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Table I
$\langle s^2\rangle/nl^2$ Obtained by Largest Eigenvalue Method

n	$\langle s^2\rangle/nl^2$	n	$\langle s^2\rangle/nl^2$
64	0.975 238	1 000	1.203 88
128	1.087 01	5 000	1.218 93
258	1.152 14	10 000	1.220 82
500	1.185 47	100 000	1.222 54
		1 100 000	1.222 72

notation used is precisely that of Flory's book[8] unless otherwise stated. The mean-square radius of gyration then reads

$$\langle s^2\rangle_0 = (n+1)^{-2}\left[\sum_{\alpha=1}^{s} F_\alpha m_\alpha^{\,2} + 2\sum_{\alpha,\beta=1}^{s} \mathbf{m}_\alpha^{\mathrm{T}}(\mathbf{B}_\alpha{}^* \otimes \mathbf{E}_3) \times \left(\sum_{r=0}^{3} C_r \boldsymbol{S}_\alpha{}^r + \mathbf{S}_\alpha{}^{x-1}\sum_{r=0}^{3} D_r \boldsymbol{S}_\alpha{}^r\right)(\mathbf{E}_{3\nu} - \mathbf{S}_\alpha)^{-4}\mathbf{R}_{\alpha\beta}(\mathbf{A}_\alpha \otimes \mathbf{E}_3)\mathbf{m}_\beta\right] \tag{3}$$

$$F_\alpha = (\alpha+1)x(sx-\alpha+1) + (sx-2\alpha)s(x-1)x/2 - s^2(x-1)x(2x-1)/6$$

$$C_0 = a_0 + a_1 + a_2 + a_3$$

$$C_1 = -(3a_0 + 2a_1 - 4a_3)$$

$$C_2 = 3a_0 + a_1 - a_2 + a_3$$

$$C_3 = -a_0$$

$$D_0 = -(a_0 + a_1 + a_2 + a_3) - (a_1 + 2a_2 + 3a_3)(x-1) - (a_2 + 3a_3)(x-1)^2 - a_3(x-1)^3$$

$$D_1 = (3a_0 + 2a_1 - 4a_3) + (3a_1 + 4a_2)(x-1) + 3(a_2 + 2a_3)(x-1)^2 + 3a_3(x-1)^3$$

$$D_2 = -(3a_0 + a_1 - a_2 + a_3) - (3a_1 + 2a_2 - 3a_3)(x-1) - 3(a_2 + a_3)(x-1)^2 - 3a_3(x-1)^3$$

$$D_3 = a_0 + a_1(x-1) + a_2(x-1)^2 + a_3(x-1)^3$$

$$a_0 = -(\alpha+1)(\beta-1)x + sx[\alpha+\beta+x(\alpha-\beta+2)]/2 + s^2x(x^2-1)/6$$

$$a_1 = (\alpha+1)(\beta-1) - s[\alpha+\beta+2x(\alpha-\beta+2)]/2 - s^2(3x^2-1)/6$$

$$a_2 = s(sx+\alpha-\beta+2)/2$$

$$a_3 = -s^2/6$$

When $\alpha < \beta$, then x is replaced by $x + 1$ in the second term of eq 3 but not in F_α.

As a simple test of eq 3, the reduction of $\langle s^2\rangle$ to $\langle r^2\rangle/6$ is obtained, when x becomes infinitely large. $\langle s^2\rangle/nl^2$ of polymethylene calculated from eq 3 are shown in Table I.

