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Distribution Functions for Gaussian Semilinear Polymers

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ABSTRACT: Distribution functions of the square radius of gyration have been calculated numerically for a class of Gaussian semilinear polymers consisting of branched or cyclic structural elements linked together by single bonds into a linear chain. In the calculations, only the characteristic polynomials of the Kirchhoff matrices of graphs representing these polymers were used. It has been shown that the first moments of the distribution, the mean square radii of gyration of the semilinear polymers, are readily obtainable directly from the analytically expressed characteristic polynomials. Purely graph-theoretical arguments have been used to determine the mean square radius of gyration for any sufficiently long semilinear molecule.

Introduction

Gaussian molecules provide a useful model for studying configurational behavior of real polymers. The disadvantages of the model, related to the approximations involved in it, are balanced, to some extent, by the relative simplicity of expressions describing various experimentally verifiable configurational properties of a polymer molecule.[1,2]

The calculations of the distribution functions of the square radius of gyration for Gaussian molecules of arbitrary connectivity becomes relatively easy when applying the graph–matrix method developed, principally, by Eichinger.[3–7] If the connectivity within a molecule follows a pattern of symmetry, the moments of the distribution can be expressed analytically,[4] and the calculation of the distribution function itself requires a simple numerical integration.[8] It has been done for linear,[9,10] comblike,[7,9] and ring[11] chains, as well as for star molecules[8,11] and regular nets.[8]

It has been shown[12,13] that for Gaussian cyclopolymers, too, the mean square radius of gyration can be calculated by merely inspecting the structure of the cycle-containing repeating elements of a polymer chain.

The dimensions of cycle-containing polymer molecules are of particular interest since it has been found that the size of cyclic molecules may affect the course of cross-linking in vinyl–divinyl polymerization.[14]

So far, two quite different estimates of the effect of cycles on dimensions of volumeless models of polymer molecules have been published.[15–18] The first, given by Allen et al.,[16] predicts a substantial collapse of randomly cyclized molecules, while the calculations by Martin and Eichinger[18] predict a much more moderate decrease in the dimensions of cyclic molecules compared with their linear analogues.

In fact, in the estimation by Martin and Eichinger,[18] the formation of small rings has been assigned a higher probability compared with formation of larger ones, and therefore this latter approach seems better suited for the cyclization occurring during polymer growth in vinyl–divinyl polymerization.

In this context, the cyclopolymerization constitutes the extreme case where only the smallest cycles are formed along essentially linear chains.

This paper deals with the evaluation of distribution functions of the square radius of gyration for a general class of Gaussian semilinear polymer molecules, including comblike and cyclopolymers. Numerically calculated distribution functions for such molecules differing in connectivity within repeating structural elements are compared.

Theoretical Background

Consider a molecule consisting of N beads connected pairwise with at least $N - 1$ identical springs. Assume[11,19] (i) the vector linking any two beads follows a Gaussian distribution (that is why the molecule is called the Gaussian), and (ii) the contribution of springs to the configurational potential is additive.

An instantaneous configuration of a molecule in a d-dimensional Cartesian system is fully described by the $d \times N$ matrix $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$, where $\mathbf{r}_j$ is the vector linking the center of mass of the molecule with the jth bead.

The assumption (ii) implies the following form of the configurational potential of the molecule:[4,8]

$$V(R) = kT\gamma \sum_{i-j} (\mathbf{r}_i - \mathbf{r}_j)^2 = kT\gamma \,\mathrm{Tr}\,(\mathbf{RKR}^{\mathrm{T}}) \qquad (1)$$

while the assumption (i) imposes the condition $\gamma = d/2\langle l^2\rangle_0$, where $\langle l^2\rangle_0$ is the mean square spring extension. The summation in eq 1 runs over all springs directly

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connecting beads i and j ($i, j = 1, 2, ..., N$). Also, the elements of **K** in the trace of the quadratic form on the right-hand side are chosen in such a way that a proper summation of the products of vector coordinates occurs.

