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Dimensions of Intramolecularly Cross-Linked Polymers. 1. Theory[†]

James E. Martin*

Division 1152, Sandia National Laboratories, Albuquerque, New Mexico 87185

B. E. Eichinger

Department of Chemistry, BG-10, University of Washington, Seattle, Washington 98195.

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ABSTRACT: A method is developed for the computation of the unperturbed radius of gyration of a class of nonlinear polymers. These polymers may be branched or may contain circuits. The method is applied to star and comb polymers and to the cyclized chain. The latter is defined as a homopolymer intramolecularly cross-linked in dilute solution. The contraction in polymer dimensions with increasing cross-link density is calculated and discussed in relation to the work of others.

Introduction

Early work in the calculation of the mean square radius of gyration $\langle s^2\rangle_0$ of nonlinear Gaussian polymers was initiated by Kramers[1] and developed by Zimm and Stockmayer.[2] Although Zimm and Stockmayer were able to calculate $\langle s^2\rangle_0$ for the circular chain, the remainder of their work dealt with the configurational statistics of branched or ramified polymers. Following Zimm and Stockmayer, researchers[3–10] have calculated the mean square dimensions of star and comb polymers and have applied these calculations to experimentally realizable ensembles of heterogeneous, random, stars and combs. Others[6] have undertaken the calculation of higher moments of the radius of gyration of ramified polymers. At the present time, the configurational statistics of unperturbed branched Gaussian polymers is reasonably well understood.

Polymers with circuits, however, do not lend themselves to such a tractable development. Eichinger[11] has shown that the mean square unperturbed radius of gyration of any Gaussian polymer, regardless of topological complexity, can always be expressed in terms of the eigenvalues of its associated Kirchhoff matrix. Eichinger has also given a method for determining the characteristic function of the distribution function of the radius of gyration for any polymer. These two methods of determining $\langle s^2\rangle_0$ can be applied to polymers containing circuits, as long as the technical difficulties encountered in calculating the eigenvalue spectra can be surmounted. The first of these methods has been used extensively in the numerical calculation of the mean square dimensions of polymer networks. In certain cases, however, a simplified technique can be used to calculate $\langle s^2\rangle_0$ analytically for multiple-ring polymers. The purpose of this contribution is to show one way in which this is possible and to apply the resultant formulation to an ensemble of intramolecularly cross-linked polymers.

The intramolecular cross-linking of a polymer chain was first treated by Kuhn,[12,13] who obtained an expression for the decrease in the intrinsic viscosity as a function of cross-link number. Kuhn's treatment, which is based on a heuristic argument, is not in agreement with the results of this paper. Edwards and Freed[14–16] calculated the Zimm–Stockmayer contraction factor, g, for a randomly cross-linked polymer chain and found that $g = (m + 1)^{-1}$, where m denotes the number of cross-links. The Zimm–Stockmayer contraction factor of a nonlinear polymer is defined as the ratio of $\langle s^2\rangle_0$ of the nonlinear chain to that of the linear chain of the same degree of polymerization. In fact, the randomly cross-linked polymers considered by Edwards and Freed exhibit the anomaly of network collapse;[17] the mean square dimensions depend only on the cross-link density and not on the polymer molecular weight.

When this theory was applied to intramolecularly cross-linked chains, large discrepancies were found. These were partially rectified by the inclusion of excluded volume effects in the theory,[18] and a physically reasonable result was found.

The calculation presented here includes the effect of ring weighting, or monomer–monomer contact probabilities, so that the result is substantially different from that of Allen et al. In the following paper, experimental data are compared with the calculated results to verify the extension of the Gaussian model to the complex polymers considered here.

General Development

In certain cases, a branched or cross-linked Gaussian polymer can be decomposed into a number of subpolymers having separable configuration statistics. In the Gaussian approximation a description of each subpolymer can be given in terms of its Kirchhoff matrix and its Moore–Penrose or generalized inverse. If the generalized inverse for each subpolymer can be computed, and this is possible in a number of useful cases, then the mean square unperturbed radius of gyration may easily be found for the entire molecule. To clarify the class of polymers under consideration, the following graphical construction is useful.

Divide a polymer into a number of subpolymers, the νth of which is denoted by G_ν, with the subscript running from 0 to p. A graphical relation between these subpolymers is clear: if G_ν and G_μ are connected at a junction, then an edge (line) is drawn between nodes labeled ν and μ, respectively. In Figure 1 such a graphical representation of a polymer is shown, its particular division into subpolymers being nonunique. If the subpolymer graph of a polymer is treelike, then in the Gaussian approximation the subpolymers have independent configuration statistics. A tree is defined as a connected graph without circuits.

It will prove useful to introduce a new matrix that describes the rooted paths on this subpolymer graph. In this connection, a rooted path is defined to be a walk that originates at node zero (the root) and proceeds without reversal to any other node ν. Having specified the root, such a rooted path is then unique for a tree. To describe these paths one may define a $p \times p$ path matrix **H** such that the element $h_{\alpha\nu}$ is given the value 1 if node α lies on the rooted path to node ν, hereafter called the ν-path, and

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[†] This work performed at the University of Washington.