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References and Notes

(1) Matsuo, K. *Macromolecules* **1977**, *10*, 498.
(2) Flory, P. J.; Jernigan, R. L. *J. Chem. Phys.* **1965**, *42*, 3509.
(3) Lifson, S. *J. Chem. Phys.* **1958**, *29*, 80; **1959**, *30*, 964.
(4) Nagai, K. *J. Chem. Phys.* **1959**, *31*, 1169.
(5) Hoeve, C. A. *J. Chem. Phys.* **1960**, *32*, 888.
(6) (a) Flory, P. J.; Crescenzi, V.; Mark, J. E. *J. Am. Chem. Soc.* **1964**, *86*, 146. (b) Allegra, G.; Bennedetti, E.; Pedone, C. *Macromolecules* **1970**, *3*, 727.
(7) Mark, J. E.; Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1415.
(8) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience: New York, 1969; p 106 footnote.
(9) Nagai, K. *J. Chem. Phys.* **1966**, *45*, 838; **1961**, *34*, 887; **1965**, *42*, 516; **1967**, *47*, 2052.

Unperturbed Dimensions of Wormlike Stars

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Introduction

The characterization of branched macromolecules by means of their dilute-solution properties continues to be an active and important enterprise. Recent careful measurements of gyration radii and intrinsic viscosities for well-defined star molecules under Θ-solvent conditions[1] are not in good agreement with the classical theoretical predictions for unperturbed random-flight chains, so that further work is needed. Undoubtedly a major reason for these discrepancies is the unusually severe volume exclusion in the neighborhood of a branch point, but in some cases it may be advisable to take full cognizance of the effects of chain stiffness as well, and the present exercise contributes to this latter purpose.

Previous theoretical calculations on stiff branched polymers include those of Kajiwara and Ribeiro[2] and of Burchard[3] for randomly branched and star polymers. These authors considered the complete particle scattering factor in the first Daniels[4] approximation to the Kratky–Porod wormlike chain model,[5,6] and thus their results are not applicable over the full range of contour length or chain stiffness. Alternatively, Tonelli[7] and Mattice[8,9] have used rotational-isomeric-state (RIS) theory to formulate the mean-square radius of gyration for starlike branched structures; and some related numerical calculations have been exhibited by Mattice and Carpenter[10] and by Mattice.[11] For molecules with short branches, the RIS approach is doubtless much superior, but for the treatment of moderately long branches the development of the relative simple analytical formula corresponding to the full Kratky–Porod model is a useful objective. In some systems, agreement between wormlike and RIS treatments can be secured over a wide range of chain lengths by introduction of an appropriate "shift factor" connecting the persistence length of the wormlike chain to an actual number of skeletal bonds in the RIS chain.[12] Here we present results for wormlike *star* molecules of any functionality and compare them briefly with the RIS calculations of Tonelli[7] and of Mattice and Carpenter[10] for regular stars with three or four rays.

Mean-Square Radius of Gyration

The wormlike chain model can be described as an ensemble of space curves in which the correlation of tangential directions of two points on the curve decays exponentially with their separation along the contour.[6] If $\mathbf{u}(s)$ is a unit vector tangent to the curve at the contour distance s from a specified origin, the aforementioned correlation function is

$$\langle \mathbf{u}(s')\cdot\mathbf{u}(s'')\rangle = \exp(-|s'-s''|/a) \tag{1}$$

where a is the "persistence length" and $2a$ is the "Kuhn length". (In notations employed elsewhere, $a \equiv 1/2\lambda \equiv 1/2D$.) The mean-square distance between two points at s_1 and s_2 is then

$$\langle R^2(s_1, s_2)\rangle = \int_{s_1}^{s_2} \mathrm{d}s' \int_{s_1}^{s_2} \mathrm{d}s'' \exp(-|s'-s''|/a) \tag{2}$$

Now for a star molecule of f rays and total contour length L, in which L_i is the contour length of the ith ray, the mean-square radius of gyration is given by

