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 $\mathbf{U}'$ 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 $\mathbf{U}'$.

Acknowledgment. This work was carried out while on sabbatical leave at Stanford University, with support provided by a John Simon Guggenheim Memorial Foundation Fellowship. The author thanks Professor Flory for his hospitality during this period. Supported in part by National Science Foundation Grant DMB-73-07655 A02.

References and Notes

(1) P. J. Flory, "Statistical Mechanics of Chain Molecules", Wiley, New York, N.Y., 1969.
(2) P. J. Flory, *Macromolecules*, **7**, 381 (1974).
(3) P. J. Flory, J. E. Mark, and A. Abe, *J. Am. Chem. Soc.*, **88**, 639 (1966).
(4) (a) A. Abe, *Polym. J.*, **1**, 232 (1970); (b) A. Abe, *J. Polym. Sci., Polym. Symp.*, **No. 54**, 135 (1976); (c) A. Abe, *Macromolecules*, **10**, 34 (1977).
(5) W. L. Mattice, *Macromolecules*, **8**, 644 (1975).
(6) W. L. Mattice, *Macromolecules*, **9**, 48 (1976).
(7) W. L. Mattice and D. K. Carpenter, *Macromolecules*, **9**, 53 (1976).
(8) W. L. Mattice, *Macromolecules*, **10**, 511 (1977).
(9) W. L. Mattice, *Macromolecules*, **10**, 516 (1977).
(10) P. J. Flory, P. R. Sundararajan, and L. C. DeBolt, *J. Am. Chem. Soc.*, **96**, 5015 (1974).
(11) A. Abe, R. L. Jernigan, and P. J. Flory, *J. Am. Chem. Soc.*, **88**, 631 (1966).
(12) J. E. Mark, *J. Am. Chem. Soc.*, **88**, 3708 (1966).
(13) J. E. Mark, *J. Polym. Sci., Part B*, **4**, 825 (1966).
(14) J. E. Mark and P. J. Flory *J. Am. Chem. Soc.*, **87**, 1415 (1965).
(15) J. E. Mark and P. J. Flory, *J. Am. Chem. Soc.*, **88**, 3702 (1966).
(16) Manuscript in preparation.

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

Wayne L. Mattice

Department of Chemistry, Louisiana State University,
Baton Rouge, Louisiana 70803.
Received April 5, 1977

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, $\mathbf{r}$. Matrix methods permit computation of $\mathbf{r}$, its self-direct products, $\mathbf{r}^{\times p}$, 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 $\mathbf{r}$ 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

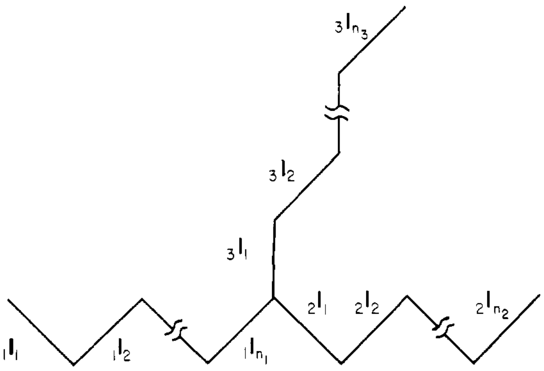

Figure 1. Diagrammatic representation of a molecule which consists of three chains emanating from a common atom. The vector for bond i in branch j is denoted by ${}_j\mathbf{l}_i$.

inertia tensor about the center of gravity, $\mathbf{S}_{x2}$.[4] The configurational average of this tensor for linear polymethylene chains shows that molecules containing fewer than about 50 methylene units approximate a prolate ellipsoid whose asymmetry increases as the molecular weight decreases.[10]

Information concerning the effect of branching on the spatial distributions for molecules of finite molecular weight is contained in $\mathbf{g}$, $\mathbf{S}_{x2}$, and their configurational averages. Matrix methods required for their evaluation are available for linear chain molecules.[4] The present objective is to develop the matrix methods required to accomplish the analogous computations for the prototype of a branched molecule, i.e., a molecule consisting of three branches emanating from a common atom. A comparison of the numerical results obtained for linear polymethylenes[10] and various branched polymethylenes will be presented subsequently.[11]

Relationship of the Persistence Vectors to the Center of Mass Vectors

Consider a molecule which consists of three branches emanating from a common atom (Figure 1). Branches and atoms are numbered as indicated, with ${}_jA_i$ (and ${}_j\mathbf{l}_i$) representing atom (and bond vector) i in branch j.[5] The molecule contains three chains, which consist of branches 1 + 2, 1 + 3, and 2 + 3. The number of chains becomes six if attention is paid to their directionality.

The vector connecting skeletal atoms 0 and i in the chain consisting of branch k followed by branch l is denoted by ${}_{kl}\mathbf{r}_{0i}$.[7] When each bond vector is expressed in its own coordinate system,

$$ {}_{kl}\mathbf{r}_{0i} = \sum_{j=1}^{i} {}_{kl}\mathbf{T}_1^{(j-1)}{}_{kl}\mathbf{l}_j \tag{1} $$

The product of the first $j - 1$ transformation matrices in the chain composed of branches k and l is denoted by ${}_{kl}\mathbf{T}_i^{(j-1)}$. The more compact notation ${}_{kl}\mathbf{r}$ is reserved for the chain vectors ($i = n_k + n_l$, where n_k is the number of bonds in branch k). There are six different ${}_{kl}\mathbf{r}$ for the molecule in Figure 1, corresponding to the six ways of assigning k and l. Each is expressed in the coordinate system defined by the first two bonds in branch k.[4]

Six *persistence vectors*, ${}_{kl}\mathbf{a}$, are defined as

$$ {}_{kl}\mathbf{a} = \langle {}_{kl}\mathbf{r} \rangle \tag{2} $$

Let ${}_{kl}\rho$ represent the vector from ${}_{kl}\mathbf{a}$ to the remote terminus of the chain consisting of branch k followed by branch l.