Now, visualize the molecule as a graph with the beads being its vertices and springs being edges. It is not difficult to recognize the matrix **K** in eq 1 as the Kirchhoff matrix,[3] called sometimes the graph,[20] tree,[21] or admittance matrix,[22] that describes connectivity within molecular graph.

Kirchhoff matrices are symmetric and often sparse matrices that are frequently used in graph theory, especially when information on the number of spanning trees of a graph is required.[21,23] The number of spanning trees is the number of all connected subgraphs of a given graph containing all its vertices but have no cycle.[24] The number of spanning trees in any connected graph on N points is equal[23] to the value of any $(N - 1) \times (N - 1)$ principal minor of its Kirchhoff matrix.

The elements of the Kirchhoff matrix, k_{ij}, are defined thus $k_{ij} = k_{ji} = \delta_i$ if $i = j$, $-\epsilon$ if vertex i is directly connected to vertex j with ϵ edges, and 0 otherwise, where δ_i is the degree of vertex i, i.e., the number of edges incident on it.

Eichinger has shown[4] that the analysis of dimensions of a Gaussian molecule is equivalent to the problem of embedding its graph into d-dimensional space. Consequently, the distribution function of the square radius of gyration, s^2 for any molecule with N beads

$$P(s^2) = (2\pi)^{-1} \int_{-\infty}^{\infty} e^{i\beta s^2} [D(\beta)]^d \, \mathrm{d}\beta \qquad (2)$$

depends solely on the eigenvalue spectrum, $\{\lambda\}$, of the Kirchhoff matrix of its graph, since the characteristic function $D(\beta)$ has the form

$$D(\beta) = \prod_j^{N-1} [1 + (i\beta/\gamma N)\lambda_j^{-1}]^{-1/2} \qquad (3)$$

Similarly, the first moment of the distribution is

$$\langle s^2 \rangle_0 = N^{-1} \langle l^2 \rangle_0 \sum_j^{N-1} \lambda_j^{-1} \qquad (4)$$

The product in eq 3 and sum in eq 4 have only $N - 1$ components, since **K** is singular and has exactly one zero eigenvalue, $\lambda_N = 0$. The subscript "0" refers quantities to the unperturbed state of a molecule.

Results and Discussion

Characteristic Polynomials. The product in eq 3, rewritten in matrix form, can be rearranged to (cf. ref 4)

$$\mathrm{Det}\,(\mathrm{I} + \xi \Lambda^{-1}) = \mathrm{Det}\,(\Lambda + \xi \mathrm{I})/\mathrm{Det}\,(\Lambda) = \mathrm{Det} \begin{bmatrix} \Lambda + \xi \mathrm{I} & 0 \\ 0^{\mathrm{T}} & \xi \end{bmatrix} / \xi\, \mathrm{Det}\,(\Lambda) = \mathrm{Det}\,(\mathrm{K} + \xi \mathrm{I})/\xi\, \mathrm{Det}\,(\Lambda) = Q(-\xi)/\xi\, \mathrm{Det}\,(\Lambda) \qquad (5)$$

where $\xi = i\beta/\gamma N$, $\mathbf{\Lambda}$ is the $(N - 1) \times (N - 1)$ matrix with the nonzero eigenvalues of **K** in diagonal, **I** is the identity matrix, and $Q(\lambda)$ is the characteristic polynomial of **K** ($Q = \mathrm{Det}\,(\mathbf{K} - \lambda \mathbf{I})$).

Applying the relation first derived by Kelmans[25]

$$\mathrm{Det}\,(\mathbf{\Lambda}) = N\, \mathrm{Det}\,(\mathbf{K}_j) \qquad (6)$$

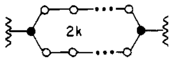
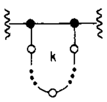
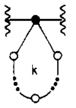
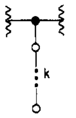
where Det $(\mathbf{K}_j)$ is the principal minor of **K** obtained by deleting its jth row and column, one gets

$$D(\beta) = [Q(-\xi)/\xi N S_t]^{-1/2} \qquad (7)$$

where S_t is the number of spanning trees of the graph describing connectivity within the molecule.