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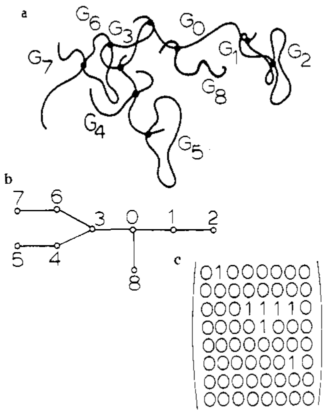

$$\begin{pmatrix}0&1&0&0&0&0&0&0\\0&0&0&0&0&0&0&0\\0&0&0&1&1&1&1&0\\0&0&0&0&1&0&0&0\\0&0&0&0&0&0&0&0\\0&0&0&0&0&0&1&0\\0&0&0&0&0&0&0&0\\0&0&0&0&0&0&0&0\end{pmatrix}$$

Figure 1. (a) Representation of a complex molecule containing linear chains and rings. Subpolymers G_1, G_2, G_5, and G_6 are circular chains, subpolymer G_4 is a tetrafunctional star, and the remainder are linear chains. (b) Graphical representation of the molecule depicted in Figure 1a. The submolecules G_μ are the nodes of the tree, and the multivalent junctions of Figure 1a are the edges. (c) The path matrix of the rooted tree of Figure 1b.

is zero otherwise. Properties of this path matrix are easily derived and hence are given without proof. Some properties of $\mathbf{H}$ are as follows:

(i) The matrix $\mathbf{H}$ and all its powers are traceless. The diagonal elements of any power of $\mathbf{H}$ are zero.

(ii) The eigenvalues of $\mathbf{H}$ are zero. This is easily seen, since $\mathbf{H}$ can always be written as an upper triangular matrix.

(iii) $(\mathbf{H}^{k+1})_{\alpha\beta} = j!/(j-k)!k!$ if there are j nodes between α and β and α lies on the β-path. Otherwise this element is zero.

(iv) $\mathbf{H}^p = \mathbf{0}$, since no rooted path can pass through more than $p - 1$ nodes. Conversely, the minimum value of k that renders $\mathbf{H}^{k+1}$ null is the length of the longest rooted path on the graph.

(v) $(\mathbf{H}^t\mathbf{H})_{\alpha\beta} = k$, where k is the number of nodes shared in common by the rooted paths to α and to β. The path to α does not include α.

(vi) $(\mathbf{H}\mathbf{H}^t)_{\alpha\beta} = q$, where q is the number of rooted paths that include both α and β.

A detailed labeling of the polymer subunits must now be introduced. Taking the coordinate origin to lie at the center of mass of G_0, we denote the position vector of the ith vertex of G_ν by $\mathbf{r}_i^{(\nu)}$, where the vertices of G_ν are labeled $v_i^{(\nu)}$, $1 \le i \le l_\nu$. If $v_i^{(\nu)}$ on G_ν is connected to $v_j^{(\mu)}$ on G_μ, then $\mathbf{r}_i^{(\nu)} = \mathbf{r}_j^{(\mu)}$ and the delta function constraint $\delta^3(\mathbf{r}_i^{(\nu)} - \mathbf{r}_j^{(\mu)})$ must multiply the product of Boltzmann factors for subpolymers in the configuration integral. If q subpolymers intersect at a junction, this junction will have a relative weighting of q since each subpolymer contributes a vertex. This extra contribution of subpolymer junctions to the mean square radius can be corrected for, and in general any relative weighting can be assigned to the junctions. With these conventions, the expression for the mean square radius of gyration becomes

$$\langle s^2\rangle_0 = N^{-1}\sum_{\nu=0}^{p}\sum_{k=1}^{l_\nu}\langle|\mathbf{r}_k^{(\nu)} - \mathbf{a}_t|^2\rangle_0 \tag{1a}$$

$$\mathbf{a}_t = \sum_{\nu=0}^{p}(l_\nu/N)\mathbf{a}_\nu; \qquad N = \sum_{\nu=0}^{p} l_\nu \tag{1b}$$

where $\mathbf{a}_\nu$ is the center of mass of G_ν, $\mathbf{a}_t$ is the center of mass of the entire polymer, and $\mathbf{a}_0 = 0$. Completion of the second summation in eq 1a yields

$$\langle s^2\rangle_0 = N^{-1}\sum_{\nu=0}^{p} l_\nu[\langle s_\nu{}^2\rangle_0 + \langle|\mathbf{a}_t - \mathbf{a}_\nu|^2\rangle_0] \tag{2}$$

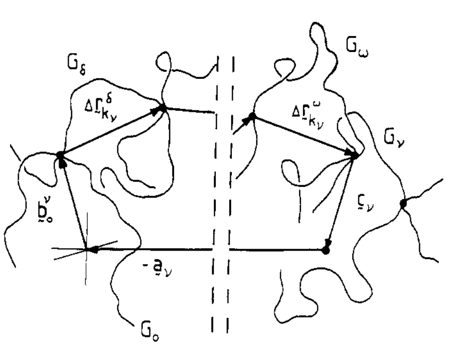

Figure 2. The vector $\mathbf{a}_\nu$ is decomposed into a sum of vectors that start at $\mathbf{a}_0$ (the coordinate origin) and pass from cross-link point to cross-link point. Note that the subpolymers are not end-linked but continue through the cross-link points.

where $\langle s_\nu{}^2\rangle_0$ is the mean square unperturbed radius of gyration of G_ν.