$$ {}_{kl}\rho = {}_{kl}\mathbf{r} - {}_{kl}\mathbf{a} \tag{3} $$

The analogous vector for atom i in this chain is

$$ {}_{kl}\rho_i = {}_{kl}\mathbf{r}_{0i} - {}_{kl}\mathbf{a} \tag{4} $$

The *center of gravity vector* expressed in the coordinate system defined[4] by the first two bonds in branch k is denoted by ${}_k\mathbf{g}$,

$$ {}_k\mathbf{g} = N^{-1}\left(\sum_{i=0}^{n_k+n_l} {}_{kl}\mathbf{r}_{0i} + \sum_{i=n_k+1}^{n_k+n_m} {}_{km}\mathbf{r}_{0i}\right) \tag{5} $$

where the total number of atoms, $n_k + n_l + n_m + 1$, is abbreviated to N. Three such vectors can be defined for the molecule in Figure 1, corresponding to the three ways of selecting branch k. The average over all configurations is

$$ \begin{aligned} \langle {}_k\mathbf{g} \rangle &= N^{-1}\left(\sum_{i=0}^{n_k+n_l} \langle {}_{kl}\mathbf{r}_{0i} \rangle + \sum_{i=n_k+1}^{n_k+n_m} \langle {}_{km}\mathbf{r}_{0i} \rangle\right) \\ &= N^{-1}\Bigg[(n_k + n_l)_{kl}\mathbf{a} + (n_m)_{km}\mathbf{a} \\ &\qquad + \sum_{i=1}^{n_k+n_l} \langle {}_{kl}\rho_i \rangle + \sum_{i=n_k+1}^{n_k+n_m} \langle {}_{km}\rho_i \rangle\Bigg] \end{aligned} \tag{6} $$

As i becomes large the average of ${}_{kl}\rho_i$ vanishes. Consequently

$$ N^{-1}\left(\sum_{i=1}^{n_k+n_l} \langle {}_{kl}\rho_i \rangle + \sum_{i=n_k+1}^{n_k+n_m} \langle {}_{km}\rho_i \rangle\right) \tag{7} $$

will vanish as n_k, n_l, and n_m become large. More precisely, $n_k \rightarrow \infty$ is a sufficient condition for (7) to vanish. Since ${}_{kl}\mathbf{a} \rightarrow {}_{km}\mathbf{a}$ as $n_k \rightarrow \infty$,

$$ \langle {}_k\mathbf{g} \rangle_{n_k\rightarrow\infty} = {}_{kl}\mathbf{a} = {}_{km}\mathbf{a} \tag{8} $$

This relationship is valid for any values of n_l and n_m. Furthermore, $\langle {}_k\mathbf{g} \rangle_{n_k\rightarrow\infty}$ is identical with the average value of the center of mass vector for a linear chain molecule consisting simply of branch k.

The expression in (7) will also vanish if $n_l \rightarrow \infty$, even if n_k is small, due to the division by N. If both n_k and n_m remain small while $n_l \rightarrow \infty$, $N \rightarrow n_l$ and $(n_k + n_l)_{kl}\mathbf{a} + (n_m)_{km}\mathbf{a} \rightarrow (n_l)_{kl}\mathbf{a}$, yielding

$$ \langle {}_k\mathbf{g} \rangle_{n_l\rightarrow\infty} = {}_{kl}\mathbf{a}\ (\neq {}_{km}\mathbf{a}) \qquad n_m \text{ and } n_k \text{ small} \tag{9} $$

The vector in eq 9 is different from the average center of mass vector for a linear chain molecule consisting of either branch k or branch k followed by branch l.

Permitting n_l and n_m to become large while n_k remains small will also cause the expression in (7) to vanish. Under these circumstances

$$ \langle {}_k\mathbf{g} \rangle_{n_l\rightarrow\infty, n_m\rightarrow\infty} = (n_l + n_m)^{-1}[(n_l)_{kl}\mathbf{a} + (n_m)_{km}\mathbf{a}] \qquad n_k \text{ small} \tag{10} $$

If we further stipulate that $n_l = n_m$,

$$ \langle {}_k\mathbf{g} \rangle_{n_l=n_m, n_l\rightarrow\infty} = \tfrac{1}{2}({}_{kl}\mathbf{a} + {}_{km}\mathbf{a}) \tag{11} $$

The vector ${}_{kl}\mathbf{a}$ will generally differ from ${}_{km}\mathbf{a}$ when n_k is small. Neither vector in eq 10 and 11 is identical with the average center of mass vector for a linear chain molecule consisting of branch k, branch k followed by branch l, or branch k followed by branch m.

Equation 6 must be used as it stands if n_k, n_l, and n_m are small.

The asymptotic limit for the characteristic ratio, $(\langle r^2\rangle_0/nl^2)_\infty$, of a *linear* chain molecule can be obtained from l and the X component, $\langle x\rangle_\infty$, of the persistence vector

$$ \langle x\rangle_\infty = \tfrac{1}{2}[(\langle r^2\rangle_0/nl^2)_\infty + 1]l = \tfrac{1}{2}[(6\langle s^2\rangle_0/nl^2)_\infty + 1]l \tag{12} $$

($\langle x\rangle_\infty$ is also the X component of the average center of mass vector).[10,12] Here n represents the number of bonds of length l. The result attained in eq 8 demonstrates that no corresponding relationship exists between $(\langle s^2\rangle_0/nl^2)_\infty$, l, and the components of the various persistence vectors and center of mass vectors for *branched* molecules. The value of $(\langle s^2\rangle_0/nl^2)_\infty$ for the branched molecule will depend on n_l/n_k and n_m/n_k,[7,13,14] but $\langle {}_k\mathbf{g}\rangle_{n_k\to\infty}$ is independent of n_l and n_m.

