Mean-Square Unperturbed Radii of Gyration for Molecules Containing a Single Trifunctional or Tetrafunctional Branch Point and Having Short-Range Interactions Represented by a Symmetric Threefold Rotation Potential[1]

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ABSTRACT: The mean-square unperturbed radius of gyration, $\langle s^2\rangle_0$, for a molecule containing a single trifunctional or tetrafunctional branch point has been computed using rotational isomeric state theory. Various symmetric threefold rotation potentials have been used. Bond lengths are all assumed to be identical, and bond angles are all tetrahedral. Mean-square unperturbed radii of gyration for the corresponding linear molecule, $\langle s_{\text{lin}}^2\rangle_0$, are also computed. The asymptotic limit for $g = \langle s^2\rangle_0/\langle s_{\text{lin}}^2\rangle_0$ as the number of bonds increases is in agreement with results obtained using random flight statistics. However, the number of bonds required for g to attain the asymptotic limit, as well as the nature of the approach to that limit, are extremely sensitive to the three-bond and four-bond interactions present in the branched macromolecule. Statistical weights appropriate for polyethylene cause g to approach the asymptotic limit from below.

The rotational isomeric state approximation has been used successfully to treat several properties of linear macromolecules.[2–4] Recently methods have been developed which produce the configuration partition function for branched macromolecules subject to the rotational isomeric state approximation.[5] The expressions required to compute the mean-square unperturbed radius of gyration for a macromolecule consisting of three branches which emanate from a common atom are described in the preceeding paper.[6] They can readily be extended to treat molecules with additional branches and branch points of higher functionality. It is assumed that the short-range interactions are adequately represented by three-bond and four-bond interactions. The branches need not be of the same length nor of the same chemical composition, and a particular branch may be a homopolymer or a copolymer with the monomer units occurring in any desired sequence. The present objective is to obtain numerical results for the case where the branched macromolecule is a homopolymer characterized by tetrahedral geometry at each chain atom and a symmetric threefold rotation potential. These results will be compared with those obtained using random flight statistics.[7,8]

Computations

Molecules consisting of three or four branches which emanate from a common atom are shown diagrammatically in a preceeding paper.[5] The branches in the case where the branch point is trifunctional will be numbered so that $n_1 \geq n_2 \geq n_3$, where n_j is the number of bonds in branch j. The atom from which branching occurs is considered to be a part of branch 1. This procedure leads to the main chain being branch 1 plus branch 2. The molecules treated which have a tetrafunctional branch point will have $n_1 = n_2 = n_3 = n_4$. The symbols ${}_jA_i$, ${}_j\mathbf{l}_i$ and ${}_j\mathbf{U}_i$ refer to atom, bond vector, and statistical weight matrix i in branch j. The total number of bonds is represented by n. The mean-square unperturbed radius of gyration of branch j, the main chain, and the entire branched macromolecule are represented by $\langle s_j^2\rangle_0$, $\langle s_{\text{mc}}^2\rangle_0$, and $\langle s^2\rangle_0$, respectively. These quantities were computed by the procedures described in ref 6. The mean-square unperturbed radius of gyration for the corresponding linear macromolecule, $\langle s_{\text{lin}}^2\rangle_0$, was computed via the customary procedure.[3]

The statistical weight matrix for the nonterminal bonds which are sufficiently remote from a branch point is shown in (1).[3] Near a trifunctional branch point the statistical weight matrices shown in eq 2–5 are required.[5] The term σ has been factored out of ${}_1\mathbf{U}_{n_1}$, and σ^2 has been factored out of ${}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1$. The matrices in eq 6–8 are required near a

$$\mathbf{U} = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\omega & \sigma\psi \end{bmatrix} \quad (1)$$

$${}_1\mathbf{U}_{n_1} = \begin{bmatrix} 1 & 1 & \sigma \\ \omega & \psi & \sigma\psi\omega \\ \psi & \omega & \sigma\psi\omega \end{bmatrix} \quad (2)$$

$${}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1 = \begin{bmatrix} \omega & \omega & \sigma\psi^2 & \sigma\psi & \sigma\omega & \sigma^2\psi\omega & 1 & \omega & \sigma\psi \\ \omega & 1 & \sigma\psi & \sigma\psi^2 & \sigma\psi & \sigma^2\psi\omega & \omega & \omega & \sigma\omega \\ \omega & \psi & \sigma\psi\omega & \sigma\psi\omega & \sigma\psi\omega & \sigma^2\omega^3 & \psi & \psi^2 & \sigma\psi\omega \end{bmatrix} \quad (3)$$

