Persistence Vectors, Average Center of Mass Vectors, and Moment of Inertia Tensors for Branched Polymethylenes

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ABSTRACT: Rotational isomeric state theory has been used to compute the persistence vectors, average center of mass vectors, and average moment of inertia tensors for unperturbed polymethylenes containing a trifunctional branch point. In each case averaging occurs in an internal coordinate system defined by the first two bonds in a particular branch. Results may depend upon the selection of this branch if the three branches contain different numbers of bonds. Spherical symmetry is always attained at sufficiently high molecule weight. If all branches contain the same number of bonds, asymmetry exists when the total number of bonds is less than about 50. The corresponding linear polymethylene has a larger asymmetry. In contrast, the asymmetry obtained in a coordinate system defined by a short (e.g., ethyl) branch may be *larger* than that attained for the corresponding linear polymethylene. Furthermore, the asymmetry sensed by the ethyl group persists to much higher molecular weight. The type of asymmetry also differs. Prolate ellipsoids are attained for small linear polymethylenes and branched polymethylenes in which all branches are of equal length. However, an oblate ellipsoid may be attained if a butyl group is present, while the asymmetry sensed by the ethyl groups cannot be represented by a prolate or oblate ellipsoid.

The mean-square unperturbed radius of gyration, $\langle s^2\rangle_0$, for a linear chain molecule becomes proportional to the number, n, of skeletal bonds at sufficiently large n.[1] A similar statement applies to branched molecules provided the various n_i/n_j are held constant while n increases (n_i and n_j denote the number of skeletal bonds in branches i and j, respectively).[2,3] Calculation of the second moments as a function of n for linear[1] and branched[4–6] polymers demonstrates that the proportionality is lost at small n. In the case of polymethylene, $\langle s^2\rangle_0/n$ approaches to within 5% of its asymptotic limit when n is about 500 for linear molecules[1,4,7] and about 300 for molecules containing a trifunctional or tetrafunctional branch point and having all branches of the same length.[4]

Distribution of atoms about the center of mass must depart from spherical symmetry at low molecular weight. Asymmetry about the first two bonds of an unperturbed polymethylene of low molecular weight suggests a prolate ellipsoid, as revealed by the average moment of inertia tensor, $\langle \mathbf{S}_{x2}\rangle$.[8] The effect of branching on the asymmetry at low molecular weight, as well as its effect on the value of n required for the loss of asymmetry in $\langle \mathbf{S}_{x2}\rangle$, are unknown. These considerations are the subject of investigation in the present work. Numerical calculations appropriate for unperturbed polymethylenes are carried out using rotational isomeric state theory in the form presented in the preceding paper.[9] Calculations are also performed which demonstrate certain relationships between the persistence vectors and average center of mass vectors for linear and branched molecules.

Rotational States and Statistical Weight Matrices

All ∠CCC are 112°[10–13] except angles at the branch point, which are assigned the value found in isobutane (111°).[14] Dihedral angles for rotational states occur at 0 and ±120° for bonds which do not involve the carbon atom at the branch point. Rotational states for bonds involving the branch point carbon atom have their dihedral angles separated by 120°. One rotational state is assigned the dihedral angle which will produce a planar trans orientation for the CCCH group, the hydrogen atom in question being the one bonded to the carbon atom at the branch point.

Statistical weight matrices for bonds near the trifunctional branch point (see Figure 1 of the preceding paper) are

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

$$ {}_2\mathbf{U}_2 = \begin{bmatrix} 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \tag{2}$$

$$ {}_3\mathbf{U}_2 = \begin{bmatrix} 1 & \sigma\omega & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma\omega \end{bmatrix} \tag{3}$$

and eq 4.

$$ {}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1 = \begin{bmatrix} \omega & \omega & \tau & \tau & \tau\omega & \tau^2\omega & 1 & \omega & \tau \\ \omega & 1 & \tau & \tau & \tau & \tau^2\omega & \omega & \omega & \tau\omega \\ \omega & 1 & \tau\omega & \tau\omega & \tau\omega & \tau^2\omega^3 & 1 & 1 & \tau\omega \end{bmatrix} \tag{4}$$