The Moment of Inertia Tensor

The vector from ${}_k\mathbf{g}$ to atom i in the chain composed of branch k followed by branch l is denoted by ${}_{kl}\mathbf{s}_i$.

$$ {}_{kl}\mathbf{s}_i = {}_{kl}\mathbf{r}_{0i} - {}_k\mathbf{g} \tag{13} $$

If atom i lies in branch k, this vector is

$$ {}_{kl}\mathbf{s}_{i,i\le n_k} = -N^{-1}\left(\sum_{j=0}^{n_k+n_l} {}_{kl}\mathbf{r}_{ij} + \sum_{j=n_k+1}^{n_k+n_m} {}_{km}\mathbf{r}_{ij}\right) \tag{14} $$

$$ = N^{-1}\left(\sum_{j=0}^{n_k+n_l} {}_{kl}\mathbf{r}_{ji} + \sum_{j=n_k+1}^{n_k+n_m} {}_{km}\mathbf{r}_{ji}\right) \tag{15} $$

However, if atom i lies in branch l, the appropriate expression is

$$ {}_{kl}\mathbf{s}_{i,i>n_k} = -N^{-1}\left[\sum_{j=0}^{n_k+n_l} {}_{kl}\mathbf{r}_{ij} + \sum_{j=n_k+1}^{n_k+n_m} ({}_{km}\mathbf{r}_{0j} - {}_{kl}\mathbf{r}_{0i})\right] $$

$$ = -N^{-1}\left[\sum_{j=0}^{n_k+n_l} {}_{kl}\mathbf{r}_{ij} + \sum_{j=n_k+1}^{n_k+n_m} {}_{km}\mathbf{r}_{0j} - (n_m)\,{}_{kl}\mathbf{r}_{0i}\right] \tag{16} $$

The sum in eq 17, of course, is zero.

$$ 0 = \sum_{i=0}^{n_k+n_l} {}_{kl}\mathbf{s}_i + \sum_{i=n_k+1}^{n_k+n_m} {}_{km}\mathbf{s}_i \tag{17} $$

From eq 13 we obtain

$$ {}_k\mathbf{g} = {}_{kl}\mathbf{s}_0 \tag{18} $$

$$ \Delta({}_k\mathbf{g}) = {}_k\mathbf{g} - \langle {}_k\mathbf{g}\rangle = -\Delta({}_{kl}\mathbf{s}_0) \tag{19} $$

The latter is similar in form to the analogous relationship for a linear chain molecule.[4] The displacement $\Delta({}_k\mathbf{g})$ can be identified with $-\Delta({}_{kl}\mathbf{s}_0)$, the negative of the displacement of the initial atom in branch k from its mean position relative to the center of mass.

The moment of inertia tensor for a specified configuration is

$$ {}_k\mathbf{S}_{x2} = N^{-1}\left(\sum_{i=0}^{n_k+n_l} {}_{kl}\mathbf{s}_i^{\,x2} + \sum_{i=n_k+1}^{n_k+n_m} {}_{km}\mathbf{s}_i^{\,x2}\right) \tag{20} $$

where ${}_{kl}\mathbf{s}_i^{\,x2}$ denotes the self-direct product of ${}_{kl}\mathbf{s}_i$. The formalism adopted generates ${}_k\mathbf{S}_{x2}$ as a column containing nine elements. This column is obtained from the 3 × 3 representation of ${}_k\mathbf{S}_{x2}$ by arranging the nine elements in "reading order".[3,4] Use of eq 13 yields

$$ {}_k\mathbf{S}_{x2} = N^{-1}\left[\sum_{i=0}^{n_k+n_l} ({}_{kl}\mathbf{r}_{0i}^{\,x2} - {}_{kl}\mathbf{r}_{0i}\otimes{}_k\mathbf{g} - {}_k\mathbf{g}\otimes{}_{kl}\mathbf{r}_{0i} + {}_k\mathbf{g}^{x2}) + \sum_{i=n_k+1}^{n_k+n_m} ({}_{km}\mathbf{r}_{0i}^{\,x2} - {}_{km}\mathbf{r}_{0i}\otimes{}_k\mathbf{g} - {}_k\mathbf{g}\otimes{}_{km}\mathbf{r}_{0i} + {}_k\mathbf{g}^{x2})\right] \tag{21} $$

Simplification via eq 5 produces

$$ {}_k\mathbf{S}_{x2} = N^{-1}\left(\sum_{i=0}^{n_k+n_l} {}_{kl}\mathbf{r}_{0i}^{\,x2} + \sum_{i=n_k+1}^{n_k+n_m} {}_{km}\mathbf{r}_{0i}^{\,x2}\right) - {}_k\mathbf{g}^{x2} \tag{22} $$

which has an obvious parallel to the moment of inertia tensor for a rigid linear chain molecule.[4]

Matrix Evaluation of ${}_{kl}\mathbf{r}$, ${}_{kl}\mathbf{r}_{0i}$, ${}_k\mathbf{g}$, ${}_k\mathbf{g}^{x2}$, ${}_k\mathbf{S}_{x2}$, and Their Configurational Averages

Chain Displacement Vector. The chain displacement vectors for branched molecules were treated in ref 6. The result can be written as

$$ {}_{kl}\mathbf{r}_{0i} = \mathbf{C}_r^*({}_{kl}\mathbf{A}_i^{(i-1)})\mathbf{C}_r \tag{23} $$

using the matrices defined in eq 24–26.

$$ {}_{kl}\mathbf{A}_i = {}_{kl}\begin{bmatrix} \mathbf{T} & \mathbf{l} \\ 0 & 1 \end{bmatrix}_i \tag{24} $$

$$ \mathbf{C}_r^* = [\mathbf{E}_3 \quad \mathbf{0}] \tag{25} $$

$$ \mathbf{C}_r = \mathrm{col}(0, 0, 0, 1) \tag{26} $$

Symbolism of the type ${}_{kl}\mathbf{A}_1^{(i-1)}$ denotes the product of $i-1$ successive matrices commencing with ${}_{kl}\mathbf{A}_1$, and $\mathbf{E}_i$ denotes the unit matrix of order i. The vector in eq 23 is expressed in the coordinate system defined by the first two bonds in branch k.