Consider a construction of the vector $\mathbf{a}_\nu$. If subpolymer G_α lies on the ν-path and an enumeration of the ν-path is given by the sequence 0, δ, ..., β, α, γ, ..., ω, ν, then a vector can be constructed that runs from the G_β,G_α junction to the G_α,G_γ junction, as in Figure 2. As a simple mnemonic, these junction vertices on G_α are labeled $k_{\nu-}$ and $k_{\nu+}$, respectively. Thus this vector that runs through G_α is $\Delta\mathbf{r}_k^\alpha \equiv \mathbf{r}_{k_{\nu+}}^\alpha - \mathbf{r}_{k_{\nu-}}^\alpha$. Defining $\mathbf{b}_0^\nu$ to be the vector that runs from $\mathbf{a}_0$ to the G_0,G_δ junction and $\mathbf{c}_\nu$ to be the vector that runs from the G_ω,G_ν junction to $\mathbf{a}_\nu$ gives an expression for $\mathbf{a}_\nu$:

$$\mathbf{a}_\nu = \mathbf{b}_0^\nu + \mathbf{T}_\nu + \mathbf{c}_\nu \tag{3a}$$

$$\mathbf{T}_\nu \equiv \sum_{\alpha=1}^{p} h_{\alpha\nu}\Delta\mathbf{r}_{k_\nu}^{(\nu)} \tag{3b}$$

This decomposition of the vector $\mathbf{a}_\nu$ is shown in Figure 2. The sum in eq 2 involves terms like $\langle\mathbf{a}_\nu\cdot\mathbf{a}_\mu\rangle_0$. These are simply evaluated in terms of the generalized inverse $\mathbf{A}^{(\nu)}$ of the Kirchhoff matrix $\mathbf{K}^{(\nu)}$ for each of the subpolymers G_ν. In Appendix A it is shown that $(\mathbf{A}^{(\nu)})_{ij} = \langle(\mathbf{r}_i^{(\nu)} - \mathbf{a}_\nu)\cdot(\mathbf{r}_j^{(\nu)} - \mathbf{a}_\nu)\rangle/\langle l^2\rangle_0$, where $\langle l^2\rangle_0$ is the mean square unperturbed Gaussian bond length. Use of this result along with eq 3a and 3b gives

$$\langle\mathbf{a}_\nu\cdot\mathbf{a}_\mu\rangle_0/\langle l^2\rangle_0 = \mathbf{A}_{k_\mu,k_\nu}^{(0)} + \delta_{\mu\nu}\mathbf{A}_{k_0,k_0}^{(\nu)} + h_{\mu\nu}\Delta\mathbf{A}_{k_\nu,k_0}^{(\mu)} + h_{\nu\mu}\Delta\mathbf{A}_{k_\mu,k_0}^{(\nu)} + \sum_{\alpha=1}^{p} h_{\alpha\nu}h_{\alpha\mu}\Delta\mathbf{A}_{k_\nu,k_\mu}^{(\alpha)} \tag{4a}$$

$$\Delta\mathbf{A}_{k_\nu,k_\mu}^{(\alpha)} \equiv \mathbf{A}_{k_{\nu+},k_{\mu+}}^{(\alpha)} + \mathbf{A}_{k_{\nu-},k_{\mu-}}^{(\alpha)} - \mathbf{A}_{k_{\nu+},k_{\mu-}}^{(\alpha)} - \mathbf{A}_{k_{\nu-},k_{\mu+}}^{(\alpha)} \tag{4b}$$

$$\mathbf{A}_{k_\mu,k_0}^{(\nu)} \equiv \mathbf{A}_{k_{\mu+},k_0}^{(\nu)} - \mathbf{A}_{k_{\mu-},k_0}^{(\nu)} \tag{4c}$$

where vertex k_μ on G_0 is the junction on G_0 leading to G_μ and vertex k_0 on G_μ is the junction on G_μ leading to G_0. Combining eq 4 with eq 2 and 1b gives as an expression for the radius of gyration

$$\begin{aligned} N\langle s^2\rangle_0/\langle l^2\rangle_0 = {} & \sum_{\nu=0}^{p} l_\nu\langle s_\nu{}^2\rangle_0/\langle l^2\rangle_0 + \sum_{\nu=1}^{p}[\mathbf{A}_{k_\nu,k_\nu}^{(0)} + \mathbf{A}_{k_0,k_0}^{(\nu)} + \sum_{\alpha=1}^{p} h_{\alpha\nu}\Delta\mathbf{A}_{k_\nu,k_\nu}^{(\alpha)}] - \\ & \sum_{\mu=1}^{p}\sum_{\nu=1}^{p}(l_\mu l_\nu/N)\Big[\mathbf{A}_{k_\mu,k_\nu}^{(0)} + \delta_{\mu\nu}\mathbf{A}_{k_0,k_0}^{(\nu)} + h_{\mu\nu}\Delta\mathbf{A}_{k_\mu,k_0}^{(\nu)} + \\ & h_{\nu\mu}\Delta\mathbf{A}_{k_\mu,k_0}^{(\nu)} + \sum_{\alpha=1}^{p} h_{\alpha\mu}h_{\alpha\nu}\Delta\mathbf{A}_{k_\nu,k_\mu}^{(\alpha)}\Big] \end{aligned} \tag{5}$$