To evaluate the distribution function of a Gaussian molecule, it is therefore not necessary to calculate the entire eigenvalue spectrum of the Kirchhoff matrix if its characteristic polynomial can be expressed analytically.

Table I
Characteristic Polynomials, $Q(\lambda) = \varphi(x) U_{m-1}[\psi(x)]$, $x = 1 - \lambda/2$, of the Kirchhoff Matrices for Gaussian Semilinear Polymer Graphs Having m Repeating Structural Elements[a]

	structural element	$\varphi(x)$	$\psi(x)$
symmetric cyclopolymer		$(x^2 - 1) \times (2U_k)^{m+1}$	$(x^2 - 1)U_k + \mathrm{T}_{k+1}$
spanning-path cyclopolymer		$2(T_{k+2} - 1) \times (U_k + 1)^{m-1}$	$(T_{k+2} + U_{k+1} - 1)/U_k + 1)$
pending-cycle cyclopolymer		$2(T_{k+1} - 1) \times (U_k)^{m-1}$	$(T_{k+1} + U_k - 1)/U_k$
comblike polymer		$2(x - 1) \times U_k(U_k - U_{k-1})^{m-1}$	$T_{k+1}/(U_k - U_{k-1})$
linear chain		$2(x - 1)$	x

[a] $T_j(x)$ and $U_j(x)$ are the Chebyshev polynomials of the first and second kind, respectively.[27] The parameter k counts only the off-main-chain beads in the structural elements (open circles).

It has been shown[26] that for a certain class of semilinear polymer graphs, the characteristic polynomials of their Kirchhoff matrices can be expressed in the form

$$Q(\lambda) = \varphi(x) U_{m-1}[\psi(x)]; \qquad x = 1 - \lambda/2 \qquad (8)$$

where

$$U_{m-1}[...] = \sin\,(m \arccos\,[...])/\sin\,(\arccos\,[...])$$

is the $(m - 1)$th order Chebyshev polynomial of the second kind[27] and m is the number of identical branched or cyclic structural elements linked together via single bonds into a linear chain.

The function $\varphi(x)$ and the argument of U_{m-1}, $\psi(x)$, are also combinations of Chebyshev polynomials of the first, $T_j(x) = \cos\,(j \arccos x)$, and second, $U_j(x)$, kind.[27] The actual forms of $\varphi(x)$ and $\psi(x)$ are presented in Table I.

Mean Square Radii of Gyration. What is usually of primary interest is the first moment of the square radius distribution, the mean square radius of gyration of a polymer molecule. As shown in the Appendix, the sum of the reciprocal eigenvalues appearing in eq 4 can be readily calculated for any molecule given an analytically expressed characteristic polynomial of the Kirchhoff matrix of its graph.

For the semilinear polymers, the structures of which are shown schematically in Table I, the appropriate sums of the reciprocals are presented in Table II.

Certain special cases seem to be worth pointing out. Thus, the known expressions[4,12,26] for the characteristic polynomial and for the mean square radius of gyration for a ring molecule with N beads can be derived from any of the three cyclopolymer structures (Tables I and II) by putting $m = 1$

$$Q(\lambda) = 2[T_N(1 - \lambda/2) - 1] = -\lambda\{U_{N-1}[(1 - \lambda/4)^{1/2}]\}^2 \qquad (9)$$

and

$$\langle s^2 \rangle_0 / \langle l^2 \rangle_0 = (N - 1/N)/12 \qquad (10)$$

It is also not difficult to verify that for $m = 2$, the characteristic polynomials and expressions for $\langle s^2 \rangle_0$ are the