Persistence vectors can be obtained by the formulation of generator matrices which combine eq 24–26 with the appropriate statistical weight matrices. If the configuration partition function[5] is written as

$$ Z = {}_{kl}\mathbf{U}_1^{(n_k+1)}[{}_{kl}\mathbf{U}_{n_k+2}^{(n_l-1)} \otimes {}_{km}\mathbf{U}_{n_k+2}^{(n_m-1)}] \tag{27} $$

the persistence vector is given by

$$ {}_{kl}\mathbf{a} = Z^{-1}({}_{kl}\boldsymbol{F}_1^{(n_k+1)})[({}_{kl}\boldsymbol{F}_{n_k+2}^{(n_l-1)}) \otimes_{4,1} ({}_{km}\mathbf{U}_{n_k+2}^{(n_m-1)})] \tag{28} $$

The generator matrices ${}_{kl}\boldsymbol{F}_i$ are constructed from ${}_{kl}\mathbf{U}_i$, ${}_{kl}\mathbf{A}_i$, $\mathbf{C}_r^*$, and $\mathbf{C}_r$ according to the procedures defined by eq 31–38b of ref 6. We have adopted here a more compact notation for handling terminal matrices, as exemplified by $({}_{kl}\boldsymbol{F}_{[1})({}_{kl}\boldsymbol{F}_2^{(n_k)})$ being written as ${}_{kl}\boldsymbol{F}_1^{(n_k+1)}$. The modified direct product, $\otimes_{a,b}$, is defined in ref 6. Dimensions of ${}_{kl}\boldsymbol{F}_1$, ${}_{kl}\boldsymbol{F}_{n_k+1}$, and ${}_{kl}\boldsymbol{F}_{n_k+n_1}$ are $3 \times 4\nu$, $4 \times 4\nu^2$, and $4\,\nu \times 1$, respectively, where ν denotes the number of rotational states. All other ${}_{kl}\boldsymbol{F}_i$ are $4\nu \times 4\nu$.

Center of Gravity Vector. The matrix expression for ${}_k\mathbf{g}$ obtained from eq 5 is

$$ {}_k\mathbf{g} = N^{-1}\mathbf{C}_r^*\left(\sum_{i=1}^{n_k+n_l} {}_{kl}\mathbf{A}_1^{(i)} + \sum_{i=n_k+1}^{n_k+n_m} {}_{km}\mathbf{A}_1^{(i)}\right)\mathbf{C}_r \tag{29} $$

Evaluation is simplified through the definition[4] of a new generator matrix, ${}_{kl}\mathbf{F}_{g;i}$.

$$ {}_{kl}\mathbf{F}_{g;i} = {}_{kl}\begin{bmatrix} \mathbf{A} & \mathbf{A}\mathbf{C}_r \\ 0 & 1 \end{bmatrix}_i \tag{30} $$

The center of gravity vector is then obtained as

$$ {}_k\mathbf{g} = N^{-1}\mathbf{C}_g^*({}_{kl}\mathbf{F}_{g;1}^{(n_k+n_l)} + {}_{km}\mathbf{F}_{g;1}^{(n_k+n_m)} - {}_{km}\mathbf{F}_{g;1}^{(n_k)})\mathbf{C}_g \tag{31} $$

with $\mathbf{C}_g^*$ and $\mathbf{C}_g$ defined by eq 32 and 33.

$$ \mathbf{C}_g^* = [\mathbf{E}_3 \quad \mathbf{0}] \tag{32} $$

$$ \mathbf{C}_g = \mathrm{col}(0, 0, 0, 0, 1) \tag{33} $$

The last term in eq 31 is required to compensate for the double counting of the atoms in branch k by the first two terms. An alternative expression, which does not require this subtraction, is

$$ {}_k\mathbf{g} = N^{-1}[\mathbf{C}_g^*({}_{kl}\mathbf{F}_{g;1}^{(n_k+n_l)}) + \mathbf{C}_r^*({}_{km}\mathbf{A}_1^{(n_k)})\mathbf{C}_a^*({}_{km}\mathbf{F}_{g;n_k+1}^{(n_m)})]\mathbf{C}_g \tag{34} $$

$$ \mathbf{C}_a^* = [\mathbf{E}_4 \quad \mathbf{0}] \tag{35} $$

The average value of the center of mass vector, obtained from eq 34, is

$$ \langle {}_k\mathbf{g}\rangle = Z^{-1}N^{-1}\{{}_{kl}\boldsymbol{F}_1^{(n_k+1)} \times [({}_{kl}\boldsymbol{F}_{n_k+2}^{(n_l-1)}) \otimes_{5,1} ({}_{km}\mathbf{U}_{n_k+2}^{(n_m-1)})] + {}_{km}\boldsymbol{F}_1^{(n_k+1)}[({}_{kl}\boldsymbol{U}_{n_k+2}^{(n_l-1)}) \otimes ({}_{km}\boldsymbol{F}_{n_k+2}^{(n_m-1)})]\} \tag{36} $$