If consideration is restricted to the special case $\mathbf{H} = \mathbf{0}$, a considerable simplification occurs. Polymers in this category include stars, combs, and cyclized chains. For these polymers, eq 5 simplifies to

$$N\langle s^2\rangle_0/\langle l^2\rangle_0 = \sum_{\nu=0}^{p} l_\nu \langle s_\nu{}^2\rangle_0/\langle l^2\rangle_0 + \sum_{\nu=1}^{p}[l_\nu(N-l_\nu)/N\mathbf{A}^{(\nu)}_{k_0,k_0} + l_\nu \mathbf{A}^{(0)}_{k_\nu,k_\nu}] - \sum_{\nu=1}^{p}\sum_{\mu=1}^{p}(l_\nu l_\mu/N)\mathbf{A}^{(0)}_{k_\nu,k_\mu} \quad (6)$$

If each junction is given only a single weighting, then $N = (\sum_{\nu=0}^{p} l_\nu) - p$ and a term Δ must be subtracted from the right-hand side of eq 6, where

$$\Delta = \sum_{\nu=1}^{p}\sum_{\mu=1}^{p} N^{-2}(pl_\nu l_\mu - 2l_\nu N)\mathbf{A}^{(0)}_{k_\nu,k_\mu} + \sum_{\nu=1}^{p}[(pl_\nu{}^2/N^2)\mathbf{A}^{(\nu)}_{k_0,k_0} + \mathbf{A}^{(0)}_{k_\nu,k_\nu}] \quad (7)$$

To make use of eq 5–7 requires the elements of the $\mathbf{A}^{(\nu)}$. In Appendix B it is shown that for the linear and circular chains of n vertices, $\mathbf{A}$ is easily found. The k,l element of $\mathbf{A}$ is given by

$$\text{(linear)} \quad \mathbf{A}_{k,l} = (1/2n)[k(k-1) + l(l-1) + (n-1) \times (2n-1)/3] + (2-l-k)/2 - |l-k|/2 \quad (8a)$$

$$\text{(circular)} \quad \mathbf{A}_{k,l} = |l-k|(|l-k|-n)/2n + (n+1)(n-1)/12n \quad (8b)$$

These results are used in the following sections to solve some problems of practical importance.

Stars and Combs

To illustrate the utility of the formulation, we apply eq 6, 7, and 8a to star and comb polymers. The regular f-branched star with n elements per branch is treated as f linear chains of $n+1$ elements each, with a single end of each coincident to form a junction. Giving the junction single weighting, with $N = nf + 1$, the contraction factor is immediately obtained as

$$g_{\text{star}} = f(n+1)^2/(nf+1)^2 + n(1 - 1/f(n+1))(f-1)(2n+1)/(nf+1)^2 \quad (9a)$$

$$\cong (3 - 2/f)/f \qquad \text{if } n \gg 1 \quad (9b)$$

which agrees with the result obtained by Zimm and Stockmayer.

Equally simple is the calculation of the contraction factor for the comb polymer with uniform arm length but with random attachment of these f arms to the polymer backbone. If the backbone, G_0, has r elements and each arm, G_μ, has n elements, then

$$g = (r^2 + n^2 f)/(nf+r)^2 - 6n^2/(nf+r)^3\Big[\sum_{\nu=1}^{f}\sum_{\mu=1}^{f}\mathbf{A}^{(0)}_{k_\nu,k_\mu}\Big] + 6n/(nf+r)^2[\sum_{\nu=1}^{f}\mathbf{A}^{(0)}_{k_\nu,k_\nu}] + 6nf((f-1)n+r)/(nf+r)^3\mathbf{A}_{1,1} \quad (10a)$$

Random placement of the arms on the polymer backbone is equivalent to letting

$$\sum_{\nu=1}^{f}\sum_{\mu=1}^{f}\mathbf{A}^{(0)}_{k_\nu,k_\mu} = (f/r)^2\sum_{i=1}^{r}\sum_{j=1}^{r}\mathbf{A}^{(0)}_{i,j} \quad (10b)$$

After the appropriate matrix elements are substituted, this reduces to

$$g_{comb} = (1 + 2fq + (2f+f^2)q^2 + (3f^2 - 2f)q^3)/(1+fq)^3 \qquad n \gg 1, \quad r \gg 1 \quad (10c)$$

where $q \equiv n/r$. This result is in agreement with that obtained by Casassa and Berry.[19]

The Cyclized Chain

It is of some interest to obtain an expression for the dimensions of a polymer intramolecularly cross-linked in very dilute solution. A polymer with a single cross-link can be thought of as a circular chain, G_0, of l elements attached to a linear chain, G_1, of n elements, so that $N = n + l$. A combination of eq 6, 8a, and 8b gives

$$\langle s^2\rangle_0/\langle l^2\rangle_0 = (n^2 + l^2/2)/6N + nl(l/12 + n/3 + k(k-1)/n + (1-k) - 1/2)/N^2 \quad (11)$$

where the junction is taken to be at the kth element of the linear chain. Introducing the variable $\alpha = l/N$, the fraction of elements in the loop, and averaging over all k, the expression for the contraction factor becomes

$$g(\alpha) = 1 - \alpha + \alpha^3/2 \quad (12)$$

If $\alpha = 1$, then $g = {}^1/_2$, which is just the contraction factor for the circular chain. If the contraction factor is indiscriminately averaged over all loop sizes without regard to ring weighting, then

$$\langle g\rangle = \int_0^1 g(\alpha)(1-\alpha)\,\mathrm{d}\alpha \Big/ \int_0^1 (1-\alpha)\,\mathrm{d}\alpha = 43/60 \quad (13a)$$