These matrices were formulated as described in ref 15. A value of unity has been assigned to ψ, while σ and σ^2 have been factored from eq 1 and 4, respectively. Columns are indexed by t, g$^+$, and g$^-$ when there are three and tt, tg$^+$, tg$^-$, g$^+$t, g$^+$g$^+$, g$^+$g$^-$, g$^-$t, g$^-$g$^+$, and g$^-$g$^-$ when there are nine. Rows are t, g$^+$, g$^-$ for the preceding bond. Statistical weights for individual first- and second-order interactions are denoted by σ and ω, respectively, while two simultaneous first-order interactions merit a statistical weight of $\sigma\tau$.[1] Statistical weight matrices for the remaining nonterminal bonds are the ones used for a linear polymethylene.[16]

$$ \mathbf{U} = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \tag{5}$$

Condensation of eq 5 to a 2 × 2 matrix can be effected due to the symmetry of the *linear* polymethylene chain.[17,18] The requisite symmetry is destroyed by the presence of the branch point, forcing use of eq 5 as it stands.

Numerical values for σ and ω of 0.54 and 0.088, respectively, reproduce the experimental characteristics of unperturbed linear polymethylene chains at 140 °C.[1,16,19] The appropriate value for τ is uncertain, although it certainly does not exceed σ.[1] Calculations were performed for $\tau = \sigma$ and $\tau = \sigma/10$. A few calculations were also carried out for small molecules using $\sigma = 0.43$ and $\omega = 0.034$, values appropriate for an unperturbed polymethylene at 25 °C.[20]

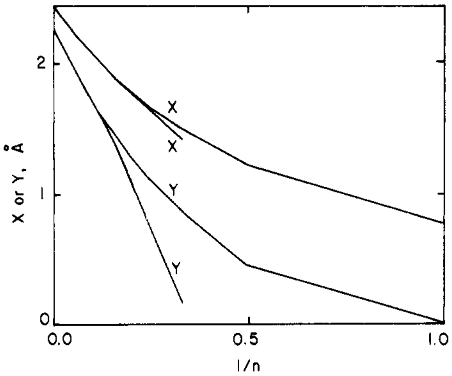

Figure 1. Components of the averaged center of mass vector when all conformations are equally probable. Branched molecules have $n_1 = n_2 = n_3$. Results for linear molecules, which commence at $n = 1$, are from ref 8. The Z component is −0.30 Å for isobutane and zero in all other cases.

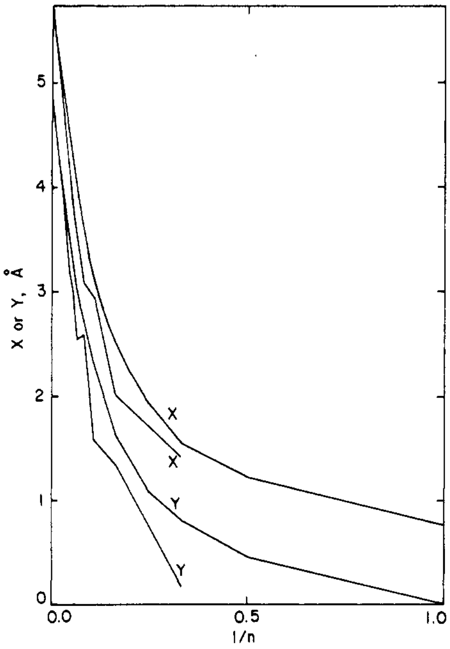

Figure 2. Same as Figure 1 except that rotations are interdependent ($\sigma = \tau = 0.54$, $\omega = 0.088$). Z components are −0.30 Å for isobutane, 0.01–0.02 Å for 3-ethylpentane, 4-propylheptane, and 5-butylnonane, and 0.00 Å in all other cases.