$${}_2\mathbf{U}_2 = \begin{bmatrix} 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\psi\omega & \sigma\psi\omega \\ 1 & \sigma\omega & \sigma\psi \end{bmatrix} \quad (4)$$

$${}_3\mathbf{U}_2 = \begin{bmatrix} 1 & \sigma\omega & \sigma\psi \\ 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\psi\omega & \sigma\psi\omega \end{bmatrix} \quad (5)$$

$${}_1\mathbf{U}_{n_1} = \begin{bmatrix} 1 & 1 & 1 \\ \psi\omega & \psi\omega & \psi\omega \\ \psi\omega & \psi\omega & \psi\omega \end{bmatrix} \quad (6)$$

$${}_2\mathbf{U}_2 = {}_3\mathbf{U}_2 = {}_4\mathbf{U}_2 = \begin{bmatrix} 1 & \sigma\psi\omega & \sigma\psi\omega \\ 1 & \sigma\psi\omega & \sigma\psi\omega \\ 1 & \sigma\psi\omega & \sigma\psi\omega \end{bmatrix} \quad (7)$$

$$({}_2\mathbf{U}_1 \ominus {}_3\mathbf{U}_1) \ominus {}_4\mathbf{U}_1 = \left[\begin{matrix} \omega^3 & \psi^2\omega & \psi\omega^2 & \psi\omega^2 & \psi^2\omega & \omega^3 & \psi^2\omega & \psi^4 & \psi^2\omega & \psi\omega & \psi^2 & \psi^2\omega & \psi\omega \\ \omega^3 & \psi\omega^2 & \psi^2\omega & \psi\omega & \psi\omega & \psi\omega & \psi\omega & \psi^2\omega & \psi^2 & \psi^2\omega & \psi^2\omega & \psi^4 & \psi^2 \\ \omega^3 & \psi\omega & \psi\omega & \psi^2\omega & \psi^2 & \psi\omega & \psi\omega^2 & \psi^2\omega & \psi\omega & \psi\omega^2 & \psi\omega & \psi^2\omega & \psi^2\omega \end{matrix}\right.$$

$$\left.\begin{matrix} \psi\omega & \omega^3 & \psi\omega & \psi^2\omega & \psi\omega^2 & \psi\omega & \psi\omega & \psi\omega & \psi^2\omega & \psi\omega^2 & \omega^3 & \psi^2 & \psi^2\omega & \psi\omega \\ \psi\omega & \psi^2\omega & \psi\omega & \psi\omega^2 & \psi^2\omega & \psi\omega^2 & \omega^3 & \psi^2\omega & \psi^2\omega & \omega^3 & \psi\omega^2 & \psi\omega & \omega^3 & \psi\omega \\ \psi\omega & \psi\omega^2 & \omega^3 & \omega^3 & \omega^3 & \psi^2\omega & \psi\omega & \psi^2 & \psi^4 & \psi^2\omega & \psi^2\omega & \psi^2\omega & \psi\omega^2 & \psi\omega \end{matrix}\right] \quad (8)$$

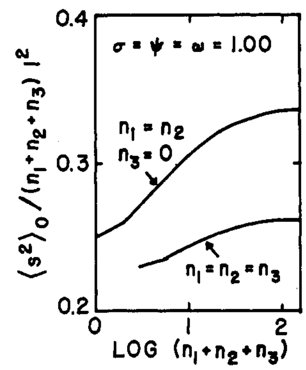

Figure 1. Characteristic ratios for a linear molecule and a branched molecule in which all branches are of equal length. The statistical weights are $\sigma = \psi = \omega = 1$.

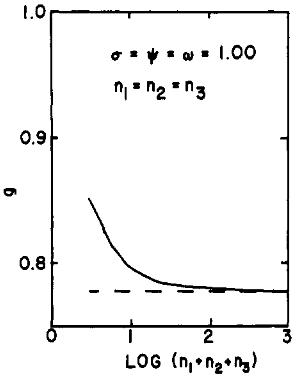

Figure 2. The parameter g for the polymer treated in Figure 1 (solid line). The dashed line is the result predicted using random flight statistics.

tetrafunctional branch point. A gauche three-bond interaction is assigned the statistical weight σ, while ψ and ω are the statistical weights for four-bond interactions generated by two successive gauche placements of the same and opposite sign, respectively.[3] Bond angles are fixed at 110° for the molecules with a trifunctional branch point, and at 109.5° for those with a tetrafunctional branch point. The rotational angles for the trans, gauche+, and gauche$^-$ states are 0, 120, and 240°, respectively. All bonds are of the same length.