With the effect of ring weighting included the single cross-link result is substantially different, and

$$\langle g\rangle = \int_{N^{-1}}^1 g(\alpha)(1-\alpha)/\alpha^{3/2}\,\mathrm{d}\alpha \Big/ \int_{N^{-1}}^1 (1-\alpha)/\alpha^{3/2}\,\mathrm{d}\alpha = 1 - (67/105)N^{-1/2} \quad (13b)$$

This expression involves the variable N, which is proportional to the degree of polymerization, DP. The numerical factor[20] 67/105 appears in the same manner in the single contact term in the cluster expansion of the excluded volume effect for the linear chain. For chains of large DP, the contraction in dimensions is very small since the average loop size $\alpha \cong (2/3)N^{-1/2}$. Therefore, for such large chains a single cross-link constitutes a relatively small portion of its structure and it is relatively unlikely that a second cross-link will involve this loop.

A picture now emerges of a multiply intramolecularly cross-linked polymer. It is a linear chain with a number of loops attached thereto. A reasonable upper limit to the number of cross-links, m, allowable in this low cross-link density model is given by $m\langle\alpha\rangle = 1$ or $m = 3N^{1/2}/2$. The appropriate expression for the chain contraction factor of this cyclized chain can be obtained from eq 6, 8a, and 8b. The result is

$$g(\{\alpha_k\}) = 1 - (\sum_{k=1}^{m}\alpha_k)(1 - \sum_{k=1}^{m}\alpha_k{}^2) - (1/2)\sum_{k=1}^{m}\alpha_k{}^3 \quad (14)$$

where α_k denotes the fraction of elements in the kth loop.

The loops have already been averaged over all positions on the linear chain. To obtain the value of the contraction factor that would be measured in an actual experiment, $\langle g\rangle$, requires that eq 14 be averaged over all possible loop sizes. With ring weighting, the approximate integral form of this average is

$$\langle g\rangle = Z^{-1}\int_{N^{-1}}^{1-(m-1)/N}\alpha_1{}^{-3/2}\,\mathrm{d}\alpha_1 \int_{N^{-1}}^{1-\alpha_1-(m-2)/N}\alpha_2{}^{-3/2}\,\mathrm{d}\alpha_2 \int\cdots\int_{N^{-1}}^{1-\Sigma_1{}^{m-1}\alpha_j}\alpha_m{}^{-3/2}g(\{\alpha_k\})(1 - \sum_{1}^{m}\alpha_j)^m\,\mathrm{d}\alpha_m \quad (15)$$

where Z is the appropriate normalization constant. The more exact expression, in the form of a sum, is

$$\langle g\rangle = Z^{-1}\sum_{\{l_k\}} g(\{\alpha_k\})(N - \sum_{1}^{m} l_j)^m W(\{l_k\}) \quad (16)$$

such that

$$\sum_{l_m \geq l_{m-1} \geq \ldots \geq l_1} l_k \leq N$$

Table I
Computational Results

$\rho \times 10^2$	m	N	g
2.50	3	120	0.8942
2.50	4	160	0.8914
2.50	5	200	0.8918
3.33	3	90	0.8777
3.33	4	120	0.8739
3.33	5	150	0.8742
5.00	3	60	0.8504
5.00	4	80	0.8445
5.00	5	100	0.8441
5.00	6	120	0.8450
5.88	3	51	0.8379
5.88	4	68	0.8308
5.88	5	85	0.8300
5.88	6	102	0.8309
7.14	3	42	0.8217
7.14	4	56	0.8130
7.14	5	72	0.8115
7.14	6	84	0.8122
7.14	7	98	0.8132
8.33	4	48	0.7977
8.33	5	60	0.7954
8.33	6	72	0.7959
8.33	7	84	0.7969
8.33	8	96	0.7977
10.00	4	40	0.7780
10.00	5	50	0.7746
10.00	6	60	0.7747
10.00	7	70	0.7756
10.00	8	80	0.7765
10.00	9	90	0.7771
10.00	10	100	0.7774
12.50	5	40	0.7464
12.50	6	48	0.7455
12.50	7	56	0.7462
12.50	8	64	0.7471
12.50	9	72	0.7479
12.50	10	80	0.7484
12.50	11	88	0.7487
12.50	12	96	0.7487

where $l_j = N\alpha_j$ and $W(\{l_k\})$ is the appropriate weighting of terms when the constraint $l_m \geq l_{m-1} \geq \ldots \geq l_1$ is applied. The summation in eq 16 is subject to the additional constraint that $\sum l_k \leq N$. $W(\{l_k\})$ is just the order of the permutation group for a set of m objects composed of various subsets of indistinguishable objects. Since the volume of the space in the integral is found to be $N^m/m!$, the number of terms in the sum is very nearly $N^m/m!^2$. This estimate of the number of terms assumes that $N \gg m$ so that $W(\{l_k\}) = m!$. This great reduction in the number of terms in the sum makes the numerical computation of $\langle g \rangle$ very feasible.