Persistence vectors, average center of mass vectors, and average moment of inertia tensors were calculated using eq 27, 28, 36, 39, 45, and 46 of the preceding manuscript.[9]

Center of Mass Vectors and Persistence Vectors

Branches of Equal Length. X and Y components of the average center of mass vector, $\langle {}_1\mathbf{g}\rangle$, expressed in the coordinate system defined[21] by the first two bonds in branch 1, are shown in Figure 1 for the case where all branches contain the same number of bonds and all rotational states are equally probable. Corresponding results for linear polymethylene chains are from ref 8. The Z component is zero except for the branched molecule with $n = 3$. Branches 1 and 2 define the coordinate system for isobutane. It is readily apparent that the center of mass does not lie in the plane defined by these two bonds; it is 0.30 Å out of this plane. Asymptotic values, $\langle x\rangle_\infty$ and $\langle y\rangle_\infty$, are identical for the branched and linear molecules. These limiting values are also obtained for the persistence vector of the linear chain[8] and for ${}_{12}\mathbf{a}_\infty$ and ${}_{13}\mathbf{a}_\infty$, results which are in accord with eq 8 of the preceding paper.[9]

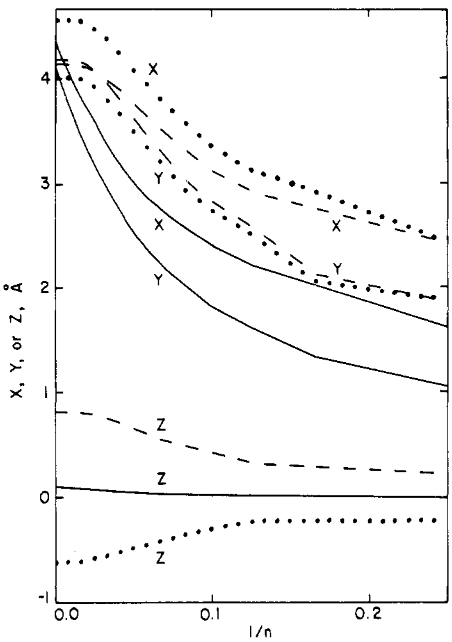

Figure 3. Components of ${}_{12}\mathbf{a}$ (dots), ${}_{13}\mathbf{a}$ (dashes), and $\langle {}_1\mathbf{g}\rangle$ (solid) when $n_1 = 2$, $n_2 = n_3$, $\sigma = \tau = 0.54$, $\omega = 0.088$.

$$\mathbf{a}_\infty = \langle \mathbf{g}\rangle_\infty = {}_{12}\mathbf{a}_\infty = {}_{13}\mathbf{a}_\infty = \langle {}_1\mathbf{g}\rangle_\infty = \begin{bmatrix} 2.45\ \text{Å} \\ 2.28\ \text{Å} \\ 0 \end{bmatrix} \qquad (6)$$

$$\sigma = \tau = \omega = 1$$

Absence of presubscripts distinguishes the persistence vector and center of mass vector for the linear chain. X and Y components of the average center of mass vector are unaffected by the trifunctional branch point when nine or more bonds are present. For smaller molecules $\langle \mathbf{g}\rangle$ is larger than $\langle {}_1\mathbf{g}\rangle$.

Inclusion of the first- and second-order interactions produces the results depicted in Figure 2. The Z component of the center of mass vector for the branched molecule is slightly out of the XY plane at small n but enters this plane as $n \to \infty$. A Z component of 0.02 Å is obtained for 3-ethylpentane. As in the previous case, the various vectors have a common asymptotic limit.

$$\mathbf{a}_\infty = \langle \mathbf{g}\rangle_\infty = {}_{12}\mathbf{a}_\infty = {}_{13}\mathbf{a}_\infty = \langle {}_1\mathbf{g}\rangle_\infty = \begin{bmatrix} 5.75\ \text{Å} \\ 4.86\ \text{Å} \\ 0 \end{bmatrix} \qquad (7)$$

$$\sigma = \tau = 0.54;\ \omega = 0.088$$

Approximately 50 bonds are now required to make the X and Y components identical for branched and linear molecules. Smaller molecules have $\langle \mathbf{g}\rangle$ larger than $\langle {}_1\mathbf{g}\rangle$.

A tenfold reduction in τ produces small effects (up to about 0.1 Å) on the X and Y components of $\langle {}_1\mathbf{g}\rangle$ when the branches each contain 2–5 bonds. These effects vanish as the number of bonds increases.