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$$\langle S^2\rangle_{\text{star}} = (1/2L^2)\sum_i^f\sum_j^f \int_0^{L_i} \mathrm{d}s_i \int_0^{L_j} \mathrm{d}s_j' \, \langle R^2(s_i, s_j')\rangle \quad (3)$$

$$L = \sum_i^f L_i$$

in which s_i and s_j' refer to contour lengths along rays i and j, respectively. This formula can be decomposed as follows:

$$\langle S^2\rangle_{\text{star}} = \sum_i^f Y_i + \sum_i^f\sum_j^f Z_{ij} \qquad (i < j) \quad (4)$$

where each ray contributes independently to the first term and each pair of rays to the second term. For the first term we have

$$Y_i = (1/2L^2)\int_0^{L_i} \mathrm{d}s_i \int_0^{L_i} \mathrm{d}s_i' \, \langle R^2(s_i, s_i')\rangle \quad (5)$$

and with the aid of eq 2 we obtain

$$Y_i = (a/L^2)[(L_i^3/3) - L_i^2 a + 2L_i a^2 - 2x_i a^3] \quad (6)$$

where

$$x_i = 1 - \exp(-L_i/a) \quad (7)$$

It can be seen that for the linear chain, where $f = 1$ and $L_1 = L$, eq 4–7 reduce to the result long ago obtained by Benoît and Doty.[13]

The second term of eq 4 involves the mean-square distance between points on different rays which is given by the following formula:

$$\begin{aligned}\langle R^2(s_i, s_j)\rangle &= \int_0^{s_i}\mathrm{d}s_i' \int_0^{s_i} \mathrm{d}s_i'' \, \langle \mathbf{u}(s_i')\cdot\mathbf{u}(s_i'')\rangle - \\ &\quad 2\int_0^{s_i} \mathrm{d}s_i' \int_0^{s_j} \mathrm{d}s_j' \, \langle \mathbf{u}(s_i)\cdot\mathbf{u}(s_j')\rangle + \\ &\quad \int_0^{s_j} \mathrm{d}s_j' \int_0^{s_j} \mathrm{d}s_j'' \, \langle \mathbf{u}(s_j')\cdot\mathbf{u}(s_j'')\rangle \\ &= \int_0^{s_i} \mathrm{d}s_i' \int_0^{s_i} \mathrm{d}s_i'' \exp(-|s_i' - s_i''|/a) - \\ &\quad 2\cos\theta_{ij}\int_0^{s_i} \mathrm{d}s_i' \int_0^{s_j} \mathrm{d}s_j' \exp[-(s_i' + s_j')/a] + \\ &\quad \int_0^{s_j} \mathrm{d}s_j' \int_0^{s_j} \mathrm{d}s_j'' \exp(-|s_j' - s_j''|/a) \\ &= 2a(s_i + s_j) - 2a^2(x_i + x_j) - 2a^2\cos\theta_{ij}x_i x_j \quad (8)\end{aligned}$$

it being assumed that rays i and j are constrained at the angle θ_{ij} at the junction point. Then we obtain

$$\begin{aligned}Z_{ij} &= L^{-2}\int_0^{L_i} \mathrm{d}s_i \int_0^{L_j} \mathrm{d}s_j \, \langle R^2(s_i, s_j)\rangle \\ &= (a/L^2)[L_i^2L_j + L_iL_j^2 - 2aL_iL_j(2 + \cos\theta_{ij}) + \\ &\quad 2a^2(1 + \cos\theta_{ij})(L_ix_j + L_jx_i) - 2a^3\cos\theta_{ij}x_ix_j] \quad (9)\end{aligned}$$

The relations (6), (7), and (9) permit the calculation of $\langle S^2\rangle_{\text{star}}$ for any particular wormlike star. For the special case of rays of equal length $L_i = L_1 = L/f$ they yield

$$\begin{aligned}\langle S^2\rangle_{\text{star}} &= f^{-1}a^2[(3f - 2)(L_1/3a) + \\ &\quad 1 - 2f + 2(a/L_1) + 2(f - 1)x_1(a/L_1) - \\ &\quad 2x_1(a/L_1)^2 - (2F/f)(1 - x_1aL_1^{-1})^2] \quad (10)\end{aligned}$$

where

$$F = \sum_{i<j} \cos\theta_{ij} \quad (11)$$

The mean-square radius of gyration thus depends on the initial directions of the rays only through F. We show in the Appendix that the minimum possible value of F is $-f/2$ and that this is achieved only when the initial directions of all the rays cancel. This corresponds to a maximum in $\langle S^2\rangle_{\text{star}}$ and is what one might expect for molecules in which steric effects force the rays to be symmetrically disposed about the center of the star. When $F = -f/2$, eq 10 becomes