The quantity g will be defined in the customary manner,[7] (9), where the number of bonds is identical in the

$$g = \langle s^2\rangle_0/\langle s_{\mathrm{lin}}^2\rangle_0 \tag{9}$$

branched and linear molecule. Related quantities g_j and g_{mc} are defined in (10) and (11), with the understanding

$$g_j = \langle s_j^2\rangle_0/\langle s_{\mathrm{lin}}^2\rangle_0 \tag{10}$$

$$g_{\mathrm{mc}} = \langle s_{\mathrm{mc}}^2\rangle_0/\langle s_{\mathrm{lin}}^2\rangle_0 \tag{11}$$

that the number of bonds is identical in the fragment of the branched molecule and in the corresponding linear chain.

Trifunctional Branch Point, Branches of Equal Length

All Rotational States Equally Probable. Figure 1 presents the manner in which the characteristic ratio depends upon the number of bonds for the linear and branched molecule when $\sigma = \psi = \omega = 1$. These statistical weights correspond to the case where trans, gauche$^+$, and gauche$^-$ states are equally probable. Identical results are obtained for free rotation about bonds. The characteristic ratio increases with n, at low n, for both the linear and branched molecule, attaining the asymptotic limit at $n > 10^2$. The result for the branched molecule is always smaller than that obtained with the linear molecule of identical n.

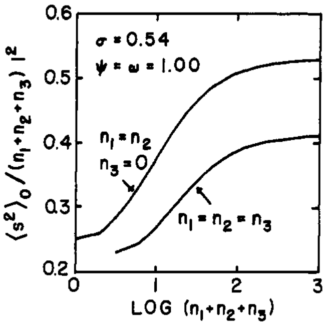

Figure 3. Characteristic ratios for a linear molecule and a branched molecule in which all branches are of equal length. The statistical weights are $\sigma = 0.54$, $\psi = \omega = 1$.

The parameter g at a particular n is given by the ratio of the two characteristic ratios. It is presented as the solid line in Figure 2. The dashed line is the result predicted from (12), which was obtained using random flight statistics.[7,8]

$$g = n^{-3}\sum_j (3nn_j^2 - 2n_j^3) \tag{12}$$

In the present case its numerical value is $7/8$, and it is independent of n. The results obtained for g using the three equally probable rotational states exceed the random flight prediction at small n. The random flight result is obtained as the asymptotic limit, and dg/dn is negative as this limit is approached. The parameter g is within 1% of its asymptotic limit when $n > 21$.

Random flight statistics predict that the g_j and g_{mc} should be unity for all n. This result is also obtained using the equally probable trans, gauche$^+$, and gauche$^-$ states, as expected.

Effect of the Three-Bond Interactions Requiring $\sigma = 0.54$. Three-bond interactions which result in the energy of a gauche state exceeding that for a trans state yield $\sigma < 1$. The value selected here, $\sigma = 0.54$, is the result appropriate for polyethylene.[9] Maintaining ψ and ω at unity corresponds to the case where there are independent hindered rotations about bonds. (We do not wish to imply that such is the case in polyethylene, but to simply examine the effect of this three-bond interaction.) Figure 3 shows the characteristic ratios for the linear and branched molecule in this case. As in the case where $\sigma = 1$, both characteristic ratios increase with n at low n, and the result for the linear molecule always exceeds that obtained for the branched molecule of the same n. However, the asymptotic limit increases when σ is reduced to 0.54, and the number of bonds required in order to attain the asymptotic limit increases to $n > 10^3$.

The values of g are presented in Figure 4. The result of $7/8$, predicted using random flight statistics, is approached as the asymptotic limit. However, the nature of the approach to the asymptotic limit is drastically affected when σ changes from unity to 0.54. When $\sigma = 0.54$, g drops below the result predicted using random flight statistics, reaches a minimum of 0.716 when $n = 12$, and approaches the asymptotic limit with dg/dn being positive. The parameter g is within 1% of the asymptotic limit for $n > 250$, which is an increase of an order of magnitude from the n required when $\sigma = 1$.