Branch 1 Ethyl, $n_2 = n_3$. Components of ${}_{12}\mathbf{a}$, ${}_{13}\mathbf{a}$, and $\langle {}_1\mathbf{g}\rangle$ are shown in Figure 3 for the case where $n_1 = 2$ and $n_2 = n_3$. Statistical weights were those used to obtain Figure 2 and eq 7. Several alterations in behavior occur. Asymptotic limits for the vectors no longer lie in the XY plane.

$${}_{12}\mathbf{a}_\infty = \begin{bmatrix} 4.55\ \text{Å} \\ 4.01\ \text{Å} \\ -0.60\ \text{Å} \end{bmatrix} \qquad (8)$$

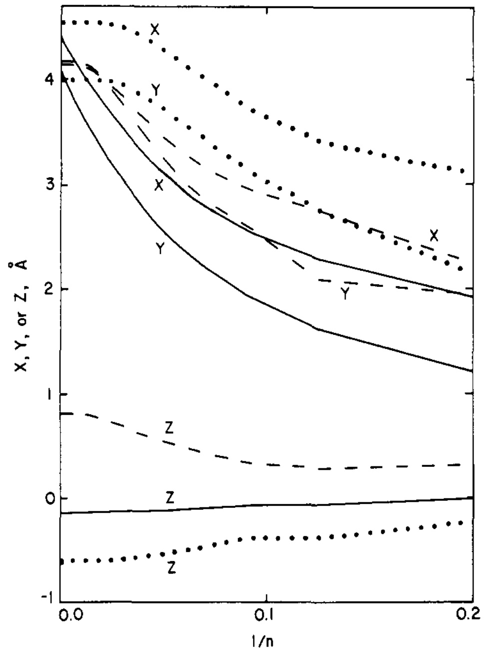

Figure 4. Same as Figure 3 except $n_1 = 2$ and $n_2 = 2n_3$.

$$ {}_{13}\mathbf{a}_\infty = \begin{bmatrix} 4.14\ \text{Å} \\ 4.18\ \text{Å} \\ 0.81\ \text{Å} \end{bmatrix} \qquad (9)$$

$$ \langle {}_1\mathbf{g} \rangle_\infty = \begin{bmatrix} 4.35\ \text{Å} \\ 4.09\ \text{Å} \\ 0.10\ \text{Å} \end{bmatrix} \qquad (10)$$

A priori probabilities for the gauche states of opposite sign are unequal for bonds near the branch point.[15] Effects of these probabilities on the vectors persist as n_2 and n_3 approach infinity if n_1 remains small. In contrast to the previous cases, asymptotic values for $_{12}\mathbf{a}$, $_{13}\mathbf{a}$, and $\langle {}_1\mathbf{g} \rangle$ are no longer identical (eq 8–10). Differences lie in their magnitudes as well as their orientations. Lengths of 6.12, 5.96, and 6.00 Å are obtained for $_{12}\mathbf{a}_\infty$, $_{13}\mathbf{a}_\infty$, and $\langle {}_1\mathbf{g} \rangle_\infty$, respectively. Each of these is smaller than 7.53 Å, the length of the vectors expressed in eq 7. The asymptotic value for the components of $\langle {}_1\mathbf{g} \rangle$ is the average of the corresponding component for the two asymptotic persistence vectors, in accord with eq 11 of the preceding paper.[9] One of these vectors, $_{13}\mathbf{a}_\infty$, has its largest component along the Y axis. Vectors $\langle {}_i\mathbf{g} \rangle_\infty$, $_{i1}\mathbf{a}_\infty$, and $_{ij}\mathbf{a}_\infty$ ($i = 2$ or 3, $j = 2$ or 3, $i \neq j$) are, of course, identical with the result presented in eq 7.

Branch 1 Ethyl, $n_2 = 2n_3$. Components of $_{12}\mathbf{a}$, $_{13}\mathbf{a}$, and $\langle {}_1\mathbf{g} \rangle$ are depicted in Figure 4 for the case where $n_1 = 2$ and $n_2 = 2n_3$. Asymptotic values for the persistence vectors are identical with those expressed in eq 8 and 9. The vector $\langle {}_1\mathbf{g} \rangle_\infty$ is now $\frac{2}{3}\,{}_{12}\mathbf{a}_\infty + \frac{1}{3}\,{}_{13}\mathbf{a}_\infty$, in accord with eq 10 of the preceding manuscript.