Generator matrices ${}_{kl}\boldsymbol{F}_i$ are formulated from the statistical weight matrices and eq 30, 32, and 33, as is also the case for those ${}_{km}\boldsymbol{F}_i$ for which $i > n_k + 1$. The generator matrices ${}_{km}\boldsymbol{F}_i$ for which $i \leq n_k$ are formulated from the statistical weight matrices and eq 24 and 25, while ${}_{km}\boldsymbol{F}_{n_k+1}$ is formulated from the rectangular statistical weight matrix, eq 30, and eq 35. In all cases the applicable rules are those summarized by eq 31–38b of ref 6. Dimensions for the generator matrices used in eq 36 are as follows: ${}_{kl}\boldsymbol{F}_1$ and ${}_{km}\boldsymbol{F}_1$ are $3 \times 5\nu$ and $3 \times 4\nu$, respectively, while ${}_{kl}\boldsymbol{F}_{n_k+n_l}$ and ${}_{km}\boldsymbol{F}_{n_k+n_m}$ are both $5\nu \times 1$. Branch point matrices ${}_{kl}\boldsymbol{F}_{n_k+1}$ and ${}_{km}\boldsymbol{F}_{n_k+1}$ are $5\nu \times 5\nu^2$ and $4\nu \times 5\nu^2$, respectively. Those ${}_{km}\boldsymbol{F}_i$ for which $1 < i \leq n_k$ are $4\nu \times 4\nu$. All remaining generator matrices are $5\nu \times 5\nu$.

Self-Direct Product of the Center of Gravity Vector. Procedures for the matrix evaluation of ${}_{k}\mathbf{g}^{x2}$ can be obtained starting either from eq 31 or 34. The latter shall be adopted as the starting point because it yields a final expression which demands appreciably less numerical labor.

$$\begin{aligned}{}_{k}\mathbf{g}^{x2} = N^{-2}\{&[\mathbf{C}_g{}^*({}_{kl}\mathbf{F}_{g;1}{}^{(n_k+n_l)})\mathbf{C}_g]^{x2} \\ &+ [\mathbf{C}_r{}^*({}_{km}\mathbf{A}_1{}^{(n_k)})\mathbf{C}_a{}^*({}_{km}\mathbf{F}_{g;n_k+1}{}^{(n_m)})\mathbf{C}_g]^{x2} \\ &+ [\mathbf{C}_g{}^*({}_{kl}\mathbf{F}_{g;1}{}^{(n_k+n_l)})\mathbf{C}_g] \otimes [\mathbf{C}_r{}^*({}_{km}\mathbf{A}_1{}^{(n_k)}) \\ &\qquad \times \mathbf{C}_a{}^*({}_{km}\mathbf{F}_{g;n_k+1}{}^{(n_m)})\mathbf{C}_g] \\ &+ [\mathbf{C}_r{}^*({}_{km}\mathbf{A}_1{}^{(n_k)})\mathbf{C}_a{}^*({}_{km}\mathbf{F}_{g;n_k+1}{}^{(n_m)})\mathbf{C}_g] \\ &\qquad \otimes [\mathbf{C}_g{}^*({}_{kl}\mathbf{F}_{g;1}{}^{(n_k+n_l)})\mathbf{C}_g]\}\end{aligned} \qquad (37)$$

Application of the theorem on direct products yields

$$\begin{aligned}{}_{k}\mathbf{g}^{x2} = N^{-2}[&\mathbf{C}_g{}^{*x2}({}_{kl}\mathbf{F}_g{}^{x2})_1{}^{(n_k+n_l)}\mathbf{C}_g{}^{x2} \\ &+ \mathbf{C}_r{}^{*x2}({}_{km}\mathbf{A}^{x2})_1{}^{(n_k)}\mathbf{C}_a{}^{*x2}({}_{km}\mathbf{F}_g{}^{x2})_{n_k+1}{}^{(n_m)}\mathbf{C}_g{}^{x2} \\ &+ (\mathbf{C}_g{}^* \otimes \mathbf{C}_r{}^*)({}_{kl}\mathbf{F}_g \otimes {}_{km}\mathbf{A})_1{}^{(n_k)}\{{}_{kl}\mathbf{F}_g \otimes [\mathbf{C}_a{}^*({}_{km}\mathbf{F}_g)]\}_{n_k+1} \\ &\quad \times \{[({}_{kl}\mathbf{F}_{g;n_k+2}{}^{(n_l-1)})\mathbf{C}_g] \otimes [({}_{km}\mathbf{F}_{g;n_k+2}{}^{(n_m-1)})\mathbf{C}_g]\} \\ &+ (\mathbf{C}_r{}^* \otimes \mathbf{C}_g{}^*)({}_{km}\mathbf{A} \otimes {}_{kl}\mathbf{F}_g)_1{}^{(n_k)}\{[\mathbf{C}_a{}^*({}_{km}\mathbf{F}_g)] \otimes {}_{kl}\mathbf{F}_g\}_{n_k+1} \\ &\quad \times \{[({}_{km}\mathbf{F}_{g;n_k+2}{}^{(n_m-1)})\mathbf{C}_g] \otimes [({}_{kl}\mathbf{F}_{g;n_k+1}{}^{(n_l-1)})\mathbf{C}_g]\}]\end{aligned} \qquad (38)$$

The terms in eq 38 appear in a fashion which provides the basis for the evaluation of $\langle {}_{k}\mathbf{g}^{x2} \rangle$ as

$$\begin{aligned}\langle {}_{k}\mathbf{g}^{x2} \rangle = Z^{-1}N^{-2}\{&{}_{kl}\boldsymbol{F}_1{}^{(n_k+1)}[({}_{kl}\boldsymbol{F}_{n_k+2}{}^{(n_l-1)}) \\ &\quad \otimes_{a,1} ({}_{km}\mathbf{U}_{n_k+2}{}^{(n_m-1)})] + {}_{km}\boldsymbol{F}_1{}^{(n_k+1)} \\ &\quad \times [({}_{kl}\mathbf{U}_{n_k+2}{}^{(n_l-1)}) \otimes ({}_{km}\boldsymbol{F}_{n_k+2}{}^{(n_m-1)})] \\ &+ {}_{k[lm]}\boldsymbol{F}_1{}^{(n_k+1)}[({}_{kl}\boldsymbol{F}_{n_k+2}{}^{(n_l-1)})\ {}_5\otimes_5\ ({}_{km}\boldsymbol{F}_{n_k+2}{}^{(n_m-1)})] \\ &+ {}_{k[ml]}\boldsymbol{F}_1{}^{(n_k+1)}[({}_{km}\boldsymbol{F}_{n_k+2}{}^{(n_m-1)})\ {}_5\otimes_5\ ({}_{kl}\boldsymbol{F}_{n_k+2}{}^{(n_l-1)})]\}\end{aligned} \qquad (39)$$