Table II
Sums of Eigenvalue Reciprocals for the Kirchhoff Matrices and Numbers of Spanning Trees of Semilinear Polymer Graphs

	$\sum\lambda_j^{-1}$	S_t
symmetric cyclopolymer	$[(m^2 - 1)(k + 1)(k + 3) + (m + 1)k(k + 2) + 1.5]/6$	$(2k + 2)^m$
spanning-path cyclopolymer	$[(m^2 - 1)(2k + 3) + (m - 1)k(k + 1) + (k^2 + 4k + 3)/2]/6$	$(k + 2)^m$
pending-cycle cyclopolymer	$[(m^2 - 1)(k + 1) + (m - {}^1/_2)k(k + 2)]/6$	$(k + 1)^m$
comblike polymer	$[(m^2 - 1)(k + 1) + 3(m - 1)k(k + 1) + k\ (k + 2)]/6$	1
linear chain	$(m^2 - 1)/6$	1

same for all cyclopolymer structures, as they should be.

The substitution $k = 0$ yields for the symmetric and spanning-path cyclopolymers the characteristic polynomal

$$Q(\lambda) = 2^{m-1}\lambda(\lambda - 4)U_{m-1}[(\lambda^2 - 6\lambda + 4)/4] \quad (11)$$

and the mean square radius of gyration

$$\langle s^2\rangle_0/\langle l^2\rangle_0 = (N - 2/N)/8 \quad (12)$$

for a Gaussian linear molecule with $m = N/2$ "conjugated double bonds". More realistically, such a molecule should be considered rather as a linear progression of chains and rings with all interbead linear fragments having the same configurational properties.

Similarly, substituting $k = 1$ into the expressions for the pending-cycle cyclopolymer (Tables I and II) yields a characteristic polynomial and mean square radius of gyration for a linear molecule with "double bonds" pending from each bead of the chain.

For $k = 0$, the expressions for the characteristic polynomials for the pending-cycle cyclopolymer and for the comblike polymer reduce to that of a linear chain.

For $m \to \infty$, the limiting value of the mean square radius of gyration for a semilinear polymer molecule is given by the generalized Debye equation[12]

$$\langle s^2\rangle_0/\langle l^2\rangle_0 = (1/6)N\frac{A - B}{nB} \quad (13)$$

where n is the number of beads in a structural element and A and B are the $n \times n$ principal minors of the Kirchhoff matrix of the molecular graph. The minors A and B are related to the Kirchhoff submatrices of the structural elements in the interior of the molecule and at its end, respectively.

Equation 13 is valid for semilinear polymers with structural elements (super units) of arbitrary structure, without restrictions on the length of the linear portion of the chain between them.[12]

Graph theory provides an easy method for calculating the values of A and B simply by inspecting the structure of repeating elements.[21] As shown in Figure 1a, the value of B is the number of spanning trees in the structural element itself.

This is easy to see, since the Kirchhoff submatrix corresponding to the structural element occurring at the end of the chain is identical with that of its graph having one dummy vertex saturating the edge through which the element is connected to the rest of the molecule and subsequently deleted row and column corresponding to this vertex. For an acrylic structure, such as for comblike molecules, the value of B is 1. For a unicyclic structure, the value of B is the number of beads (or bonds) in the cycle, etc.

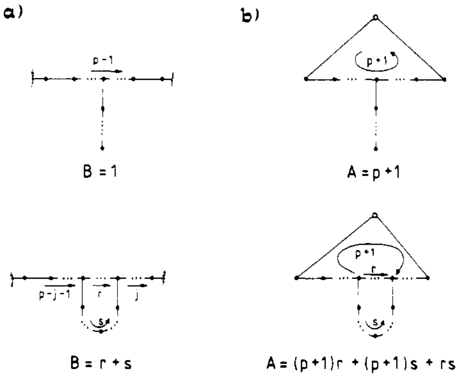


Figure 1. Examples of branched and cyclic structural elements in a semilinear polymer (a) and their contracted versions (b). The values of B and A required in eq 13 are the numbers of spanning trees in the graphs of the elements themselves and in their contracted graphs, respectively. j, p, r, and s are the path lengths (numbers of edges) in the graphs.

