & \tau\omega_1 & 1 \\ \eta & \tau\omega_1 & \omega \\ \eta\omega_1 & \tau\omega\omega_2 & \omega_1 \end{bmatrix} \quad (21)$$

$$ {}_j\mathbf{U}'_{dl} = \begin{bmatrix} \eta\tau^* & 1 & \tau f_1 \\ \eta f_1 & f_2 & \tau\omega f_4 \\ \eta & \omega(2-\tau^*) & \tau f_2 \end{bmatrix} \begin{bmatrix} \eta & \omega_1 & \tau\omega_2 \\ \eta\omega_1 & 1 & \tau\omega \\ \eta\omega_2 & \omega & \tau\omega_1{}^2 \end{bmatrix} \quad (22)$$

$$ {}_j\mathbf{U}'_{ld} = \begin{bmatrix} \eta\tau^* & \tau f_1 & 1 \\ \eta & \tau f_2 & \omega(2-\tau^*) \\ \eta f_1 & \tau\omega f_4 & f_2 \end{bmatrix} \begin{bmatrix} \eta & \tau\omega_2 & \omega_1 \\ \eta\omega_2 & \tau\omega_1{}^2 & \omega \\ \eta\omega_1 & \tau\omega & 1 \end{bmatrix} \quad (23)$$

$$ {}_j\mathbf{U}'_{ll} = \begin{bmatrix} \eta\tau^* & \tau f_1 & 1 \\ \eta & \tau f_2 & \omega(2-\tau^*) \\ \eta f_1 & \tau\omega f_4 & f_2 \end{bmatrix} \begin{bmatrix} \eta\omega_2 & 1 & \tau\omega_1 \\ \eta\omega_1 & \omega_1 & \tau\omega\omega_2 \\ \eta & \omega & \tau\omega_1 \end{bmatrix} \quad (24)$$

Leading statistical weight matrices differ from those presented by Flory and co-workers[1,3] only in the appearance of the f_i.

Behavior of τ^* and the f_i

The second atom in an articulated side chain affects the conformation of the main chain, and hence $\langle r^2 \rangle_0$, through τ^* and the f_i. It is of interest to determine the extent to which these factors might differ from unity.

Table I presents permissible ranges for τ^* and the f_i. The definition of τ^* in eq 13 yields $0 \leq \tau^* \leq 2$. The upper limit is attained when $\omega_3 \gg 1 + \tau_1$, while the lower limit corresponds to $1 \gg \tau_1 + 2\omega_3$. In those cases where $1 > \omega_3$, τ^* is also less than unity. In principal, the f_i might differ dramatically from unity. However, if attention is restricted to those circumstances for which τ_1 and ω_3 both lie between zero and unity, the f_i differ from unity by no more than a factor of 2.

Behavior of the f_i and τ^* when ω_3 is vanishingly small is summarized in Table I and depicted in Figure 2. In the region for which $0 < \tau_1 < 1$, it is apparent that $0 < \tau^* < f_1 < 1 < f_2 = f_4 < f_3 < 2$. Simpler behavior arises when τ_1 becomes vanishingly small, as summarized by Table I and depicted by the dashed lines in Figure 3. When $0 < \omega_3 < 1$ we find $0 < \tau^* < f_1 = 1 < f_2 = f_3 = f_4 < 2$. Figure 3 also demonstrates the behavior of τ^* and the f_i when τ_1 is 0.5. The following conclusions hold for the numerous polymers for which τ_1 and ω_3 lie between zero and unity: (1) τ^* and f_1 will be less than unity, with $\tau\text{¢}$

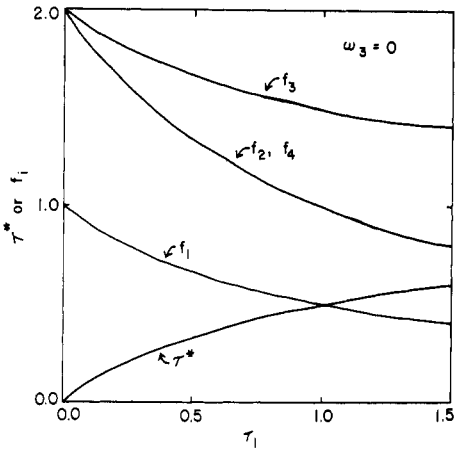

Figure 2. Dependence of τ^* and the f_i on τ_1 when $\omega_3 = 0$.