The generator matrices ${}_{kl}\boldsymbol{F}_i$ in the first term are formed from $\mathbf{C}_g{}^{*x2}$, ${}_{kl}\mathbf{F}_{g;i}{}^{x2}$, $\mathbf{C}_g{}^{x2}$, and the statistical weight matrices. The value of a is 25 or 15, depending upon whether ${}_{kl}\mathbf{F}_{g;i}{}^{x2}$ is used as generated (25×25) or is reduced to 15×15.[4] The generator matrices ${}_{km}\boldsymbol{F}_i$, $i \leq n_k$, in the second term are formed from $\mathbf{C}_r{}^{*x2}$, ${}_{km}\mathbf{A}_i{}^{x2}$, and the statistical weight matrices, while ${}_{km}\boldsymbol{F}_i$, $i > n_k$, are formed from $\mathbf{C}_a{}^{*x2}$, ${}_{km}\mathbf{F}_{g;i}{}^{x2}$, $\mathbf{C}_g{}^{x2}$, and the statistical weight matrices. Generator matrices ${}_{k[lm]}\boldsymbol{F}_i$ and ${}_{k[ml]}\boldsymbol{F}_i$ in the third and fourth terms are formulated using ${}_{kl}\mathbf{F}_g \otimes {}_{km}\mathbf{A}$ and ${}_{km}\mathbf{A} \otimes {}_{kl}\mathbf{F}_g$, respectively. The ${}_{km}\boldsymbol{F}_i$ and ${}_{kl}\boldsymbol{F}_i$, $i > n_k$, in the third and fourth terms are formulated using ${}_{km}\mathbf{F}_{g;i}$ and ${}_{kl}\mathbf{F}_{g;i}$.

The operation $\mathbf{X}\,{}_a\otimes_b\,\mathbf{Y}$ in the third and fourth terms of eq 39 is defined as follows: Let $\mathbf{X}$ be a column consisting of *ma* elements and $\mathbf{Y}$ a column consisting of *nb* elements. Then $\mathbf{X}\,{}_a\otimes_b\,\mathbf{Y}$ is a column consisting of *manb* elements arranged as shown in eq 40.

$$\mathbf{X}\,{}_a\otimes_b\,\mathbf{Y} = \begin{bmatrix} \begin{bmatrix} X_1 \\ X_2 \\ \vdots \\ X_a \end{bmatrix} & \otimes & \begin{bmatrix} Y_1 \\ Y_2 \\ \vdots \\ Y_b \end{bmatrix} \\ \begin{bmatrix} X_1 \\ X_2 \\ \vdots \\ X_a \end{bmatrix} & \otimes & \begin{bmatrix} Y_{b+1} \\ Y_{b+2} \\ \vdots \\ Y_{2b} \end{bmatrix} \\ \vdots & & \vdots \\ \begin{bmatrix} X_1 \\ X_2 \\ \vdots \\ X_a \end{bmatrix} & \otimes & \begin{bmatrix} Y_{nb-b+1} \\ Y_{nb-b+2} \\ \vdots \\ Y_{nb} \end{bmatrix} \\ \begin{bmatrix} X_{a+1} \\ X_{a+2} \\ \vdots \\ X_{2a} \end{bmatrix} & \otimes & \begin{bmatrix} Y_1 \\ Y_2 \\ \vdots \\ Y_b \end{bmatrix} \\ \vdots & & \vdots \\ \begin{bmatrix} X_{a+1} \\ X_{a+2} \\ \vdots \\ X_{2a} \end{bmatrix} & \otimes & \begin{bmatrix} Y_{nb-b+1} \\ Y_{nb-b+2} \\ \vdots \\ Y_{nb} \end{bmatrix} \\ \vdots & & \vdots \\ \begin{bmatrix} X_{ma-a+1} \\ X_{ma-a+2} \\ \vdots \\ X_{ma} \end{bmatrix} & \otimes & \begin{bmatrix} Y_{nb-b+1} \\ Y_{nb-b+2} \\ \vdots \\ Y_{nb} \end{bmatrix} \end{bmatrix} \qquad (40)$$

Special attention is required for ${}_{k[ml]}\boldsymbol{F}_{n_k+1}$ in the fourth term in eq 39. The generator matrices for bond $n_k + 1$ in chains $k + l$ and $k + m$ assume a different pattern from that normally obtained (e.g., in the third term), due to the reversal of the terms in the operation denoted ${}_5\otimes_5$ (compare the third and fourth terms). For this reason a corresponding rearrangement must be made in the columns of the rectangular statistical weight matrix used at the branch point. The manner in which the columns are interchanged can be specified as follows: Let each column be indexed by two integers (1, 2, . . . , ν) according to the ν rotational states for bonds $n_k + 1$ in the two chains. Those columns which are to be interchanged are indexed by the same two digits in permuted order. The necessity of making this change is eliminated by noting the relationship between the third and fourth terms of eq 39. If the nine elements obtained from the third term are arranged as a 3×3 matrix, the result obtained from the fourth term will be the transpose of this matrix.