Moment of Inertia Tensors

Branches of Equal Length. Consider first the case where all rotational states are equally probable. Averaged moment of inertia tensors consist of four distinct elements provided each branch contains two or more bonds. Six distinct elements are encountered for isobutane. In each case averaging takes place in the internal coordinate system used to express $\langle {}_1\mathbf{g} \rangle$. Diagonalization may be accomplished through rotation about the Z axis for molecules other than isobutane. Principal axis a makes an angle of 45° with the X axis when n_1 is greater than six, while principal axis c is coincident with the Z axis. Components along the principal axes are presented in Figure 5. The components along principal axes a and c are identical for isobutane and exceed the remaining component by nearly a factor of 20. For all other members of this series the elements along principal axes b and c are nearly identical. The remaining component is larger until n becomes about 50, at which point the moments converge.

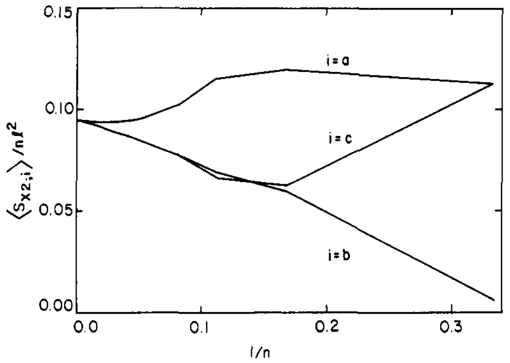

Figure 5. Components of the moment of inertia tensor along principal axes a, b, and c when $n_1 = n_2 = n_3$ and all conformations are equally probable. Averaging occurs in the coordinate system defined by two terminal bonds.

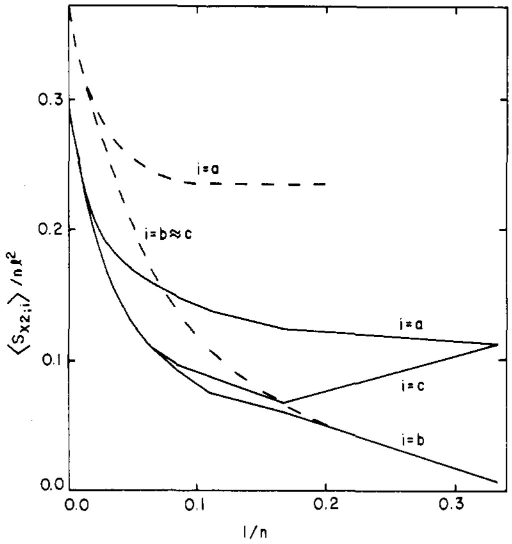

Figure 6. Components of the moment of inertia tensor along principal axes a, b, and c for linear[8] (dashed) and branched (solid) polymethylenes ($\sigma = \tau = 0.54$, $\omega = 0.088$). Branched molecules have $n_1 = n_2 = n_3$.

Incorporation of first- and second-order interactions yields the results depicted in Figure 6. For comparison the principal moments computed[8] for linear polymethylene chains are also shown. Principal axis a makes an angle of 43° with the X axis for the high molecular weight molecules, both branched and linear.[8] Values of $\langle S_{2;b} \rangle$ and $\langle S_{2;c} \rangle$ are nearly identical for 3-ethylpentane and n-heptane. Increasing molecular weight serves to decrease the differences in the components along principal axis a, although a higher result is always obtained for the linear molecule. Components along principal axes b and c for the linear molecule exceed those for the branched molecule when the number of bonds exceeds six. Convergence of the components for each type of molecule occurs when the number of bonds becomes about 50. The ratio of the asymptotic limits for the branched molecules in Figures 5 and 6 is in accord with the ratio of their $(\langle s^2 \rangle_0 / nl^2)_\infty$.[4] The asymptotic