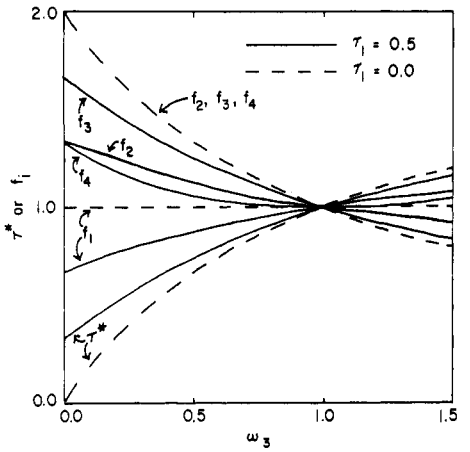

Figure 3. Dependence of τ^* and the f_i on ω_3 when τ_1 is 0 or 0.5.

being the smaller; (2) f_2, f_3, and f_4 will lie between unity and two (nearly equal values will be obtained for f_2 and f_4, while f_3 will tend to be somewhat larger); (3) ln τ^* will show a greater difference from zero than will any of the ln f_i. The final of the above conclusions suggests that τ^* will generally be the most important of the five factors.

Illustrative estimates of τ^* and the f_i for several side chains are presented in Table II.

The temperature dependence of τ^* and the f_i are summarized in Table III. In the likely event that τ_1 and ω_3 are both less than unity, d ln τ^*/d ln T will be positive while d ln f_2/d ln T and d ln f_3/d ln T will be negative. The remaining two derivatives may be either positive or negative for τ_1 and ω_3 in this range. They both become negative if either τ_1 or ω_3 is vanishingly small. Hence for many polymers containing articulated side chains the effect of temperature on the f_i will be in the opposite direction from its affect on τ^*. Temperature will generally have a greater effect on τ^* than on any of the f_i, as judged by the absolute value of the temperature coefficients. However, there is a small range of values for τ_1 and ω_3 which will yield $-$d ln f_4/dT > d ln τ^*/dT. Illustrative temperature coefficients are presented in Table IV.

Extension to Longer Side Chains. Side Chains with Three Bonds

The preceeding treatment is readily applied to longer side chains. Necessary procedures are illustrated by considering a molecule in which the side chain contains three bonds. Now

$$Z = {}_1\mathbf{U}_1({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1)[{}_2\mathbf{U}_2 \otimes ({}_3\mathbf{U}_2^{(2)})]({}_4\mathbf{U}_1 \ominus {}_5\mathbf{U}_1) \times [{}_4\mathbf{U}_2 \otimes ({}_5\mathbf{U}_2^{(2)})] \ldots ({}_{2x-2}\mathbf{U}_1 \ominus {}_{2x-1}\mathbf{U}_1) \times [{}_{2x-2}\mathbf{U}_2 \otimes ({}_{2x-1}\mathbf{U}_2^{(2)})]({}_{2x-1}\mathbf{U}_3)({}_{2x-1}\mathbf{U}_4) \quad (25)$$

Equation 7 is replaced by

$${}_2\mathbf{U}_2 = {}_4\mathbf{U}_2 = \ldots = {}_{2x-2}\mathbf{U}_2 = \begin{bmatrix} 1 & \sigma_1 & \sigma_1\omega_4 \\ 1 & \sigma_1\omega_4 & \sigma_1 \\ 1 & \sigma_1\omega_4 & \sigma_1\omega_4 \end{bmatrix} \quad (26)$$

and

$${}_2\mathbf{U}_3 = {}_4\mathbf{U}_3 = \ldots = {}_{2x-2}\mathbf{U}_3 = {}_{2x-1}\mathbf{U}_4 = \text{col}\,(1, 1, 1) \quad (27)$$

Here σ_1 and ω_4 denote first- and second-order interactions of the third atom in the side chain with atoms in the main chain. States for the second bond in side chain j are defined by an imaginary methyl group bonded to ${}_jA_2$ meso to ${}_{j+1}A_1$.