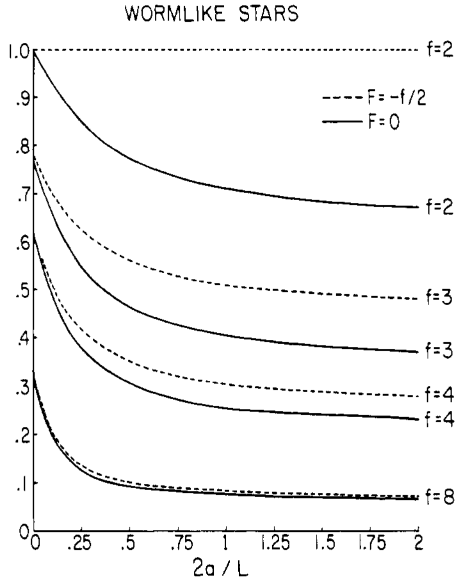

Figure 1. Ratios of mean-square radii, $g = \langle S^2\rangle_{\text{star}}/\langle S^2\rangle_{\text{linear}}$, for different directional restrictions at the branch point: $F = 0$ corresponds to uncorrelated initial directions of the rays emanating from the vertex, while $F = -f/2$ corresponds to the maximum mutual avoidance of the rays. The values of g for $a/L = 0$ are the random-coil limits, and for large a/L they approach those for rigid rodlike rays.

$$\begin{aligned}\langle S^2\rangle_{\text{star}} &= f^{-1}a^2[(3f - 2)(L_1/3a) + 2(1 - f) + \\ &\quad 2(fx_1 - 2x_1 + 2)(a/L_1) + x_1(x_1 - 2)(a/L_1)^2] \quad (12)\end{aligned}$$

In the Gaussian and in the rod limits we find

$$\langle S^2\rangle_{\text{Gaussian}} = \lim_{L/a\to\infty} \langle S^2\rangle_{\text{star}} = aL_1(3f - 2)/3f \quad (13)$$

$$\langle S^2\rangle_{\text{rod}} = \lim_{L/a\to 0} \langle S^2\rangle_{\text{star}} = L_1^2/3 \quad (14)$$

The g value of a star is defined as the ratio $\langle S^2\rangle_{\text{star}}/\langle S^2\rangle_{\text{linear}}$ for star and linear molecules of the same total contour length. The limiting values for $F = -f/2$ are

$$g_{\text{Gaussian}} = (3f - 2)/f^2 \quad (15)$$

and

$$g_{\text{rod}} = 4/f^2 \quad (16)$$

as expected. In Figure 1, we display g values calculated for various values of f, F, and L/a.

We now compare our results to the RIS calculations[7,10] for paraffinic star molecules with three and four rays, which are based on the statistical weight parameters $\sigma = 0.54$, $\psi = 1$, and $\omega = 0.088$ given by Flory[14] for polymethylene. Specifying[12] a "shift factor" K by the relation $n = KL/2a$ for a chain of n bonds, we obtain a satisfactory fit of the Mattice–Carpenter[10] curves at higher n by setting $K = 5$, as shown in Figure 2. Unfortunately, this shift factor is only about half as large as that which reproduces the behavior of linear paraffin chains.[12] Doubtless one reason for the discrepancy is that a fitted wormlike space curve does not actually lie along the single bonds of the actual chain, and so the RIS models cannot correspond fully to the condition $F = -f/2$ imposed on eq 12. It can be seen from Figure 1 that this effect can cause large changes for short chains.