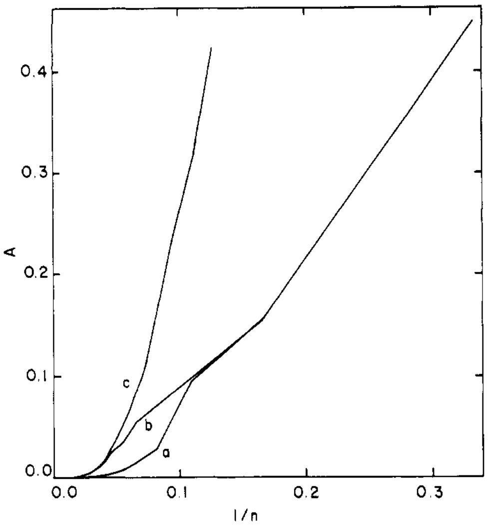

Figure 7. Asymmetry parameter, A, for branched molecules ($n_1 = n_2 = n_3$) using $\sigma = \tau = \omega = 1$ (curve a) and $\sigma = \tau = 0.54$, $\omega = 0.088$ (curve b). Curve c presents results for unperturbed linear polymethylenes.

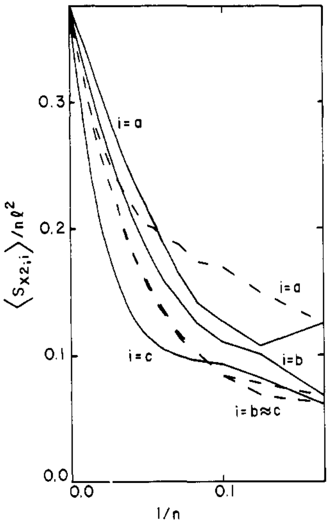

Figure 8. Components along the principal axes of the averaged moment of inertia tensor for polymethylenes which have an ethyl group attached to the central atom in the main chain. The internal coordinate system is provided by the ethyl group (solid line) or by the terminal two bonds in the main chain (dashed lines).

limit for the components along the principal axes for the branched polymethylene is 7/9 of that for the linear polymethylene, as required by eq 11.[2,3]

$$(\langle s^2\rangle_{0,\text{branched}}/\langle s^2\rangle_{0,\text{linear}})_{n\to\infty} = n^{-3}\sum_{j=1}^{3}(3nn_j^2 - 2n_j^3) \quad (11)$$

The preceding moment of inertia tensors for flexible branched and linear polymethylenes containing fewer than 50 bonds have the asymmetry of a prolate ellipsoid. Ellipsoids for the small linear molecules have larger axial ratios than ellipsoids for the corresponding branched molecules.

Moments along the principal axes in Figures 5 and 6 differ for a specified n because of differences in $\langle s^2\rangle_0$ and differences in asymmetry. Attention is focused on the latter through the definition of a parameter A as

$$A = \frac{(\langle S_{2;a}\rangle - \langle S_{2;b}\rangle)^2 + (\langle S_{2;a}\rangle - \langle S_{2;c}\rangle)^2 + (\langle S_{2;b}\rangle - \langle S_{2;c}\rangle)^2}{2(\langle S_{2;a}\rangle^2 + \langle S_{2;b}\rangle^2 + \langle S_{2;c}\rangle^2)} \quad (12)$$

Figure 7 presents A for the branched molecules whose principal moments are depicted in Figures 5 and 6. Asymmetry increases as $1/n$ increases. Inclusion of first- and second-order interactions brings about an increase in asymmetry for n between 12 and 50. Molecules containing three branches of equal length have a lower asymmetry than linear polymethylenes when n is less than 24.

A tenfold reduction in τ has a minor effect on the moment of inertia tensor for branched molecules whose n is less than 18. Maximal effect is obtained with 3-ethylpentane, whose asymmetry increases when τ decreases. Calculations using $\sigma = \tau = 0.43$ and $\omega = 0.034$, values appropriate for 25 °C, yield components along the principal axes which are slightly larger than those depicted in Figure 6. This result is consistent with the sign of the temperature coefficient for the unperturbed dimensions of linear polymethylene.[22-24]

Ethyl Branch. Attention is now focused on a polymethylene which has an ethyl group bonded to the middle atom in the main chain. Two separate calculations were performed for each molecule. In the first calculation of $\langle {}_1\mathbf{S}_{x2}\rangle$ the ethyl group was considered to be branch 2, while branches 1 and 3 constituted the main chain. Four distinct elements occur in $\langle {}_1\mathbf{S}_{x2}\rangle$ as $n \to \infty$. The tensor may be rendered diagonal using the same rotation required for the linear polymethylene. In the second calculation of $\langle {}_1\mathbf{S}_{x2}\rangle$ the ethyl group was considered to be branch 1, while branches 2 and 3 constituted the main chain. The resulting tensor contains six distinct elements even when n is 200.