Previous expressions for ${}_j\mathbf{U}'_m$ and ${}_j\mathbf{U}'_r$ apply without

Table II
Illustrative Estimates of the Effect of Side Chain Elongation on τ^* and the f_i at 298 K (Energies are in cal/mol)[a]

Side chain	τ^*	f_1	f_2	f_3	f_4	E_{τ_1}	E_{ω_3}	E_{σ_1}	E_{ω_4}
CH_3	1.00	1.00	1.00	1.00	1.00				
CH_2CH_3	0.21	0.85	1.65	1.79	1.64	1000	2000		
$CH_2CH_2CH_3$	0.17	0.89	1.72	1.83	1.72	1000	2000	500	2000
OCH_3	0.09	0.91	1.83	1.91	1.83	1400	∞		
OCH_2CH_3	0.07	0.93	1.86	1.93	1.86	1400	∞	900	∞
$OOCCH_3$	0.07	1.00	1.93	1.93	1.93	∞	2000		
CH_2OCH_3	0.79	0.89	1.11	1.21	1.05	300	340	900	∞

[a] Energies are based on results reported in ref 11–16. A penalty of 500 cal/mol has been assessed for E_{τ_1}.

Table III
d ln τ^*/d ln T and d ln f_i/d ln T for Side Chains with Threefold Rotation Potentials

Factor	Derivative × $(1 + \tau_1 + \omega_3)$	Sign, $0 < \tau_1 < 1$ and $0 < \omega_3 < 1$
τ^*	$-[(1 - \omega_3)\tau_1 \ln \tau_1 + (2 + \tau_1)\omega_3 \ln \omega_3](\tau_1 + 2\omega_3)^{-1}$	+
f_1	$\tau_1[(1 - \omega_3^2) \ln \tau_1 - (2 + \tau_1)\omega_3 \ln \omega_3](1 + \omega_3 + \tau_1\omega_3)^{-1}$	+ or −
f_2	$[(2 - \omega_3 - \omega_3^2)\tau_1 \ln \tau_1 + (2 - \tau_1 - \tau_1^2)\omega_3 \ln \omega_3](2 + \tau_1\omega_3)^{-1}$	−
f_3	$[(1 - \omega_3)\tau_1 \ln \tau_1 + (2 + \tau_1)\omega_3 \ln \omega_3](2 + \tau_1)^{-1}$	−
f_4	$[(2 - \omega_3^2 - \omega_3^3)\tau_1 \ln \tau_1 + (2 - 2\tau_1\omega_3 - 2\tau_1^2\omega_3 - \tau_1\omega_3^2)\omega_3 \ln \omega_3](2 + \tau_1\omega_3^2)^{-1}$	+ or −

Table IV
Illustrative Temperature Coefficients ($\times 10^3$) for τ^* and the f_i at 298 K[a]

Side chain	d ln τ^*/dT	d ln f_1/dT	d ln f_2/dT	d ln f_3/dT	d ln f_4/dT
CH_2CH_3	7.3	−0.85	−1.4	−0.86	−1.4
OCH_3	4.0	−0.75	−0.75	−0.36	−0.75
$OOCCH_3$	11	0	−0.39	−0.39	−0.39

[a] Using E_{τ_1} and E_{ω_3} specified in Table II.

modification provided each τ_1 in the definitions for τ^* and the f_i is replaced by $c\tau_1$, where

$$c = (1 + 2\sigma_1\omega_4)(1 + \sigma_1 + \sigma_1\omega_4)^{-1} \quad (28)$$

Definitions for τ^* and the f_i are unaffected when $c = 1$, a circumstance which arises when $\sigma_1 = 0$ or $\omega_4 = 1$. In the more likely event that $1 > \omega_4$ and $\sigma_1 > 0$, we obtain $1 > c$. The direction of the effect of side chain elongation on τ^* and the f_i under these circumstances can be deduced by differentiating eq 13–17 with respect to τ_1 and changing the sign.

$$-d\tau^*/d\tau_1 = (\omega_3 - 1)(1 + \tau_1 + \omega_3)^{-2} \quad (29)$$

$$-df_1/d\tau_1 = (1 - \omega_3^2)(1 + \tau_1 + \omega_3)^{-2} \quad (30)$$

$$-df_2/d\tau_1 = (2 - \omega_3 - \omega_3^2)(1 + \tau_1 + \omega_3)^{-2} \quad (31)$$

$$-df_3/d\tau_1 = (1 - \omega_3)(1 + \tau_1 + \omega_3)^{-2} = d\tau^*/d\tau_1 \quad (32)$$

$$-df_4/d\tau_1 = (2 - \omega_3^2 - \omega_3^3)(1 + \tau_1 + \omega_3)^{-2} \quad (33)$$

For those polymers which have $\omega_3 < 1$, lengthening of the side chain from two to three bonds will increase the f_i and decrease τ^*. Effects on τ^* and f_3 are equal in size but of opposite sign, and the effects on the f_i increase in the sequence $f_3 \leq f_1 < f_2 \leq f_4$.