Figure 4 also shows that the partial suppression of the gauche states causes appreciable deviation of g_{mc} from the result predicted from random flight statistics. This quantity reaches a minimum value of 0.954 at $n = 9$ and is within

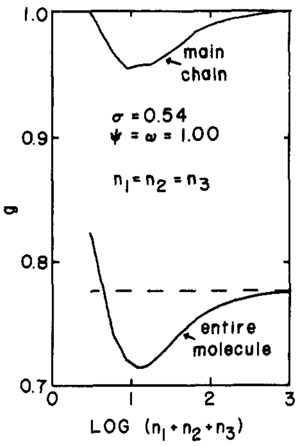

Figure 4. Parameters g and g_{mc} for the polymer treated in Figure 3. The dashed line is the result predicted for g using random flight statistics.

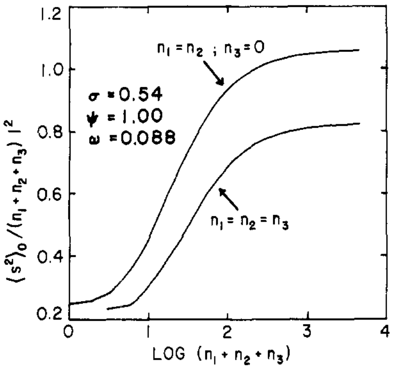

Figure 5. Characteristic ratios for a linear molecule and a branched molecule in which all branches are of equal length. The statistical weights ($\sigma = 0.54$, $\psi = 1$, $\omega = 0.088$) are those appropriate for polyethylene.[9]

1% of the random flight value of unity only when $n > 120$. The g_j (not shown) exhibit only minor deviations from unity at small n.

Addition of the Four-Bond Interaction Requiring $\omega = 0.088$. Four-bond interactions which result in high energies for adjacent bonds which adopt gauche states of opposite sign have $\omega < 1$. The result attained with polyethylene is $\omega = 0.088$.[9] The characteristic ratios obtained when $\sigma = 0.54$, $\psi = 1$, and $\omega = 0.088$ are presented in Figure 5. They exhibit an extension of the trend established in Figures 1 and 3, i.e., the asymptotic value is increased and a larger number of bonds (~10^4) is required to attain the asymptotic limit.

The corresponding g are shown in Figure 6. As before, the random flight result of $^7\!/_9$ is obtained in the asymptotic limit. However, the number of bonds required in order to be within 1% of the asymptotic limit has increased to $n > 650$. The minimum in the curve for g is more pronounced than when the rotations were independent (Figure 4). The result attained when $n = 15$ is 0.659.

In this case all of the g_j and g_{mc} also exhibit appreciable deviations from the random flight result, although in each case the asymptotic limit is unity, the result predicted using random flight statistics. This limit is attained quickly for the g_j. The results for g_2 and g_3 are identical, while a substantially larger deviation is obtained for g_1. Atom $_1A_{n_1}$ is considered to belong to branch 1, causing g_1 to differ from g_2 and g_3 when $n_1 = n_2 = n_3$. It is desirable to search for the explanation of the different behavior of g_1 and g_2 in the a priori probabilities for bond $n_1 - 1$ in branch 1. The statistical weights used here result in an enhanced a priori probability that this bond will be in the trans state in the branched macromolecule,[5] which is consistent with $g_1 > 1$ at small n. This "end effect" will quickly be overwhelmed as n increases, and consequently g_1 attains the asymptotic value at $n < 10^2$.

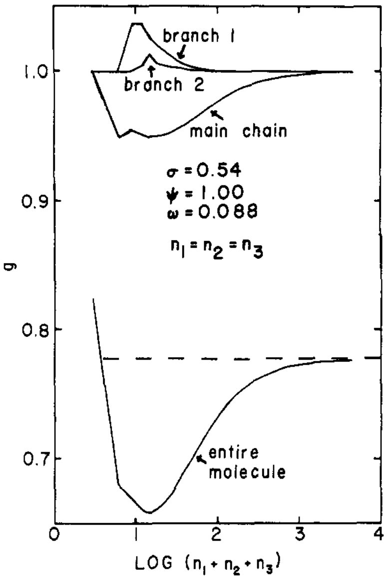

Figure 6. The parameters g, g_{mc}, and g_j for the polymer treated in Figure 5. Identical results are obtained for g_2 and g_3. The dashed line is the result predicted for g using random flight statistics.

These statistical weights also yield a reduced a priori probability that those bonds in the main chain which involve $_1A_{n_1}$ will both be in the trans state.[5] This result is consistent with $g_{mc} < 1$ for small n. Many more bonds are required for g_{mc} than for g_1 to attain the asymptotic value because the disturbances affecting $\langle s_1^2\rangle_0$ occur as an "end effect", but the disturbances affecting $\langle s_{mc}^2\rangle_0$ occur in the center of the main chain.