Components along the principal axes are depicted in Figure 8. The asymptotic limit is now that attained by linear polymethylenes. Such behavior is in accord with eq 11. Principal moments in the first calculation (branch 2 = ethyl) converge at about the same n as was required to produce convergence for linear polymethylenes. Molecules of smaller n have the distribution of a prolate ellipsoid. A much larger n is required to produce convergence of the principal moments in the second calculation (branch 1 = ethyl). Differences are well illustrated by a polymethylene consisting of an ethyl group bonded to the 50th carbon atom in a chain containing 99 carbon atoms. A symmetric distribution will be found about the terminal two bonds in the main chain, but the distribution about the ethyl group is definitely asymmetric. Furthermore, the distribution about the ethyl group cannot be represented by a prolate ellipsoid.

Asymmetry parameters are depicted in Figure 9. The tensor obtained in the first calculation (branch 2 = ethyl) has an asymmetry between that obtained for the linear polymethylene and the molecule with three branches of equal length when n is 4, 8, 10, 12, or 14. At higher n the curve merges with that for the molecule with three branches of equal length. Asymmetry about the ethyl group, obtained in the second calculation, goes through a minimum when n is 8 and experiences a maximum when n is 20. A greater asymmetry is found about the ethyl group than about the terminal two bonds in a linear chain when n exceeds 16. Molecules treated in this section provide an excellent illustration of the dependence of asymmetry on the location of the internal coordinate system in which averaging occurs.[9]

Butyl Branch. Figure 10 depicts principal moments of polymethylenes which have a butyl group attached to the central atom of the main chain. Averaging was accomplished in the coordinate system defined by the terminal two bonds in the butyl group. The asymptotic limit is that attained by linear polymethylenes, but convergence of the principal moments is delayed. Distributions for molecules with n down to about 20 approximate an oblate ellipsoid. Asymmetries, de-

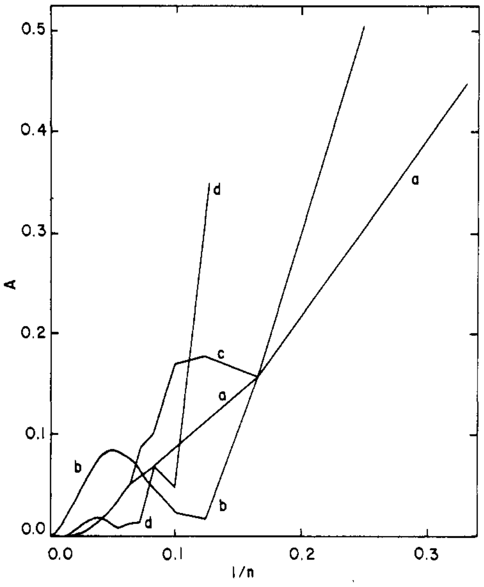

Figure 9. Asymmetry parameter for branched polymethylenes ($\sigma = \tau = 0.54$, $\omega = 0.088$). Curve a, $n_1 = n_2 = n_3$; curve b, $n_1 = 2$, $n_2 = n_3$; curve c, $n_1 = n_3$, $n_2 = 2$; curve d, $n_1 = 4$, $n_2 = n_3$. Averaging occurs in the coordinate system defined by the first two bonds in branch 1.

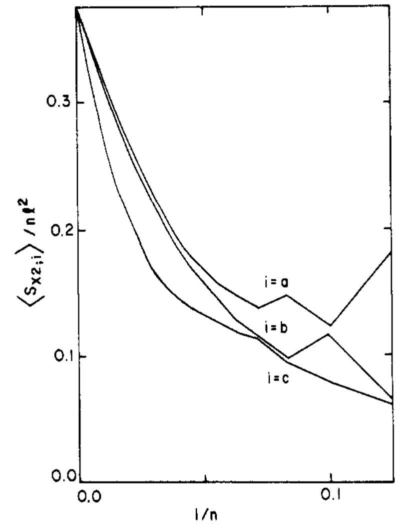

Figure 10. Components along the principal axes of the averaged moment of inertia tensor for polymethylenes which have a butyl group attached to the central atom in the main chain. The internal coordinate system is provided by the terminal two bonds in the butyl group.

picted in Figure 9, exceed those for the corresponding linear polymethylenes when n exceeds 26. However, the asymmetry is not as great as that found about an ethyl group.