The numerical evaluation of eq 16 was carried out on the VAX II Model 780 computer at the University of Washington, Department of Chemistry. Representative results are displayed in Table I. Although the calculations were done in double precision, some round-off error is noticeable in the data. Close examination of the data reveals a simple functional form for $g(N,m)$: results for a range of N at constant cross-link density m/N indicate that for $m > 3$ the chain contraction factor is very nearly constant, within the limits of the round-off error. From the calculation of the contraction factor for a single cross-link, eq 13b, we are led to write

$$\langle g(N,m) \rangle = 1 - \beta\rho^{1/2} \tag{17}$$

where $\rho \equiv m/N$ is the cross-link density. The parameter β is nearly constant for all ρ, and in light of the inherent inaccuracies of the model, we simply assign to β the value $^7/_{10}$, which fits the numerical data quite well. A graph of this function vs. the numerical data is shown in Figure 3. For the purposes of obtaining a better fit to the data the exponent may be allowed to vary, giving the alternate form

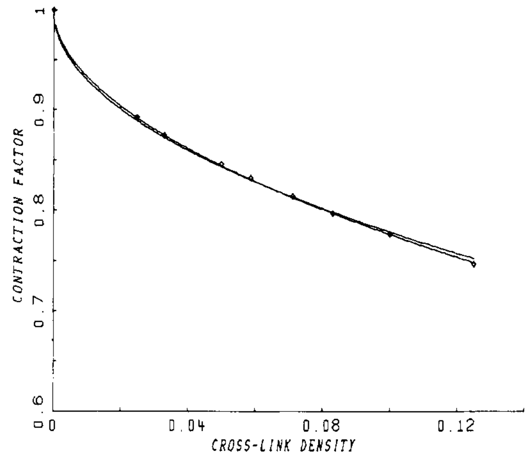

Figure 3. Chain contraction factor vs. the cross-link density for a cyclized chain. The points were obtained from the numerical computation of eq 16 whereas the lines are taken from eq 17 and 18. The better fit is the empirical eq 18. Note that to apply this to a real polymer, the cross-link density must be multiplied by the number of monomers per statistical subunit. In this way the units of the cross-link density become moles of cross-links/mole of monomer.

$$\langle g(N,m) \rangle = 1 - \beta'\rho^{\gamma} \tag{18}$$

A least-squares fit to the data gives $\beta' = 0.750$ and $\gamma = 0.525$. This function fits the data extremely well, but it is of no real physical significance to differentiate between the two equations.

A few comments are in order concerning the nature of intramolecularly cross-linked polymers and the applicability of these equations to the calculation of their dimensions. In the calculations reported here the ring weighting factor is taken to be $|i-j|^{-3/2}$. The ring weighting expresses the probability that the ith and jth segments of a linear polymer will come in contact and thus have an opportunity to cross-link. This is a good approximation if the polymer is at the Θ condition and if $|i-j|$ is large. If the chain is in a good solvent, the correct ring weighting factor will be given by $|i-j|^{-(3/2+\Delta)}$, where Δ is small, positive, increases with the goodness of the solvent, and is a monotonically increasing function of $|i-j|$. The value of Δ approaches[21] $^7/_{15}$ as $|i-j|$ goes to ∞. This will tend to reduce the magnitude of the contraction effect since small loops will be more strongly favored.

For small values of $|i-j|$ the Gaussian ring weighting factor will not generally be a good approximation. Weighting factors for small loops are highly dependent on the details of molecular structure. It is important to make a detailed consideration of steric hindrance, rotational potentials, and even the local excluded volume and cross-linker dimensions. No simple model could hope to portray these effects, which might be of some practical importance in a system in which small loops are the favored product.

Finally, it seems pertinent to discuss the randomly cross-linked polymer model in relation to the cyclized chain. In a cyclized chain any monomer is a potential cross-linking site. In the randomly cross-linked polymer only a certain fraction of the monomers are potential cross-linking sites. This is achieved[22] by making a random copolymer from reactive and unreactive monomers. For the purposes of computation it is assumed that the probability of ring formation between the ith and jth monomers is independent of i and j. The result Edwards et al.[14-16] give for a formulation of this sort of $g = (m+1)^{-1}$. As an example, consider polystyrene of DP = 10^4 cross-linked to an extent of 0.01 mol of cross-link/mol of monomer. With 10 monomers per statistical subunit, eq 15 gives a contraction factor of 0.776. The random cross-link model gives $g = 0.01$. For such large contractions in dimensions, Allen et al.[18] were aware that an excluded volume interaction had to be admitted. After this was included in the formulation, results were obtained that could account for general trends in the experimental data obtained by Allen et al.[23] The agreement was still unsatisfactory, however, since theory gave values of g that were 2–4 times lower than the experimental values.

A possible reason for the discrepancy is the nature of the quasi-random polymers on which the measurements were conducted. If $2m$ monomers are available for cross-linking at the initiation of the cross-linking reaction, as is the case in the work of Allen et al., then certainly ring weighting plays an important role in determining the mean loop size of the first and subsequent rings. The mean loop size after the first cross-link is just

$$\langle l \rangle = \binom{N}{2m}^{-1} \sum_{1 \le i_1 < i_2 \ldots \le i_{2m} < N} \cdots \sum \left[\frac{\sum\limits_{\nu<\mu}^{2m} \sum |i_\mu - i_\nu|^{-1/2}}{\sum\limits_{\nu<\mu}^{2m} \sum |i_\mu - i_\nu|^{-3/2}} \right] \tag{19}$$

In the limit $2m = N$ this gives the cyclized chain result $\langle \alpha \rangle = (2/3)N^{-1/2}$, whereas only if $2m = 2$ is the truly random result $\langle \alpha \rangle = {}^1/_3$ obtained. In the intermediate region of m the intractable sums in eq 19 must be performed. For this reason no theoretical treatment of the experimentally realizable quasi-randomly cross-linked chain has been given.