Distinction between Three-Bond Interactions. The Factor τ. The statistical weight for two gauche three-bond interactions of the type that occur in the C_s form of 2-methylbutane is assumed to be σ^2 in the statistical weight matrices used thus far. A more detailed assessment[3] suggests that the appropriate statistical weight for the C_s form of 2-methylbutane should be written as $\sigma\tau$, with $0.1 < \tau < 0.4$. The effect of this refinement will be to substitute τ for each σ in (2) and (3). The results obtained by making the distinction between σ and τ, and using $\sigma = 0.54$, $\tau = 0.20$, $\psi = 1.00$, and $\omega = 0.088$, are nearly indistinguishable from those presented in Figure 6, in which no distinction is made between σ and τ. The minimum value of g occurs at $n = 15$ in each case. The value at the minimum is 0.663 when $\sigma = 0.54$ and $\tau = 0.20$, as compared to 0.659 when $\sigma = \tau = 0.54$. Results for g_1 and g_2 ($=g_3$) always agree to within 0.5 and 0.1%, respectively. The maximum difference in g_{mc} is 1.5%, and it occurs at $n = 6$.

Since the effect of differentiating between τ and σ is small in the present case, the results in Figures 5 and 6 serve as a good approximation for a branched polyethylene. An additional refinement which could be made would be to increase the bond angle to 112°, resulting in an increase in the asymptotic limit for $\langle s_{lin}^2\rangle_0/nl^2$ of less than 10%.[3]

The Three-Bond Interaction Requiring $\sigma = 10$. Three-bond interactions which result in the energy for a trans state exceeding that for a gauche state yield $\sigma > 1$. The value selected here, $\sigma = 10$, serves as an approximation to the result required for polyoxymethylene if the rotations are viewed as independent.[10] In this section ψ and ω will be

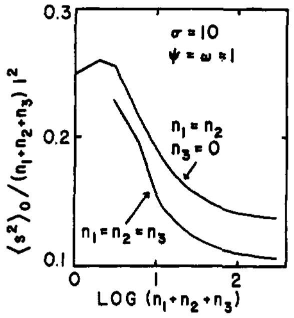

Figure 7. Characteristic ratios for a linear molecule and a branched molecule in which all of the branches are of equal length. The statistical weights are $\sigma = 10$ and $\psi = \omega = 1$.

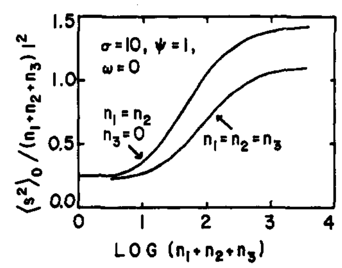

Figure 9. Characteristic ratios for a linear molecule and a branched molecule in which all branches are of equal length. The statistical weights ($\sigma = 10$, $\psi = 1$, $\omega = 0$) are an approximation to those appropriate for polyoxymethylene.[3]

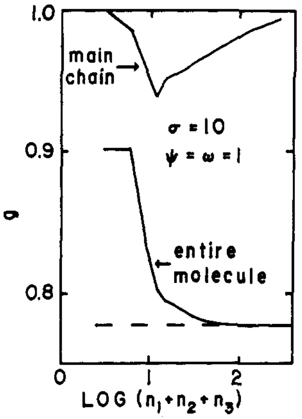

Figure 8. The parameters g and g_{mc} for the polymer treated in Figure 7. The dashed line is the result predicted for g using random flight statistics.

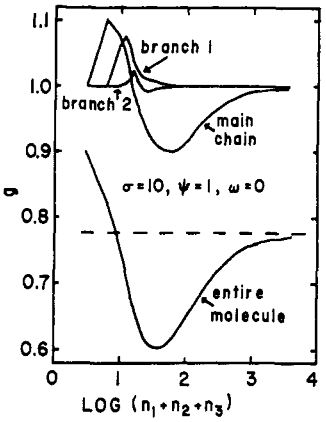

Figure 10. The parameters g, g_{mc}, and g_j for the polymer treated in Figure 9. Identical results are obtained for g_2 and g_3. The dashed line is the result predicted for g using random flight statistics.

maintained at unity. The characteristic ratios for the linear and branched molecule are shown in Figure 7. An extremely small value is obtained due to the preponderance of gauche placements and the absence of any tendency to propagate gauche placements of the same sign. The result for the linear polymer always exceeds that for the branched molecule. The asymptotic limit is approached from above, and is not attained until n exceeds 10^2.

