Notes

Second Moment of Infinite Polymer Chains

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During the past few years, and especially since the publication of Flory's book,[1] most applications of the rotational isomeric state (RIS) model to the calculation of unperturbed chain dimensions or dipole moments have been based on the so-called generalized method of Flory and Jernigan,[2] which can be used for chains of any finite length. Since the chain-length dependence of these quantities can often be observed experimentally, and since this yields more information than could be obtained only from the result for infinitely long chains, it is easy to see why the "generalized" formulas have usually been preferred to the older ones given by Lifson,[3] Nagai,[4] and Hoeve,[5] which are restricted to infinite chains.

A slight disadvantage of the generalized method, however, is an increase in computational complexity; for example, in the case of a three-state RIS model it requires 15×15 matrices, while for the older methods 9×9 matrices are sufficient. Moreover, experimental data are sometimes available only for very long chains. For this reason, it seemed useful to present a formula for the second moment (of either end-to-end chain length or dipole moment) in the case of an infinite chain with *repeat units of any size.* This exercise can be performed by straightforward generalization of previously published results for repeat units containing two[5,6] and three[7] bonds and of course it reduces to those results when appropriately specialized. It seems unnecessary to give a detailed derivation; however, as far as we are aware the formula has not been explicitly given before, and it may have occasional practical interest.

The notation used is precisely that of Flory's book[1] 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 limiting second moment formula (of course for unperturbed chains) then reads

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

Definitions of several symbols appearing in this formula follow:

$$\mathbf{S}_\alpha = \lambda_\alpha{}^{-1}\prod_{j=\alpha}^{\alpha+s-1}(\mathbf{U}_j \otimes \mathbf{E}_3)\|\mathbf{T}_j\| \qquad \alpha = 1, 2, \ldots, s \quad (2)$$

The statistical-weight matrices $\mathbf{U}_j$ are of order $\nu \times \nu$. There is no great difficulty if these orders are not all equal,[1] but in such cases the plain symbol ν appearing as part of a subscript in eq 1 denotes the largest value found in the chain. Further, λ_α is the largest eigenvalue of the matrix

$$\mathbf{Q}_\alpha = \prod_{j=\alpha}^{\alpha+s-1}\mathbf{U}_j \qquad \alpha = 1, 2, \ldots, s \quad (3)$$

Because the chain structure repeats after s links, the cyclic conditions

$$\mathbf{U}_j = \mathbf{U}_{j+s}; \quad \|\mathbf{T}_j\| = \|\mathbf{T}_{j+s}\| \quad (4)$$

necessarily hold. Also, $\mathbf{B}_\alpha{}^*$ and $\mathbf{A}_\alpha$ represent the mutually normalized eigenrow and eigenvector of $\mathbf{Q}_\alpha$ corresponding to λ_α.

Finally, the matrix $\mathbf{R}_{\alpha\beta}$ is defined as

$$\mathbf{R}_{\alpha\beta} = \lambda_\alpha{}^{-1}\prod_{j=\alpha}^{\beta+s-1}(\mathbf{U}_j \otimes \mathbf{E}_3)\|\mathbf{T}_j\|\prod_{k=\beta+s}^{\alpha+s-1}(\mathbf{U}_k \otimes \mathbf{E}_3) \quad \text{when } \alpha \geq \beta$$

$$\mathbf{R}_{\alpha\beta} = \lambda_\alpha{}^{-1}\prod_{j=\alpha}^{\beta-1}(\mathbf{U}_j \otimes \mathbf{E}_3)\|\mathbf{T}_j\|\prod_{k=\beta}^{\alpha+s-1}(\mathbf{U}_k \otimes \mathbf{E}_3) \quad \text{when } \alpha < \beta \quad (5)$$

where again the cyclic conditions of eq 4 are to be remembered.

As remarked earlier, it is easy to extract simpler earlier results as special cases of eq 1. For example, if $s = 1$ then $\alpha = \beta = 1$ and $\mathbf{S} = \lambda_1{}^{-1}(\mathbf{U} \otimes \mathbf{E}_3)\|\mathbf{T}\| = \mathbf{R}$; so the unperturbed dimensions at once reduce to the classical result

$$C_\infty = \lim_{n\to\infty}\langle r^2\rangle/nl^2 = 1 + 2[(\mathbf{B}_1{}^* \otimes \mathbf{E}_3)(\mathbf{E}_{3\nu} - \mathbf{S})^{-1}\mathbf{S}(\mathbf{A}_1 \otimes \mathbf{E}_3)]_{11} \quad (6)$$

The known results[5-7] for $s = 2$ and 3 are also easily obtained, as mentioned earlier.

For the computation of dipole-moment ratio, it will be recognized that many terms in the double sum of eq 1 may vanish; for example, in the case of poly(tetramethylene oxide),[8] with $s = 5$, in first approximation there are bond dipoles only for the two C–O bonds of the repeat unit but none for the three C–C bonds.

We have tested eq 1 numerically in a number of cases and have obtained quantitative agreement with the generalized method when the chains are sufficiently long. These tests include the following: poly(trimethylene oxide),[9] poly(tetramethylene oxide),[8] poly(*cis*-butadiene),[10] poly(*trans*-butadiene),[11] and poly(ϵ-caprolactam).[12]

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References and Notes

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