Table II presents illustrative results calculated for τ^* and the f_i for several side chains. Assumed energies are reasonable in view of studies of polymethylene,[11] polyoxyalkanes,[12-15] and triacetin.[16] Hydrocarbon side chains demonstrate that appreciable changes arise in τ^* and $f_2 - f_4$ upon lengthening the side chain from methyl to ethyl. Addition of another methylene group further reduces τ^* and increases the f_i, but the changes are comparatively small. Many articulated side chains will have $f_2 - f_4$ near two, although exceptions can be expected (see CH_2OCH_3).

Side chains containing four or more bonds can be treated within the framework used here. In only rare cases will the effects on τ^* and the f_i be large enough to render such treatment necessary.

A Priori Probabilities for Poly(1-butene)

Consequences arising from τ^* and the f_i were estimated for poly(1-butene) by calculation of the a priori probability that the main chain bonds flanking the point of side chain attachment would occupy various states. The bond pair in question is located in the center of a long chain so that it is free from end effects. Energies associated with all second-order interactions were 2000 cal/mol, $e_\tau = E_{\tau_1} = 1000$ cal/mol, $\eta = 1$, and $T = 298$ K. These energies are reasonable in view of results obtained from polymethylene.[11] Values for τ^* and the f_i are those specified in Table II except when noted to the contrary.

Isotactic Polymer. Use of eq 19 for ${}_j\mathbf{U}'_m$ produces

$$\begin{bmatrix} 0.062 & 0.436 & 0.004 \\ 0.436 & 0.038 & 0.011 \\ 0.004 & 0.011 & 0.000 \end{bmatrix} \quad (34)$$

where the a priori probabilities are presented in matrix form with the order for rows and columns being t, g, $\bar{g}$. Dominant conformations are tg and gt, which produce the helices anticipated for an isotactic vinyl polymer.

To assess the consequences of τ^* and the f_i, calculations were repeated following various alterations in the leading statistical weight matrix in eq 19. The f_i and τ^* have been set equal to unity in the calculation which produced the results in (35).

$$\begin{bmatrix} 0.118 & 0.404 & 0.003 \\ 0.404 & 0.047 & 0.011 \\ 0.003 & 0.011 & 0.000 \end{bmatrix}, \quad \tau^* = f_i = 1 \quad (35)$$

Helical states are still preferred, but the preference has been reduced. The a priori probability for tt varies by a factor of two in (34) and (35).

Restoration of a value of 0.21 for τ^*, while maintaining the f_i at unity, produces

$$\begin{bmatrix} 0.053 & 0.449 & 0.004 \\ 0.449 & 0.026 & 0.007 \\ 0.004 & 0.007 & 0.000 \end{bmatrix}, \quad f_i = 1 \quad (36)$$

Reductions in the probabilities for tt and gg occur, with the major effect being on tt. Preference for helices is greater in (36) than in either (34) or (35).

Probabilities presented in (37) were obtained using $\tau^* = 0.21$, $f_1 = 0.85$, $f_2 = 1.65$, and $f_3 = f_4 = 0$.

$$\begin{bmatrix} 0.045 & 0.460 & 0.003 \\ 0.460 & 0 & 0.014 \\ 0.003 & 0.014 & 0 \end{bmatrix}, \quad f_3 = f_4 = 0 \quad (37)$$

Null values for f_3 and f_4 completely suppress gg and $\bar{g}\bar{g}$, states in which third-order interactions are inevitable.[10] Since the a priority probability for $\bar{g}\bar{g}$ is 0.000 even in eq 34–36, changes arise primarily from the suppression of gg. The helical content increases as a consequence. There is also a reduction in the probability for tt.

Condensation of the statistical weight matrices, through rejection of the final column and final row, becomes possible whenever $\tau\omega$, $\tau\omega_1$, and $\tau\omega_2$ are negligible.[10] In the present case combined probabilities for one bond being $\bar{g}$ are 0.030, 0.028, 0.022, and 0.034 in eq 34–37, respectively. On this basis it might appear that rejection of the final row and column would be of little consequence. By so doing, however, there would be a significant change in the frequency and nature of the helix interruptions in the polymer. The final row and column in eq 34–37 account for 23, 15, 22, and 43%, respectively, of the nonhelical states.