Assuming that the procedures for matrix size reduction have been implemented, the dimensions for the generator matrices in eq 39 are as follows. First term: ${}_{kl}\boldsymbol{F}_1$, $6 \times 15\nu$; ${}_{kl}\boldsymbol{F}_{n_k+1}$, $15\nu \times 15\nu^2$; ${}_{kl}\boldsymbol{F}_{n_k+n_l}$, $15\nu \times 1$; all remaining ${}_{kl}\boldsymbol{F}_i$, $15\nu \times 15\nu$. Second term: ${}_{km}\boldsymbol{F}_1$, $6 \times 10\nu$; ${}_{km}\boldsymbol{F}_{n_k+1}$, $10\nu \times 15\nu^2$, $km\,\boldsymbol{F}_{n_k+n_m}$, $15\nu \times 1$; ${}_{km}\boldsymbol{F}_i$ with $1 < i \leq n_k$, $10\nu \times 10\nu$; ${}_{km}\boldsymbol{F}_i$ with $n_k + 1 < i < n_k + n_m$, $15\nu \times 15\nu$. Third and fourth terms: ${}_{k[lm]}\boldsymbol{F}_1$ and ${}_{k[ml]}\boldsymbol{F}_1$, $6 \times 10\nu$; ${}_{k[lm]}\boldsymbol{F}_{n_k+1}$ and ${}_{k[ml]}\boldsymbol{F}_{n_k+1}$, $20\nu \times 25\nu^2$; ${}_{kl}\boldsymbol{F}_{n_k+n_l}$ and ${}_{km}\boldsymbol{F}_{n_k+n_m}$, $25\nu \times 1$; ${}_{k[lm]}\boldsymbol{F}_i$ and ${}_{k[ml]}\boldsymbol{F}_i$ with $1 < i \leq n_k$, $20\nu \times 20\nu$; ${}_{kl}\boldsymbol{F}_i$ with $n_k + 1 < i < n_k + n_l$ and ${}_{km}\boldsymbol{F}_i$ with $n_k + 1 < i < n_k + n_m$, $5\nu \times 5\nu$.

Matrix Evaluation of the Moment of Inertia Tensor about the Center of Gravity. The starting point is eq 22. Equation 38 is used for ${}_{k}\mathbf{g}^{x2}$. For the remaining terms in eq 22 we have[4]

$$\begin{aligned}\sum_{i=0}^{n_k+n_l} {}_{kl}\mathbf{r}_{0i}{}^{x2} + \sum_{i=n_k+1}^{n_k+n_m} {}_{km}\mathbf{r}_{0i}{}^{x2} &= (\mathbf{C}_b{}^*)_{kl}\mathbf{F}_{r;1}{}^{(n_k+n_l)}\mathbf{C}_b \\ &\quad + \mathbf{C}_r{}^*({}_{km}\mathbf{A}^{x2})_1{}^{(n_k)}\mathbf{C}_c{}^*({}_{km}\mathbf{F}_{r;n_k+1}{}^{(n_m)})\mathbf{C}_b\end{aligned} \qquad (41)$$

where

$${}_{kl}\mathbf{F}_{r;i} = {}_{kl}\begin{bmatrix} \mathrm{A}^{x2} & (\mathbf{AC}_b)^{x2} \\ \mathbf{0} & 1 \end{bmatrix}_i \qquad (42)$$

$$\mathbf{C}_b{}^* = [\mathbf{C}_r{}^{*x2} \quad \mathbf{0}] \qquad (43)$$

$$\mathbf{C}_b = \mathrm{col}(0, 0, \ldots, 0, 1) \tag{44a}$$

and

$$\mathbf{C}_c{}^* = [\mathbf{E}_{16} \qquad \mathbf{0}] \tag{44b}$$

The average value is

$$\begin{aligned}\sum_{i=0}^{n_k+n_l} \langle {}_{kl}\mathbf{r}_{0i}{}^{x2} \rangle + \sum_{i=n_k+1}^{n_k+n_m} \langle {}_{km}\mathbf{r}_{0i}{}^{x2} \rangle \\ = Z^{-1}\{{}_{kl}\boldsymbol{F}_1{}^{(n_k+1)}[({}_{kl}\boldsymbol{F}_{n_k+2}{}^{(n_l-1)}) \otimes_{a,1} ({}_{km}\mathbf{U}_{n_k+2}{}^{n_m-1)})] \\ + {}_{km}\boldsymbol{F}_1{}^{(n_k+1)}[({}_{kl}\mathbf{U}_{n_k+2}{}^{(n_l-1)}) \otimes ({}_{km}\boldsymbol{F}_{n_k+2}{}^{(n_m-1)})]\}\end{aligned} \tag{45}$$

The generator matrices in the first term are formulated from the statistical weight matrices using eq 42, while those in the second term are obtained from the statistical weight matrices and either eq 42 or ${}_{km}\mathbf{A}^{x2}$. The value of a in eq 45 is 17 or 11, depending upon whether or not the matrix size has been reduced. Assuming that matrix size reduction has been effected, the dimensions of the generator matrices in eq 45 are as follows. First term: ${}_{kl}\boldsymbol{F}_1$, $6 \times 11\nu$; ${}_{kl}\boldsymbol{F}_{n_k+1}$, $11\nu \times 11\nu^2$; ${}_{kl}\boldsymbol{F}_{n_k+n_l}$, $11\nu \times 1$; all other ${}_{kl}\boldsymbol{F}_i$, $11\nu \times 11\nu$. Second term: ${}_{km}\boldsymbol{F}_1$, $6 \times 10\nu$, ${}_{km}\boldsymbol{F}_{n_k+1}$, $10\nu \times 11\nu^2$; ${}_{km}\boldsymbol{F}_{n_k+n_m}$, $11\nu \times 1$; ${}_{km}\boldsymbol{F}_i$ for which $1 < i \leq n_k$, $10\nu \times 10\nu$; ${}_{km}\boldsymbol{F}_i$ for which $n_k + 1 < i < n_k + n_m$, $11\nu \times 11\nu$.