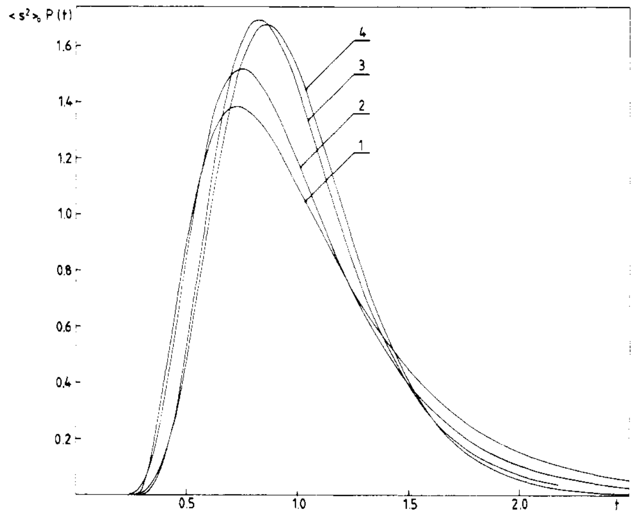


Figure 2. Distribution functions of the square radius of gyration for semilinear polymers consisting of 30 beads each having 5 identical structural elements: (1) symmetric cyclopolymer, $k = 2$; (2) spanning-path cyclopolymer, $k = 4$; (3) pending-cycle cyclopolymer, $k = 5$; (4) comblike polymer, $k = 5$.

In order to evaluate A, it is convenient to add to the graph of a structural element two auxiliary vertices saturating the two edges that connect this element with the remaining two parts of the molecule. Contraction of these two vertices into a single one (cf. Figure 1b) forms a new contracted graph containing one more cycle than the graph of the structural element itself. Now, it is easy to see that by deleting the row and column corresponding to the dummy vertex of the contracted graph, a submatrix is obtained that is exactly the Kirchhoff submatrix describing connectivity within the repeating structural element in the interior of a molecule. Thus, the value of A is the number of spanning trees in the contracted graph of the structural element.

For an acyclic structural element, A is equal to the number of bonds in the only cycle in its contracted graph, i.e., it is one more than the number of bonds in this part of the element that constitutes the fragment of the main chain. For a unicyclic structural element, the value of A is the sum of the binary products of the numbers of edges in the three paths linking the "trifunctional" vertices in the contracted graph (cf. Figure 1b), etc.

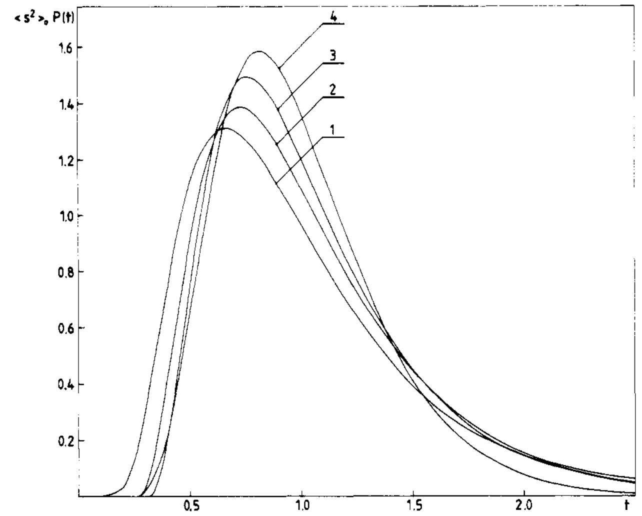


Figure 3. Distribution functions of the square radius of gyration for the symmetric cyclopolymers and the one for a linear chain (curve 1) each consisting of 30 beads. The cyclopolymers have m cycles, each of $2k + 2$ beads linked via single bonds: (2) $m = 5$, $k = 2$; (2) $m = 3$, $k = 4$; (4) $m = 1$, $k = 14$ (ring polymer).