Syndiotactic Polymer. Use of eq 20 for ${}_j\mathbf{U}'_r$, along with the τ^* and f_i in Table II, produces

$$\begin{bmatrix} 0.094 & 0.428 & 0.004 \\ 0.428 & 0.024 & 0.008 \\ 0.004 & 0.008 & 0.000 \end{bmatrix} \quad (38)$$

Preference for the tg and gt helices is readily apparent. When all of the f_i are unity the probabilities are

$$\begin{bmatrix} 0.097 & 0.434 & 0.005 \\ 0.434 & 0.013 & 0.005 \\ 0.005 & 0.005 & 0.000 \end{bmatrix}, \quad f_i = 1 \quad (39)$$

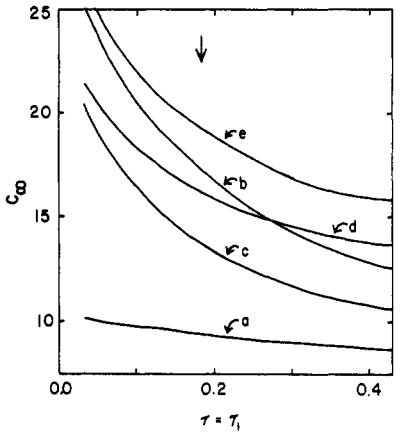

Figure 4. Characteristic ratios for an isotactic vinyl polymer at 298 K calculated using a bond angle supplement of 68°, $\Delta\phi = 10°$, $\eta = 1$, $\omega = \omega_1 = \omega_2 = \omega_3 = 0.034$, and the indicated $\tau = \tau_1$. The f_i and τ^* are those appropriate for an articulated side chain containing two bonds (see eq 13–17) with the following exceptions: (a) $\tau^* = f_i = 1$, (b) $f_i = 1$, (c) no exceptions, (d) $f_3 = f_4 = 0$, and (e) $f_1 = f_2 = 1, f_3 = f_4 = 0$. The arrow denotes the $\tau = \tau_1$ which were used to compute the a priori probabilities presented in eq 34–37.

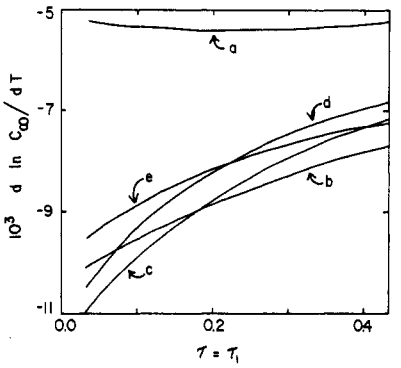

Figure 5. Temperature coefficients for the polymers treated in Figure 4. Identifying letters a–e have the same significance in both figures.

Rejection of the gg and $\bar{g}\bar{g}$ states yields

$$\begin{bmatrix} 0.100 & 0.438 & 0.005 \\ 0.438 & 0 & 0.008 \\ 0.005 & 0.008 & 0 \end{bmatrix}, \quad f_3 = f_4 = 0 \qquad (40)$$

The f_i exert a smaller effect on the probabilities for the syndiotactic polymer than on the isotactic polymer. Condensation through rejection of the last row and column is more appropriate for the syndiotactic polymer. Thus when $f_3 = f_4 = 0$, condensation for the syndiotactic polymer eliminates 21% of the nonhelical states, while for the corresponding isotactic polymer the figure would be 43%.

Characteristic Ratios for Isotactic Poly(1-butene) and Poly(1-pentene)

Characteristic ratios, $C_\infty = (\langle r^2\rangle_0/nl^2)_\infty$, were calculated for isotactic poly(1-butene) and poly(1-pentene). The objective is not to attempt to account for the properties observed with these polymers but rather to use them in order to explore the sensitivity of the unperturbed dimensions to τ^* and the f_i. Previous work has shown that calculated dimensions and temperature coefficients will be sensitive to a small proportion of racemic dyads.[1,3,4] Bond angle supplements were 68°, $\Delta\phi$ = 10°, and the temperature was 298 K. Energies associated with all second-order interactions were 2000 cal/mol, $\eta = 1$, and $E_\tau = E_{\tau_1}$ was varied from 500 to 2000 cal/mol. A range of 0.034–0.43 for $\tau = \tau_1$ results. The effect of the variation in τ_1 on the f_i and τ^* will approximate that depicted in Figure 2 since ω_3 is small (0.034). Poly(1-pentene) requires E_{σ_1}, whose value was chosen to be 500 cal/mol.[11]

When τ^* and all f_i are unity, C_∞ is only weakly dependent on τ for the range covered in Figure 4 (curve a). Here the effect of the second atom in the side chain on the main chain conformation is ignored. Probabilities at $\tau = 0.184$ are those presented in (35).