Figure 8 presents the values of g for this case. The result of $\frac{7}{9}$, predicted by random flight statistics, is approached with $\mathrm{d}g/\mathrm{d}n < 0$. When $n > 24$, g is within 1% of the asymptotic limit. Values of g_j (not shown) are always within 1% of unity and approach unity as the asymptotic limit. The results for g_{mc}, on the other hand, fall appreciably below unity and are within 1% of the asymptotic limit for $n > 240$.

Comparison with Figure 4, in which $\sigma = 0.54$, shows a qualitatively similar behavior for g_{mc}, but a substantially different behavior for g. A minimum in g is obtained when $\sigma = 0.54$, but not when $\sigma = 1$ or 10. These results suggest that the observation of a minimum for g will require discrimination against the gauche states if there is an independent symmetric threefold rotation potential.

Addition of the Four-Bond Interaction Requiring $\omega = 0$. The statistical weights $\sigma = 10$, $\psi = 1$, and $\omega = 0$ serve as an approximation for polyoxymethylene when the interdependence of rotations is considered.[3] The appropriate bond angle is 110°.[10] The characteristic ratios for this case are shown in Figure 9. They increase with n, attain the asymptotic limit at $n \sim 10^4$, and are always larger for the linear than for the branched molecule.

Results for g, g_{mc}, and g_j are shown in Figure 10. The addition of the four-bond interactions causes g to go through a minimum ($g = 0.603$ at $n = 36$). The asympotic value is approached with $\mathrm{d}g/\mathrm{d}n > 0$, and n must be greater than 2700 in order for g to be within 1% of $\frac{7}{9}$. The g_j and g_{mc} also exhibit appreciable deviations from the random flight result, but approach it as the asymptotic limit. The perturbations are larger for g_1 than for g_2 ($=g_3$), and the g_j attain the asymptotic limit before g_{mc}, as was the case in Figure 6.

In the present case, however, g_{mc} shows a new feature, rising to a maximum of 1.10 at $n = 6$, then falling to a minimum of 0.90 at $n = 54$, and finally rising to the asymptotic limit of unity. The explanation for this behavior lies in the tendency for the linear chain to contain short helices, consisting of a succession of gauche placements of the same sign,[11] and the disruption of these helices at the branch point due to markedly enhanced a priori probabilities for trans placements for bonds n_1 and $n_1 - 1$ in branch 1 and bond 2 in branch 2. For very short chains the disruption by trans placements of the succession of gauche placements of the same sign will increase the radius of gyration, and hence g_{mc} rises above unity at small n.

Bonds Required for Asymptotic Behavior. Figures 2, 4, 6, 8, and 10 show that the number of bonds required for g to reach its asymptotic limit of $\frac{7}{9}$ depends strongly on the nature of the short-range interactions. The number of bonds required for g to be within 1% of its asymptotic limit varies from $n > 21$ (Figure 2) to $n > 2700$ (Figure 10). Short-range interactions will determine the sign of $\mathrm{d}g/\mathrm{d}n$ at the approach to the asymptotic limit. The parameter g may experience a minimum either as a consequence of three-bond (Figure 4) or four-bond (Figure 10) interactions.

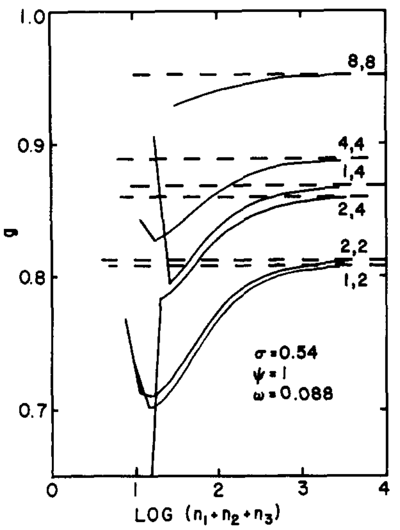

Figure 11. The parameter g for branched polyethylenes (σ = 0.54, ψ = 1, ω = 0.088) in which the number of bonds in the branches is given by $n_1 = in_2 = jn_3$. Paired numbers for each curve represent i and j. The dashed lines are the results predicted for g using random flight statistics.