In a subsequent paper the results of some experimental investigations on the contraction in dimensions of the cyclized chain will be given and the results will be compared with eq 14.

Appendix A. Computation of $\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle_0$

In the Gaussian approximation, the potential energy of a polymer molecule may be expressed in terms of a row vector containing the coordinates of its segment joints, $\mathbf{R} = (x_1, y_1, z_1, x_2, \ldots, z_n)$, and the Kirchhoff matrix. The Kirchhoff matrix, $\mathbf{K}$, is a real, symmetric, $n \times n$ matrix that describes the polymer connectivity. The expression for the potential energy of a Gaussian polymer at the Θ condition may be written as

$$V(\mathbf{R})/kT = \gamma \mathbf{R}(\mathbf{K} \otimes \mathbf{E}_3)\mathbf{R}^{\mathrm{t}}; \qquad \gamma = 3/2\langle l^2 \rangle_0 \tag{A.1}$$

where $\mathbf{E}_3$ denotes the identity of order three and $\mathbf{R}^{\mathrm{t}}$ is the transpose of $\mathbf{R}$. Computation of $\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle_0$ in a coordinate system whose origin is coincident with the molecular center of mass requires the evaluation of

$$\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = Z^{-1} \int \ldots \int \mathrm{d}^{3n}\mathbf{R} \prod_{l=x,y,z} \delta(\mathbf{J}_l \mathbf{R}^{\mathrm{t}}) \mathbf{r}_i \cdot \mathbf{r}_j e^{-\gamma \mathbf{R}(\mathbf{K} \otimes \mathbf{E}_3)\mathbf{R}^{\mathrm{t}}} \tag{A.2}$$

with Z being the appropriate normalization constant and $\mathbf{J}_x = (1, 0, 0, 1, 0, 0, \ldots, 1, 0, 0)$. The delta function product serves to keep the coordinate origin fixed at the molecular center of mass. It is convenient to write $\mathbf{r}_i \cdot \mathbf{r}_j$ in the form $\mathbf{R}(\mathbf{S}(i,j) \otimes \mathbf{E}_3)\mathbf{R}^{\mathrm{t}}$, where $\mathbf{S}(i,j)$ is a sparse $n \times n$ matrix given by the Kronecker delta product

$$\mathbf{S}(i,j)_{\alpha\beta} = \delta_{\alpha i} \delta_{\beta j} \tag{A.3}$$

Making use of the normal coordinate transformation matrix defined by $\mathbf{TKT}^{\mathrm{t}} = \mathbf{\Lambda} = \mathrm{Diag}\,(\lambda_1, \lambda_2, \ldots, \lambda_n)$ and letting $\mathbf{Q}(\mathbf{T} \times \mathbf{E}_3) = \mathbf{R}$ define the normal coordinate vector, we find

$$\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle_0 = Z^{-1} \int_{-\infty}^{+\infty} \ldots \int \mathrm{d}^{3n}\mathbf{Q} \prod_{l=1}^{3} \delta(q_1{}^l) e^{-\gamma \mathbf{Q}(\mathbf{\Lambda} \otimes \mathbf{E}_3)\mathbf{Q}^{\mathrm{t}}} \times \sum_{l=1}^{3} \sum_{\mu=1}^{n} \sum_{\nu=1}^{n} q_\mu{}^l q_\nu{}^l T_{\mu i} T_{\nu j} \tag{A.4}$$

where the elements $q_\mu{}^l$ are defined by $\mathbf{Q} = (q_1{}^1, q_1{}^2, q_1{}^3, \ldots, q_n{}^3)$. As seen from the transformation of the delta function product, the first eigenvector corresponds to the center-of-mass motion of the macromolecule. Only terms with $\nu = \mu$ contribute to the integral in eq A.4. Integration of these terms gives

$$\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle_0 = Z^{-1} \Big(\sum_{\mu=2}^{n} T_{\mu i} T_{\mu j} \lambda_\mu{}^{-1} \Big) \prod_{k=2}^{n} (\pi/\gamma\lambda_k)^{3/2} \tag{A.5}$$

Evaluation of the normalization constant yields

$$\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle_0 / \langle l^2 \rangle_0 = \sum_{\mu=2}^{n} T_{\mu i} T_{\mu j} \lambda_\mu{}^{-1} \tag{A.6}$$

The right-hand side of eq A.6 may be recognized as $\mathbf{A}_{ij}$, the i,j element of the generalized inverse of the Kirchhoff matrix. This leads to the simple expression

$$\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle_0 / \langle l^2 \rangle_0 = \mathbf{A}_{ij} \tag{A.7}$$

In Appendix B, it is shown how these elements may be found without explicit evaluation of eq A.6 or knowledge of the elements of the transformation matrix $\mathbf{T}$.