The statistical mechanical average of ${}_k\mathbf{S}_{x2}$ is obtained from eq 39, 45, and 46.

$$\langle {}_k\mathbf{S}_{x2} \rangle = N^{-1} \left(\sum_{i=0}^{n_k+n_l} \langle {}_{kl}\mathbf{r}_{0i}{}^{x2} \rangle + \sum_{i=n_m+1}^{n_k+n_m} \langle {}_{km}\mathbf{r}_{0i}{}^{x2} \rangle \right) - \langle {}_k\mathbf{g}^{x2} \rangle \tag{46}$$

Expressions for ${}_{kl}\mathbf{a}$, $\langle {}_k\mathbf{g} \rangle$, and $\langle {}_k\mathbf{S}_{x2} \rangle$ (eq 28, 36, and 46, respectively) apply to any unperturbed molecule which consists of three branches emanating from a common atom. Bonds may be of different types and may occur in any specified order. Consequently the equations apply to molecules as simple as a branched polymethylene or as complex as lipids derived from glycerol or sphingosine. Extension to molecules containing more than one branch point, or branch points of higher functionality, is possible, but the required generator matrices will become inconveniently large.

Relationship between k and the Asymmetry of $\langle {}_k\mathbf{S}_{x2} \rangle$

Consider an *unbranched* chain molecule consisting of n bonds. Associated with bond i as a tensor, $\mathbf{p}_i$, considered to be invariant to the configuration when expressed in the coordinate system defined for that bond. Let $\mathbf{P}_j$ be the tensor sum of the $\mathbf{p}_i$ for a spceified configuration, each $\mathbf{p}_i$ having been transformed to its representation in the coordinate system defined for bond j.

$$\mathbf{P}_j = \sum_{i=1}^{n} \mathbf{T}_{ij}\mathbf{p}_i\mathbf{T}_{ij}{}^{\mathrm{T}} \tag{47}$$

Here $\mathbf{T}_{ij}$ is the matrix required to transform from the coordinate system defined for bond i to that defined for bond j when the molecule is in the specified configuration. Interconversion of the various $\mathbf{P}_j$ may be affected by an appropriate similarity transform.

$$\mathbf{P}_k = \mathbf{T}_{jk}\mathbf{P}_j\mathbf{T}_{jk}{}^{\mathrm{T}} \tag{48}$$

The configurational average obtained in the coordinate system defined for bond j is

$$\langle \mathbf{P}_j \rangle = \sum_{i=1}^{n} \langle \mathbf{T}_{ij}\mathbf{p}_i\mathbf{T}_{ij}{}^{\mathrm{T}} \rangle \tag{49}$$

Similarly,

$$\langle \mathbf{P}_k \rangle = \langle \mathbf{T}_{jk}\mathbf{P}_j\mathbf{T}_{jk}{}^{\mathrm{T}} \rangle \tag{50}$$

Interconversion of $\langle \mathbf{P}_j \rangle$ and $\langle \mathbf{P}_k \rangle$ via a similarity transform can be achieved only in special cases. While identical traces must be obtained for $\langle \mathbf{P}_k \rangle$ and $\langle \mathbf{P}_j \rangle$, asymmetries deduced from their principal moments may differ.

A convenient illustration is provided by consideration of the carbon atoms in n-pentane. Assume a bond length of 1.53 Å, a bond angle of 112°, rotational states located at 0 and ±120°, and the approximation that all nine configurations are equally probable. Then the average moment of inertia tensor has principal moments of 1.71, 0.53, and 0.45 Å^2 if the internal coordinate system is that defined by a terminal bond and its neighbor. On the other hand, the principal moments are 1.81, 0.56, and 0.32 Å^2 if the internal coordinate system is defined by the two internal bonds. Each trace is 2.69 Å^2, but a greater asymmetry arises when averaging is achieved in the latter coordinate system. The preceding two tensors are different from that obtained by first diagonalizing the tensor for each configuration and then averaging the largest, second largest, and smallest principal moments. Averaged principal moments are 2.17, 0.43, and 0.09 Å^2, respectively. Once again the trace is 2.69 Å^2, but the asymmetry is larger than that obtained when averaging occurs in either of the internal coordinate systems. Averaging in an internal coordinate system suppresses the asymmetries of individual configurations.[10]

In the case of current interest, averaging takes place using the internal coordinate system defined for the first bond in branch k. With a simple symmetric linear chain molecule, such as a linear polymethylene, identical results must be obtained for either directionality along the chain. The equivalent statement applies to a polymethylene containing a trifunctional branch point only if all branches are of the same length. If branches differ in length, different asymmetries may be deduced from the principal moments of the various $\langle {}_k\mathbf{S}_{x2} \rangle$. This effect is illustrated by the numerical computations reported in the following paper.[11]

Acknowledgment. This work was carried out while on sabbatical leave at Stanford University, with support provided by a John Simon Guggenheim Memorial Foundation Fellowship. The author thanks Professor Flory for his hospitality.

References and Notes

(1) K. Nagai, *J. Chem. Phys.*, **38**, 924 (1963).
(2) R. L. Jernigan and P. J. Flory, *J. Chem. Phys.*, **50**, 4185 (1969).
(3) P. J. Flory, *Macromolecules*, **7**, 381 (1974).
(4) P. J. Flory and D. Y. Yoon, *J. Chem. Phys.*, **61**, 5358 (1974).
(5) W. L. Mattice, *Macromolecules*, **8**, 644 (1975).
(6) W. L. Mattice, *Macromolecules*, **9**, 48 (1976).
(7) W. L. Mattice and D. K. Carpenter, *Macromolecules*, **9**, 53 (1976).
(8) W. L. Mattice, *Macromolecules*, **10**, 511 (1977).
(9) W. L. Mattice, *Macromolecules*, **10**, 516 (1977).
(10) D. Y. Yoon and P. J. Flory, *J. Chem. Phys.*, **61**, 5366 (1974).
(11) W. L. Mattice, *Macromolecules*, following paper in this issue.
(12) P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience, New York, N.Y., 1969.
(13) B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, **17**, 1301 (1949).
(14) T. A. Orofino, *Polymer*, **2**, 305 (1961).