Trifunctional Branch Point, Branches of Unequal Length

Figure 11 presents the g values obtained when the branches are not of equal length, using σ = 0.54, ψ = 1, and ω = 0.088. The relative lengths of the branches are given by (13), in which i and j are integers. The pair of numbers associated with each curve in Figure 11 are the i,j appropriate for that curve. Dashed lines represent the result predicted by (12), which is based on random flight statistics.

$$n_1 = in_2 = jn_3 \qquad (13)$$

This result is always attained as the asymptotic limit at large n. The limit is approached with $\mathrm{d}g/\mathrm{d}n > 0$ for the cases shown in Figure 11. The number of bonds required in order to attain the asymptotic limit depends on the relative length of the branches. For example, g is within 1% of the asymptotic limit when $n > 150$ if $i = j = 8$, but $n > 650$ is required when $i = j = 1$ (Figure 6).

These results indicate that the asymptotic limit of g is largest and approaches unity when i and j become large. Under these circumstances the molecule is essentially a linear chain with two small branches near one chain end. On the other hand, if j is not large, then the asymptotic limit of g is lowered. If $i \neq j$ then there is an additional variation of g which is unfortunately too small to be detectable from experimental measurements of $\langle s^2\rangle_0$ (which are known typically to ±10%).

The ratio $\langle s_{\mathrm{mc}}^2\rangle_0/\langle s^2\rangle_0$ is shown for various n and combinations of i and j in Figure 12. When the branches are all of the same length, the mean-square unperturbed radius of gyration of the main chain is appreciably smaller than that of the branched macromolecule. The discrepancy is reduced when the branches are not of the same length. In the case where i = 2 and j = 4, the two radii are nearly identical.

Tetrafunctional Branch Point, Branches of Equal Length

The molecular weight dependence of g for a molecule with a single tetrafunctional branch point, and branches of equal length, is shown in Figure 13 for the combinations of statistical weights used for the cases where the branch point was trifunctional. The random flight result, calculated from (12), is $\frac{5}{8}$ and is represented by the dashed line. It is attained as the asymptotic limit in each case. However, as when the branch point was trifunctional, the number of bonds required to attain the asymptotic limit, and the sign of $\mathrm{d}g/\mathrm{d}n$ upon the approach to this limit, are sensitive to the short-range interactions present.

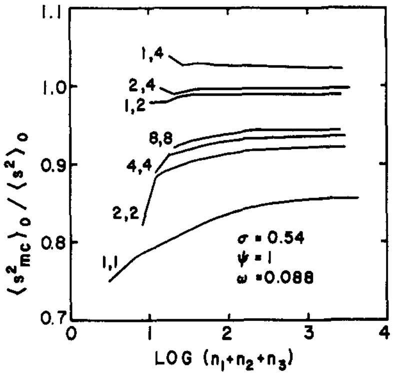

Figure 12. Relationship between the mean-square unperturbed radius of gyration for the main chain and for the entire molecule for branched polyethylenes (σ = 0.54, ψ = 1, ω = 0.088) with the indicated i and j. The number of bonds in the branches is given by $n_1 = in_2 = jn_3$.

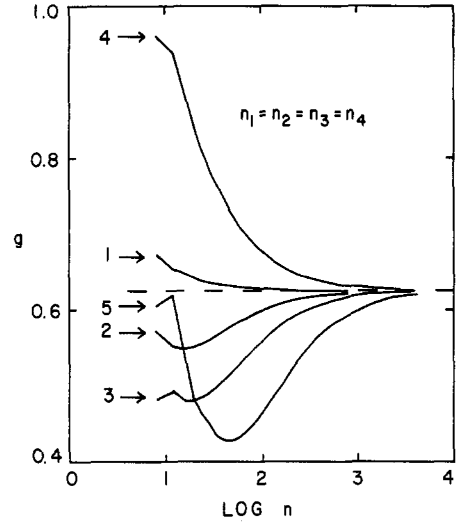

Figure 13. The parameter g for a molecule containing a single tetrafunctional branch point, branches of equal length, and having the following statistical weights: (1) $\sigma = \psi = \omega = 1$; (2) σ = 0.54, $\psi = \omega = 1$; (3) σ = 0.54, ψ = 1, ω = 0.088; (4) σ = 10, $\psi = \omega = 1$; (5) σ = 10, ψ = 1, ω = 0.

Table I summarizes the behavior for the short-range interactions considered. Several similarities are evident. The sign of $\mathrm{d}g/\mathrm{d}n$ on the approach to the asymptotic limit is identical for trifunctional and tetrafunctional branch points. If g experiences a minimum, the value of n at the minimum is only slightly different for the two branch point functionalities considered. Short-range interactions which accentuate the minimum for a trifunctional branch point also accentuate the minimum for the tetrafunctional branch point.