Unperturbed dimensions increase in the presence of an articulated paraffinic side chain. Specification of τ^* by eq 13 produces an increase of 45–150% in C_∞ (curve b). The probabilities when $\tau = \tau_1 = 0.184$ are those in (36). Extension of the molecule arises from an increase in the helices formed from tg and gt, attained at the expense of the tt and gg states. This effect becomes more pronounced as τ_1, and therefore τ^*, decreases. If in addition the f_i are now specified by eq 14–17, C_∞ decreases by 15–20% (curve c). Probabilities are given by (34). The decrease in helical content brought about by the f_i is in harmony with the contraction in dimensions. Comparison of curves a, b, and c reveals that introduction of τ^* has a greater effect on the dimensions than does the subsequent introduction of the f_i. This result is compatible with the conclusion that ln τ^* will differ from zero more than will any of the ln f_i when τ_1 and ω_3 lie between zero and unity.

Rejection of the gg and $\bar{g}\bar{g}$ states, by setting f_3 and f_4 equal to zero, produces an increase in C_∞. Approximately the same increase occurs when $f_1 = f_2 = 1$ and when f_1 and f_2 are assigned by eq 14 and 15. Refinements brought about by using eq 14 and 15 for f_1 and f_2, and by suppression of gg and $\bar{g}\bar{g}$, are partially compensatory. This conclusion follows from inspection of curves b, d, and e in Figure 4. The former refinement becomes dominant when τ and τ_1 are less than 0.27.

Unperturbed dimensions were calculated for poly(1-pentene) with and without suppression of gg and $\bar{g}\bar{g}$. They exceed the corresponding C_∞ for poly(1-butene) by only 3–7%.

Temperature coefficients for the unperturbed dimensions of isotactic poly(1-butene) are depicted in Figure 5. In all cases they are large and negative, as expected,[1,3,4] and they become more negative in the presence of an articulated paraffinic side chain. Once again τ^* is of greater consequence than the f_i.

Calculations for atactic and syndiotactic polymers were not performed. The relative insensitivity of the a priori probabilities for syndiotactic poly(1-butene), demonstrated in eq 38–40, suggests that the f_i would exert smaller effects than those calculated for the isotactic polymer.

Maximal Effect of the f_i on C_∞

Further calculations of C_∞ for an isotactic polymer were carried out in which the statistical weights were varied subject to the restrictions that E_τ and E_{τ_1} were positive, $E_\tau > E_\eta$, and the energies for second-order interactions were positive or zero. In each case τ^* was specified by eq 13, while the f_i were either unity or the values specified by eq 14–17. In some cases the ratio of the two C_∞ would approach 3:2, the higher value being obtained when the f_i were unity. For example, with $E_\eta = E_{\omega_1} = 0$, $E_\tau = E_\omega = E_{\omega_2} = 2000$ cal/mol, and $E_{\tau_1} = E_{\omega_3} = 5000$ cal/mol, the ratio of the C_∞ is 16.4:11.1, while with $E_\eta = 0$, $E_{\omega_1} = 500$ cal/mol, $E_\tau = 1000$ cal/mol, and $E_{\tau_1} = E_\omega = E_{\omega_2} = E_{\omega_3} = 2000$ cal/mol the ratio is 9.2:6.8. Temperature coefficients (10^3 d ln C_∞/dT) could be as different as −2.7:−1.7, obtained with $E_\eta = 0$, $E_\tau = E_{\omega_1} = 500$ cal/mol, $E_{\tau_1} = E_\omega = E_{\omega_2} = E_{\omega_3} = 2000$ cal/mol.

