$$\sum_{\alpha=1}^{n-1} \alpha^3 = [n(n-1)/2]^2$$

and combining certain terms together we arrive at (43) in the text.

References and Notes

(1) Daoud, M. Thesis, Université de Paris IV, 1977.
(2) de Gennes, P. G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, N.Y., 1979.
(3) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(4) Kitano, T.; Taguchi, A.; Noda, I.; Nagasawa, M. *Macromolecules* **1980**, *13*, 57.
(5) Kratky, O.; Porod, G. *Recl. Trav. Chim. Pays-Bas* **1949**, *68*, 1106.
(6) Hermans, J. J.; Ullman, R. *Physica* **1952**, *18*, 951.
(7) Koyama, R. *J. Phys. Soc. Jpn.* **1973**, *34*, 1029.
(8) Norisuye, T.; Murakama, H.; Fujita, H. *Macromolecules* **1978**, *11*, 966.
(9) Akcasu, Z.; Benmouna, M.; Han, C. C. *Polymer* **1980**, *21*, 866. *Polymer*.
(10) Richter, D.; Hayter, J.; Mezei, R.; Ewen, B. *Phys. Rev. Lett.* **1978**, *41*, 1484.
(11) Akcasu, Z.; Gurol, H. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1.
(12) Benmouna, M.; Akcasu, Z. *Macromolecules* **1978**, *11*, 1187.
(13) Akcasu, Z.; Benmouna, M. *Macromolecules* **1978**, *11*, 1193.
(14) Benmouna, M.; Akcasu, Z. *Macromolecules* **1980**, *13*, 409.
(15) (a) Schmidt, M.; Burchard, W. *Macromolecules* **1978**, *11*, 460. (b) Stockmayer, W. H.; Schmidt, M.; Burchard, W. *Ibid.* **1980**, *13*, 580. (c) Burchard, W.; Schmidt, M.; Stockmayer, W. H. *Ibid.* **1980**, *13*, 1265.
(16) Riseman, J.; Kirkwood, J. G. "Rheology, Theory and Applications"; Academic Press: New York, 1956.
(17) Hearst, J. E.; Stockmayer, W. H. *J. Chem. Phys.* **1962**, *37*, 1425.
(18) Stockmayer, W. H.; Burchard, W. *J. Chem. Phys.* **1979**, *70*, 3138.
(19) Fixman, M.; Kovac, J. *J. Chem. Phys.* **1974**, *61*, 4939.
(20) Helfand, E. *J. Chem. Phys.* **1979**, *71*, 5000.
(21) Akcasu, Z.; Higgins, J. S. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1745.
(22) Berne, B. J.; Pecora, R. "Dynamic Light Scattering"; Wiley: New York, 1976.
(23) Fixman, M.; Skolnick, J. *Macromolecules* **1978**, *11*, 863.
(24) Akcasu, Z., to be submitted for publication.
(25) Burgers, J. M. "Second Report on Viscosity and Plasticity"; 1938; Vol. 16, p 1.
(26) Wilson, R.; Bloomfield, V. *Biopolymers* **1979**, *18*, 1205.
(27) Broersma, S. *J. Chem. Phys.* **1959**, *32*, 1626.
(28) Akcasu, Z.; Han, C. C. *Macromolecules* **1979**, *12*, 276.
(29) Benoit, H.; Doty, P. *J. Phys. Chem.* **1953**, *57*, 958.
(30) Gradhteyn, I. S.; Ruzlik, I. M. Eds. "Tables of Integrals, Series, and Products"; Academic Press: New York, 1965.
(31) Zimm, B. H.; Stein, R. S.; Doty, P. *Polym. Bull.* **1945**, *1*, 90.
(32) Fixman, M., to be submitted for publication (private communication).

Notes

Second Moment of Finite Polymer Chains

KEIZO MATSUO

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755.

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A relatively simple formulation of the second moment of *infinite* polymer chains with repeat units of any size has been given.[1] In order to calculate unperturbed chain dimensions or dipole moments of *finite* linear chains, the so-called generalized method[2] by Flory and Jernigan must be used. However, the generalized method requires 15 × 15 matrices in the case of a three-state rotational isomeric state (RIS) model, while for the older methods proposed by Lifson,[3] Nagai,[4] and Hoeve,[5] 9 × 9 matrices are sufficient to get second moments of *infinite* polymer chains. We present here a formula with 9 × 9 matrices which gives very close approximations to the second moments of *finite* polymer chains.