Two features are found to be sensitive to the functionality of the branch point. The number of bonds required for g to approach to within 1% of its asymptotic limit is always appreciably larger for tetrafunctional than for trifunctional branch points. If g goes through a minimum, the minimum will be more pronounced (as measured by $g_{\mathrm{min}}/g_{n=\infty}$) for the tetrafunctional branch point than for the trifunctional branch point.

Table I
Summary of the Effect of Short-Range Interactions on g for Molecules Containing a Trifunctional (Tetrafunctional) Branch Point and Branches of Equal Length[a]

σ	ψ	ω	n, 1%[b]	dg/dn[c]	n, min[d]	g, min[d]	$g_{\min}/g_{n=\infty}$[d]
1.00	1	1.000	24 (52)	—	N.O.	N.O.	N.O.
0.54	1	1.000	250 (448)	+	12 (16)	0.716 (0.548)	0.921 (0.877)
0.54	1	0.088	650 (1200)	+	15 (16)	0.659 (0.480)	0.847 (0.768)
10.00	1	1.000	27 (960)	—	N.O.	N.O.	N.O.
10.00	1	0.000	2700 (4200)	+	36 (48)	0.603 (0.428)	0.775 (0.685)

[a] Results obtained with the tetrafunctional branch point are given in parentheses. [b] Number of bonds required for g to be within 1% of its asymptotic limit. [c] Sign of dg/dn on the approach to the asymptotic limit. [d] Results when g experiences a minimum; N.O. = not observed.

Comparison with the results for the corresponding linear molecules (Figures 1, 3, 5, 7 and 9) reveals a correlation between the characteristic ratio for the linear molecule and the sign of dg/dn upon the approach to the asymptotic limit for the branched molecule. Those short-range interactions which lead to a large characteristic ratio for the linear molecule cause dg/dn to be positive upon the approach to the asymptotic limit for the branched molecule. For the cases considered, the minimum experienced by g becomes more pronounced for those short-range interactions which lead to larger characteristic ratios for the linear molecule.

Tonelli[12] has calculated g for certain branched polyethylenes. His approach differs from that used here in that he uses an approximate, rather than the exact, expression for the configuration partition function and certain of his statistical weight matrices were formulated incorrectly.[5] Nevertheless, the results which he obtains for g for the cases where there is a single branch point are generally only slightly larger than those obtained by the present method. The close agreement may be achieved in part because his n in several cases are large enough so that g has nearly attained its asymptotic limit. Tonelli also reports that $g_{\mathrm{mc}} < 1$ only if $\Delta\phi \neq 0°$, a conclusion which is contradicted by the results we report in Figure 6.

References and Notes

(1) Supported by Grant No. BMS 72-02416 A01 from the National Science Foundation.
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Hard Block Length Distribution in Segmented Block Copolymers

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Received July 18, 1975

ABSTRACT: Further evidence is presented to show that under ideal conditions and at complete conversion under stoichiometric conditions the sequence length distribution of hard block segments in a segmented block copolymer follows the most probable distribution. A two-stage polymerization results in a narrower distribution of hard blocks than a single-stage polymerization of the same stoichiometry when the first reaction of the low molecular weight difunctional monomer is faster than the second reaction ($\mu > 1$). In the two-stage polymerization, at intermediate extents of conversion the hard block segments can be classified into six types, depending on how the segment is capped. At conversions greater than 0.10, the concentrations of all segment types follow the geometric distribution $N_i = N_1\alpha^{i-1}$, where i is the number of extender molecules in the segment under consideration, N_1 is the concentration of the first member of the series, and α is a function of conversion and is independent of the segment type.

A two-stage polymerization of segmented block copolymers is defined as the polymerization of an excess low molecular weight difunctional monomer, usually a diisocyanate, with a macrodiol to complete reaction of the macrodiol, followed by a second-stage polymerization, with a low molecular weight diol or diamine extender. Many difunctional monomers exhibit different rates of reaction for the two functional units. The reaction rate of the first isocyanate group is usually faster than that of the second; hence, the reactivity ratio μ is greater than unity.[1] The reason for the difference in reaction rates may be due to steric hindrance, alteration of the induction-resonance condition of the molecule when it is partly reacted, or the molecular configuration in the transition state. The resulting polymer consists of blocks of macrodiol separated by various amounts of a diisocyanate-extender alternating copolymer. The first paper in this series[2] was concerned with the sequence length distribution of the diisocyanate-extender copolymer within a segmented polyurethane block copolymer. In order to count the number of units in each se-

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