Elimination of f_1, f_2, and f_4 from the configuration partition function occurs whenever $\tau = 0$ or whenever $\tau\omega$, $\tau\omega_1$, and $\tau\omega_2$ are zero. These circumstances permit condensation of the statistical weight matrices to 2×2.[1,3,4,10] Suppression of the gg and $\bar{g}\bar{g}$ states for the bond pair flanking the point of side chain attachment eliminates f_3 and f_4.

Comparison with Previous Work

Abe[4] has described a treatment for vinyl polymers containing articulated side chains which shares with the present work the feature of multiplying certain elements in U′ by factors which arise from a consideration of the side chains. Specific application has been made to poly(1-olefins) and poly(alkyl vinyl ethers).[4] While the two approaches can be made to yield identical results, certain differences in detail exist. Thus Abe[4a] concludes $\tau^* = \tau_1 - \tau_1^2 + \ldots$ for poly(1-butene). This result can be contrasted with the expression found in eq 13. An important difference is the relationship between τ^* and ω_3. According to eq 13, $\tau^* = 1$ when $\omega_3 = 1$, irrespective of the value for τ_1. If instead we let $\tau^* = \tau_1 - \tau_1^2 + \ldots$, the value of τ^* depends solely on τ_1. The differences arise primarily because of certain approximations introduced by Abe,[4a] as exemplified by $\tau_1 + 2\omega_3 \approx \tau_1$ and $1 + \tau_1 + \omega_3 \approx 1 + \tau_1$ in the case of poly(1-butene).

The present work demonstrates that four distinct factors (τ^*, f_1, f_2, and f_4) need be considered for symmetric side chains containing two or three bonds, three rotational states per bond being assumed. The objective is not to account for the configurational properties observed with any particular polymer but rather to explore the manner in which the four factors will influence such properties. This objective is achieved by examination of the relationship between these factors and first- and second-order interactions present, evaluation of their effect of C_∞ and a priori probabilities for bonds in the main chain, and identification of the maximal effect on C_∞.

The present treatment corresponds exactly to that developed by Flory and co-workers[3,10] when τ^* and the f_i are unity. These circumstances will arise if (a) the side chain contains only one bond, (b) the articulated side chain contains two bonds and $\omega_3 = 1$, or (c) the articulated side chain contains three bonds, $\omega_3 = 1$, and either $\sigma_1 = 0$ or $\omega_4 = 1$. In other circumstances the factors τ^* *and* f_i appear in the statistical weight matrix U′.

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Moment of Inertia Tensors and Center of Mass Vectors for Flexible Molecules Containing a Trifunctional Branch Point

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ABSTRACT: Expressions are developed for the center of mass vectors and moment of inertia tensors for a molecule which contains a trifunctional branch point. Evaluation is achieved using rotational isomeric state theory. Configurational averages are obtained for unperturbed molecules, the averaging being accomplished in the internal coordinate system defined by the first two bonds in a branch. Under certain limiting conditions simple relationships exist between persistence vectors and averaged center of mass vectors for the branched molecule. They are identical with those obtained for the corresponding linear chain molecule only if there is a sufficiently large number of bonds in the branch used to define the internal coordinate system. Asymmetries deduced from the principal moments of the averaged moment of inertia tensor may depend on the selection of the branch whose terminal two bonds specify the internal coordinate system in which averaging takes place.

The spatial configuration of a linear polymer chain is customarily described by the end-to-end vector, **r**. Matrix methods permit computation of **r**, its self-direct products, $\mathbf{r}^{xp}$, and the even moments, r^{2p}, as well as their averages over all configurations for the unperturbed chain.[1-4] Branched macromolecules, however, are not conveniently described in terms of **r** because of the presence of more than two chain ends. The fundamental quantity for branched macromolecules is the square of the radius of gyration, s^2. Matrix methods[5,6] are available for the computation of s^2 as well as its statistical mechanical average over all configurations accessible to the unperturbed molecule, $\langle s^2 \rangle_0$. Random-flight statistics has frequently been used to calculate the ratio of the $\langle s^2 \rangle_0$ for flexible branched and linear macromolecules containing the same number of bonds, but this procedure is accurate only when the asymptotic limit at high molecular weight has been attained.[7-9] An additional quantity of interest for branched molecules is the center of mass vector expressed in the coordinate system defined by the first two bonds in branch k, ${}_k\mathbf{g}$.

Flexible linear chain molecules attain a Gaussian distribution at sufficiently high molecular weight, but deviations from Gaussian behavior occur at low molecular weight. The asymmetry of the distribution is described by the moment of