Again it seems unnecessary to give a detailed derivation since this exercise can be performed by straightforward generalization of previously published results for two-[6] and three-bond[7] repeat units, taking account of the general properties[8] of the RIS model. The notation used here is precisely that of Flory's book[8] unless otherwise stated. Let there be s bonds within a repeat unit, numbered by indices α or β running from 1 to s. With x denoting the number of repeat units of a chain, the formula of the second moment then reads

$$\langle M^2\rangle/x = \sum_{\alpha=1}^{s} m_\alpha{}^2 + (2/x) \sum_{\alpha,\beta=1}^{s} \mathbf{m}_\alpha{}^{\mathrm{T}}(\mathbf{B}_\alpha{}^* \otimes \mathbf{E}_3) \times [(x-1)\mathbf{E}_{3\nu} - x\mathbf{S}_\alpha + \mathbf{S}_\alpha{}^x](\mathbf{E}_{3\nu} - \mathbf{S}_\alpha)^{-2}\mathbf{R}_{\alpha\beta}(\mathbf{A}_\alpha \otimes \mathbf{E}_3)\mathbf{m}_\beta \quad (1)$$

When $\alpha < \beta$, x should be replaced by $x + 1$. Definitions of several symbols appearing in the formula can be found in detail in the previous paper.[1]

This formula is not an *exact* expression of the second moments of *finite* chains (because the largest eigenvalue has been used for normalization instead of the complete partition function). The generalized method, on the other hand, yields an exact expression, however.[8] When x ($=n$ for $s = 1$) is smaller than 10, there still remains a difference between the generalized and the eigenvalue method due to some end-group contributions and to the difference between the partition function and the largest eigenvalues. However, these become relatively small as x increases. This method is expected to give excellent results in all cases where the largest eigenvalue of $\mathbf{Q}\alpha$ (U matrices) is much larger than the other ones. If, however, this is not the case, convergence to the correct result is a bit slower. Readers are well-advised to refer to Nagai's earlier work[9] on the second and higher even moments using the largest eigenvalue method.

A small rearrangement of eq 1 gives

$$\langle M^2\rangle/x = \lim_{x\to\infty} \langle M^2\rangle/x - (2/x) \sum_{\alpha,\beta=1}^{s} \mathbf{m}_\alpha{}^{\mathrm{T}}(\mathbf{B}_\alpha{}^* \otimes \mathbf{E}_3) \times (\mathbf{E}_{3\nu} - \mathbf{S}_\alpha{}^x)(\mathbf{E}_{3\nu} - \mathbf{S}_\alpha)^{-2}\mathbf{R}_{\alpha\beta}(\mathbf{A}_\alpha \otimes \mathbf{E}_3)\mathbf{m}_\beta \quad (2)$$

where $\lim_{x\to\infty} \langle M^2\rangle/x$ can be obtained directly from our earlier result.[1]

Flory and Jernigan's method[2] requires 21 × 21 matrices for a three-state RIS model to evaluate the mean-square radius of gyration. Here again a slightly simpler formula is proposed, with only 9 × 9 matrices, to calculate a mean-square radius of gyration. Though the formula does not give an exact expression because of the reasons stated earlier, it reproduces more than 99% of an exact value obtained by Flory and Jernigan's method. The derivation of this formula is relatively straightforward (from the series of expansions of $\langle s^2\rangle_0 = (n+1)^{-2}\sum_{0\le h\le k\le n}\sum_{i=h+1}^{k}\cdot\sum_{j=h+1}^{k}\langle \mathbf{l}_i\cdot\mathbf{l}_j\rangle$, numerical orders were obtained). Again the

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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

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

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

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

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

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

$$C_3 = -a_0$$

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

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

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

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

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

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

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

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

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

MARC L. MANSFIELD and WALTER H. STOCKMAYER*

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755. *Received April 21, 1980*

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