Conclusion

Unperturbed polymethylenes obtain spherical symmetry as $n \rightarrow \infty$, independent of the location of the internal coordinate system and independent of branching. Asymmetry is present at low molecular weight. The same number of bonds is required for the onset of asymmetry in linear polymethylenes and in polymethylenes which consist of three branches of equal length, the internal coordinate system being that defined by two terminal bonds. Molecules of lower n have the distribution of a prolate ellipsoid, the larger axial ratio being obtained for the linear molecule. Asymmetry about the terminal bonds in short branches (ethyl or butyl) persists to much larger values of n and does not suggest a prolate ellipsoid. An ellipsoid may be found for the terminal two bonds in the butyl group, but it is oblate.

Persistence vectors and averaged center of mass vectors for branched molecules become identical with those for the corresponding linear chain molecules as $n \rightarrow \infty$, provided the free terminus of a "large" branch is used to establish the internal coordinate system for the branched molecule. The rate of the final approach to the asymptotic limit is also the same for branched and linear molecules under these conditions. Different asymptotic limits are obtained if a "small" branch is used to establish the internal coordinate system for the branched molecule.

The above conclusions concerning the asymmetry of the moment of inertia tensor and the relationships between the persistence vectors averaged center of mass vectors follow directly from rotational isomeric state theory. These phenomena cannot be investigated using random-flight statistics.

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References and Notes

(1) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N.Y., 1969.
(2) B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, **17,** 1301 (1949).
(3) T. A. Orofino, *Polymer*, **2,** 305 (1961).
(4) W. L. Mattice and D. K. Carpenter, *Macromolecules*, **9,** 53 (1976).
(5) W. L. Mattice, *Macromolecules*, **10,** 511 (1977).
(6) W. L. Mattice, *Macromolecules*, **10,** 516 (1977).
(7) R. L. Jernigan and P. J. Flory, *J. Chem. Phys.*, **50,** 4178 (1969).
(8) D. Y. Yoon and P. J. Flory, *J. Chem. Phys.*, **61,** 5366 (1974).
(9) W. L. Mattice, *Macromolecules, preceding paper* in this issue.
(10) H. J. M. Bowen and L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions", The Chemical Society, London, 1958; Supplement, 1965.
(11) H. M. M. Shearer and V. Vand, *Acta Crystallogr.*, **9,** 379 (1956).
(12) R. A. Bonham, L. S. Bartell, and D. A. Kohl, *J. Am. Chem. Soc.*, **81,** 4765 (1959).
(13) D. R. Lide, Jr., *J. Chem. Phys.*, **33,** 1514 (1960).
(14) D. R. Lide, Jr., *J. Chem. Phys.*, **33,** 1519 (1960).
(15) W. L. Mattice, *Macromolecules*, **8,** 644 (1975).
(16) A. Abe, R. L. Jernigan, and P. J. Flory, *J. Am. Chem. Soc.*, **88,** 631 (1966).
(17) K. Nagai, *J. Chem. Phys.*, **48,** 5646 (1968).
(18) P. J. Flory and Y. Abe, *J. Chem. Phys.*, **54,** 1351 (1971).
(19) P. J. Flory, *J. Polym. Sci., Polym. Phys. Ed.*, **11,** 621 (1973).
(20) G. D. Patterson and P. J. Flory, *J. Chem. Soc., Faraday Trans. 2*, **68,** 1098 (1972).
(21) P. J. Flory and D. Y. Yoon, *J. Chem. Phys.*, **61,** 5358 (1974).
(22) A. Ciferri, D. A. J. Hoeve, and P. J. Flory, *J. Am. Chem. Soc.*, **83,** 1015 (1961).
(23) P. J. Flory, A. Cieferri, and R. Chiang, *J. Am. Chem. Soc.*, 83, 1023 (1961).
(24) R. Chiang, *J. Phys. Chem.*, **70,** 2348 (1966).