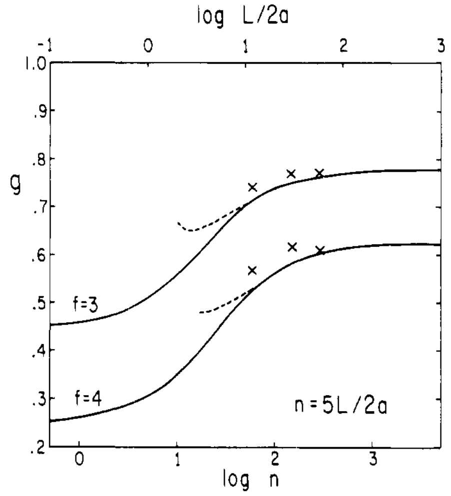

Figure 2. Mean-square radius ratios g as a function of chain length for regular paraffinic stars of three and four rays: crosses from Tonelli;[7] dashed curves from Mattice and Carpenter;[10] solid curves, wormlike stars, eq 12 with $L/2a = n/5$.

Further, it has been pointed out to us by Mattice[15] that certain RIS models, including several of those treated by him and Carpenter,[10] cannot possibly be imitated by a wormlike treatment. For example, as can be seen in Figure 1, our g values always increase with increasing L, but this is not true of some of the RIS stars, notably those with physically unusual statistical weights (e.g., excessive tolerance of g^+g^- sequences). For such chains the directional correlation functions are necessarily quite unlike the exponential form of eq 1. We expect that our results may be useful when the corresponding linear polymer can be usefully represented as a wormlike chain and when the branches are sufficiently long. But it is important to remember that excluded-volume effects near the branch point are not taken into account.

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Added Note. We have just become aware of some RIS calculations on star polypeptides by Oka and Nakajima.[16] Their results in general are very similar to those of Mattice and Carpenter.

Appendix

Here we show that $F = -f/2$ is the minimum possible F and that this occurs when the initial directions of all rays cancel. Represent by $\mathbf{u}_i$ the unit vector tangent to the ith ray at the junction point of the star. Let $\mathbf{q}_i = \sum_{j\neq i} \boldsymbol{u}_i$ and let $\mathbf{s} = \sum_j \boldsymbol{u}_j = \mathbf{q}_i + \mathbf{u}_i$ be the sum of all $\mathbf{u}_i$. We wish to show that when $\mathbf{s} = 0$, $F = -f/2$ and is minimal. Expressing $\mathbf{u}_i$ in spherical-polar coordinates provides the following:

$$F = \sum_{i<j} \sin\theta_i \sin\theta_j \cos(\phi_i - \phi_j) + \sum_{i<j} \cos\theta_i \cos\theta_j \tag{17}$$

F is extremal whenever its derivatives with respect to θ_i and ϕ_i are zero for all i. Differentiation with respect to θ_i and ϕ_i yields expressions that may be written as follows:

$$(\partial \mathbf{u}_i/\partial\theta_i)\cdot\mathbf{q}_i = 0 \tag{18}$$

$$(\mathbf{u}_i \times \mathbf{q}_i)_z = 0 \tag{19}$$

The result must be independent of coordinate system, and we may thus write eq 19 as