Distribution Functions. The distribution functions of the square radius of gyration for Gaussian semilinear polymer molecules differing in structure, but each having 30 beads, are shown in Figures 2 and 3. As usual, they are presented in reduced coordinates as the plots $\langle s^2\rangle_0 P(t)$ vs. t, where $t = s^2/\langle s^2\rangle_0$.

The functions were calculated numerically with the procedure described in detail in the next paragraph. The distribution functions for the linear and ring molecules each comprising 30 beads are also shown in Figure 3. An increase in the number of beads up to, say, 60 only negligibly affects the shape of these two latter distributions.

As it was expected, two general conclusions can be drawn by examining the distribution functions. The first is that as the structural element of a semilinear is more ramified, the narrower is the distribution function of the polymer.[4] This is illustrated by Figure 2, where the distribution functions are shown for different semilinear polymers, each having five structural elements.

The second conclusion is that with increasing number of structural elements, m, the shape of the distribution function more closely resembles that of a linear chain.[11] For a polymer with "conjugated double bonds", as well as for a chain with pending "double bonds", the distribution functions can hardly be distinguished from that of a linear chain.

This is also illustrated by Figure 3, where distribution functions for symmetric cyclopolymers are shown. As can be seen, the shapes of these functions are intermediate between that for a linear and that for a ring molecule.

The symmetric cyclopolymers are interesting, since their mean square radii of gyration provide an upper bound for the dimensions of a cyclized linear chain, similarly the result of Allen et al.[16] is a strong lower bound.[17]

For a symmetric cyclopolymer with large k and $m \to \infty$, the Zimm–Stockmayer[28] ratio approaches $^1/_4$ (not $^1/_2$ as erroneously reported[12]).

Perhaps it is worth mentioning that the Kirchhoff matrix of a symmetric cyclopolymer graph shares its eigenvalue spectrum with that of a set of disjoint linear-type graphs shown in Figure 4. This set results from splitting the cycles in the cyclopolymer without affecting the degrees of vertices but with two bonds per cycle in the "main chain" subgraph having the weight $2^{1/2}$ greater than the other bonds have.

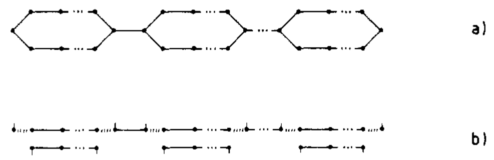


Figure 4. Two graphs for which the Kirchhoff matrices have the same eigenvalue spectra: (a) graph of a symmetric cyclopolymer; (b) a set of disjoint linear-type graphs. The edges that have the weight $2^{1/2}$ greater than the other ones are indicated.

Numerical Procedure. For a 3-dimensional space, eq 2 can be rearranged to read (cf. ref 4)

$$\langle s^2\rangle_0 P(t) = \int_0^\infty [\cos(\alpha\pi t)Z_r(\alpha) - \sin(\alpha\pi t)Z_i(\alpha)]\, d\alpha \tag{14}$$

where, according to (7)

$$Z(\alpha) = Z_r(\alpha) + iZ_i(\alpha) = [Q(-i\alpha c)/(i\alpha c N S_t)]^{-3/2} \tag{15}$$

and $c = 2\pi/\sum\lambda_j^{-1}$ is the scaling factor obtained by the substitutions $\beta = \alpha c\gamma N$ and $s^2 = \langle s^2\rangle_0 t = 3\sum\lambda_j^{-1}t/2\gamma N$.

The integral 14 was evaluated by using 13-point Gauss–Kronrod quadrature,[29] which is particularly suited for oscillating integrals.[30]

The upper limit of integration, $\alpha_{\max}$, was adjusted in such a way that the value of integrand at $\alpha_{\max}$ was about 1 order of magnitude lower than the estimate of error of integral evaluation in the most significant first subinterval out of 48 into which the range from 0 to $\alpha_{\max}$ was divided. In all cases, $|Z(\alpha_{\max})|$ was lower than 10^{-9}, while $|Z(0)|$ was 1. Then, $\alpha_{\max}$ did not exceed 30.

First, two tables containing Z_r and Z_i values were calculated in all nodes of the quadrature and in all subintervals, according to increasing α's. Then the tables were used to evaluate the integral at required t values.

To avoid the values of integrand crossing branching points in the integration contour,[8,31] the calculations were programmed as in the following example.

For the comblike molecules, the function $Z(\alpha)$ was rewritten in the form (cf. Table I)

$$Z(\alpha) = 1/\{(2^{m-1}/m)^{1/2}[U_k/(k+1)]^{1/2}\prod_{j=1}^{m-1}[T_{k+1} - \cos(j\pi/m)(U_k - U_{k-1})]^{1/2}]^3 \tag{16}$$

where the argument in all Chebyshev polynomials was $1 + i\alpha c/2$. The cosine appeared because $U_{m-1}(z) = 2^{m-1}\prod_{j=1}^{m-1}[z - \cos(j\pi/m)]$. Whenever the value of the square root of a term in product 16 attempted to move from the first to second or from the third to fourth quadrant of the complex plane, the sign of the root was reversed to enable it to do so, thus keeping the calculated values at the same Riemann sheet. Each such sign reversal corresponded to the values of the term going around the negative half of real axis.

To limit the roundoff error while calculating Chebyshev polynomials for small α, the identities A-1 and A-2 (see Appendix) rather than the usual recurrence formulas[27] were used. The calculations were performed by using 14-digit double-precision arithmetics on a desk microcomputer.

Acknowledgment. Drs. A. and S. Lewanowicz are acknowledged for advice during numerical calculations.

Appendix

The identities

$$T_k(1+z) = k\sum_{j=0}^{k}\frac{(k+j-1)!}{(2j)!(k-j)!}(2z)^j \tag{A-1}$$

$$U_k(1 + z) = \sum_{j=0}^{k} \frac{(k + j + 1)!}{(2j + 1)!(k - j)!}(2z)^j \qquad \text{(A-2)}$$

and

$$\sum_{j=1}^{m-1} [1 - \cos (j\pi/m)]^{-1} = (m^2 - 1)/3 \qquad \text{(A-3)}$$

were found very useful for evaluating the moments of the square radius of gyration distribution directly from the characteristic polynomials of the Kirchhoff matrices of semilinear polymer graphs.

In order to calculate the sum of eigenvalue reciprocals (Table II) required by eq 4, each term of the characteristic polynomial (Table I) was dealt with separately. As known from elementary algebra, the sum of reciprocals of all nonzero roots of a polynomial, $a_0 + a_1z + a_2a^2 + ...$ is simply given by $-a_1/a_0$, if $a_0 \neq 0$; $-a_2/a_1$, if $a_0 = 0$, $a_1 \neq 0$, etc.

The coefficients of λ in the Chebyshev polynomials with the argument $1 - \lambda/2$ are provided by (A-1) and (A-2).

The contribution from the term U_{m-1} (the roots of which are at $\cos(j\pi/m)$ ($j = 1, 2, ..., m - 1$)) can be calculated by using (A-3), since for each function ψ listed in Table I, the sum of the root reciprocals of a polynomial $\psi(1 - \lambda/2) = \cos (j\pi/m)$ has the form

$$f(k)[1 - \cos (j\pi/m)]^{-1} + g(k) \qquad \text{(A-4)}$$

where $f(k)$ and $g(k)$ are polynomials of parameter k of order 2, at most.

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