$$\mathbf{u}_i \times \mathbf{q}_i = 0 \tag{20}$$

The derivative $\partial\mathbf{u}_i/\partial\theta_i$ is normal to $\mathbf{u}_i$. This means that eq 18 is true whenever eq 20 is, so that eq 20 is the only condition necessary for F to be extremal. Therefore, F is extremal whenever $\mathbf{u}_i$ and $\mathbf{q}_i$ are collinear. Then $\mathbf{q}_i = \alpha_i \boldsymbol{u}_i$ for α_i some scalar. Then $\mathbf{s} = \mathbf{u}_i + \mathbf{q}_i = (1 + \alpha_i)\mathbf{u}_i$ and $\mathbf{s}$ is collinear with each $\mathbf{u}_i$. Therefore there are two cases in which F is extremal: either (1) $\mathbf{s} = 0$, or (2) the $\mathbf{u}_i$ are all collinear, with f_1 in one direction, f_2 in the opposite direction, $f_1 + f_2 = f$, and $f_1 \neq f_2$ (obviously $f_1 = f_2$ would fall under the first case). In these two cases we may evaluate F:

Case 1:

$$F = \tfrac{1}{2}\sum_i \sum_{j\neq i} \mathbf{u}_i\cdot\mathbf{u}_j = \tfrac{1}{2}\sum_i \mathbf{u}_i\cdot\mathbf{q}_i = -\tfrac{1}{2}\sum_i \mathbf{u}_i^2 = -f/2$$

Case 2:

$$F = \tfrac{1}{2}[f_1(f_1 - 1) + f_2(f_2 - 1) - 2f_1f_2]$$

The latter exceeds the former by the amount $(f_1 - f_2)^2/2$, which establishes the proof.

References and Notes

(1) Bauer, B. J.; Hadjichristidis, N.; Quack, G.; Vitus, J.; Fetters, L. J. *Polym. Prepr., Div. Polym. Chem., Am. Chem. Soc.* **1979**, *20*, 126 and references therein.
(2) Kajiwara, K.; Ribeiro, C. A. M. *Macromolecules* **1974**, *7*, 121.
(3) Burchard, W. *Macromolecules* **1974**, *7*, 835, 841.
(4) Daniels, H. E. *Proc. R. Soc. Edinburgh, Sect. A: Math. Phys. Sci.* **1952**, *63*, 290.
(5) Kratky, O.; Porod, G. *Recl. Trav. Chim. Pays-Bas* **1949**, *68*, 1106.
(6) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971; pp 52–7.
(7) Tonelli, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 2972.
(8) Mattice, W. L. *Macromolecules* **1975**, *8*, 644.
(9) Mattice, W. L. *Macromolecules* **1976**, *9*, 48.
(10) Mattice, W. L.; Carpenter, D. K. *Macromolecules* **1976**, *9*, 53.
(11) Mattice, W. L. *Macromolecules* **1977**, *10*, 511, 516.
(12) Maeda, H.; Saito, N.; Stockmayer, W. H. *Polym. J.* **1971**, *2*, 94.
(13) Benoît, H.; Doty, P. *J. Phys. Chem.* **1953**, *57*, 958.
(14) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Wiley-Interscience: New York, 1969; pp 142–7.
(15) Mattice, W. L., private communication.
(16) Oka, M.; Nakajima, A. *Polym. J.* **1977**, *9*, 573.

Polymerization of 1-Oxa-3-thiacyclopentane. Structure of the Polymer

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Introduction

The cationic polymerization of 1,3-dioxolane has been widely investigated in the past.[1-6] However, no definitive conclusion can be obtained about the polymerization mechanism of this cyclic acetal due, among other reasons, to the obscure initiation reaction and to the well-known fact that there are a few active species which carry the propagation reaction in the cationic polymerization of cyclic ethers.[7-9] A monomer similar to 1,3-dioxolane is 1-oxa-3-thiacyclopentane. The former polymer can be schematically converted to the latter by substituting a sulfur atom for one of the oxygen atoms in the 1,3-dioxolane ring. Very few studies have been reported dealing with the polymerization of 1-oxa-3-thiacyclopentane.[10,11] A very recent study[11] on the cationic polymerization of this monomer indicates that, although the polymerization seems to be initiated by quantitative formation of ethylsulfonium, the propagation is not the simple repeating formation of sulfonium ions, which are the propagating

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