Appendix B. Moore–Penrose Inverse of the Kirchhoff Matrix

The Moore–Penrose or generalized inverse,[24] $\mathbf{A}$, of a rectangular or singular matrix $\mathbf{D}$ is uniquely specified by the four conditions (i) $\mathbf{ADA} = \mathbf{A}$, (ii) $\mathbf{DAD} = \mathbf{D}$, (iii) $(\mathbf{AD})^{\mathrm{t}} = \mathbf{AD}$, and (iv) $(\mathbf{DA})^{\mathrm{t}} = \mathbf{DA}$. If, however, the matrix $\mathbf{D}$ is a Kirchhoff matrix $\mathbf{K}$ it can be shown[11] that these conditions reduce to (i) $\mathbf{KA} = \mathbf{E}_n - n^{-1}\mathbf{U}$, (ii) $\mathbf{A}^{\mathrm{t}} = \mathbf{A}$, and (iii) $\mathbf{AU} = \mathbf{0}$. The $n \times n$ matrix $\mathbf{U}$ is a matrix of ones. It is easy to show that the matrix $\mathbf{A} = \mathbf{T}_0 \mathbf{\Lambda}_0{}^{-1} \mathbf{T}_0{}^{\mathrm{t}}$ satisfies these conditions. The second set of conditions provides a method for the calculation of $\mathbf{A}$ if $\mathbf{K}$ is sufficiently regular. Such is the case for the Kirchhoff matrix of the linear or circular chain. In these cases the Kirchhoff matrix may be written

$$\text{(linear)} \qquad \mathbf{K}_{ij}{}^{\mathrm{l}} = \mathbf{K}^{\mathrm{c}} - \delta_{i1}\delta_{j1} - \delta_{in}\delta_{jn} + \delta_{i1}\delta_{jn} + \delta_{in}\delta_{j1} \tag{B.1a}$$

$$\text{(circular)} \qquad \mathbf{K}^{\mathrm{c}} = 2\delta_{i,j} - \delta_{i,j+1} - \delta_{i,j-1} (\mathrm{mod}\ n) \tag{B.1b}$$

Direct application of the second set of conditions to these matrices leads to the expressions given in eq 8a and 8b for the elements of the generalized inverses.

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Dimensions of Intramolecularly Cross-Linked Polymers. 2. Dilute Solution Thermodynamic Parameters and Photon Correlation Results on the Polystyrene/Cyclopentane System†

James E. Martin*

Division 1152, Sandia National Laboratories, Albuquerque, New Mexico 87185

B. E. Eichinger

Department of Chemistry, BG-10, University of Washington, Seattle, Washington 98195.

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ABSTRACT: In the previous paper a prediction was made for the contraction in dimensions of a homopolymer intramolecularly cross-linked in dilute solution. To test this prediction, Θ dimensions of linear and cross-linked polymers were determined for the polystyrene/cyclopentane system by means of photon correlation spectroscopy. Dilute solution thermodynamic parameters were found from the temperature dependence of the hydrodynamic radius and from viscosity measurements. Good agreement is found between the observed hydrodynamic radii of the cross-linked polymers and theoretical predictions.

Introduction

In a previous paper, a theoretical expression was proposed for the Zimm–Stockmayer[1] contraction factor, g, of a cyclized or intramolecularly cross-linked chain. The prediction is that $g = 1 - 0.7\rho^{1/2}$, where ρ is cross-link density expressed as moles of cross-links per mole of Gaussian statistical segments. It is appropriate to verify this expression experimentally. To do so requires the synthesis of intramolecularly cross-linked polymers and the subsequent determination of their dimensions in the Θ state. By way of definition, a polymer is in the Θ state when the second virial coefficient is zero.

It is of some interest to relate the work that others have done on intramolecularly cross-linked polymers. In 1962 Kuhn and Balmer[2] added terephthalaldehyde ($OCHC_6H_4CHO$) to an aqueous solution of poly(vinyl alcohol). They measured the effect of polymer concentration during the cross-linking reaction on the intrinsic viscosity of the cross-linked polymer. It was found that at low reacting solution concentration, the viscosity decreased, indicating intramolecular cross-linking, and that at higher concentrations of polymer, the intrinsic viscosity increased, indicating the usual intermolecular cross-linking. At very high concentrations of polymer, the gel point was reached and the intrinsic viscosity became infinite.

In 1968 Longi, Greco, and Rossi[3] synthesized α-olefin/allylsilane copolymers and treated these with alkali/alcohol mixtures to form quasi-random intramolecular ≡Si–O–Si≡ bridges. They were unable to observe any change in the intrinsic viscosity of the copolymers after cross-linking. This may be due to the copolymers having a block structure, which makes them prone to formation of relatively small cycles. The cross-links formed in this reaction were found to be very labile.

In 1969 Longi et al.[4] reported the synthesis of styrene/methyl acrylate copolymers, which they cross-linked with 9,10-disodio-9,10-dihydroanthracene in tetrahydrofuran. In this experiment, ca. 10% of the copolymer monomers were of the reactive methyl acrylate type. It was found that the intrinsic viscosity decreased in proportion to the number of intramolecular cross-links per polymer. It was their understanding that this was in agreement with the heuristic theory of Kuhn.[5] In fact, Kuhn's development cannot be applied to the complex statistics of the quasi-randomly cross-linked chain. Any agreement between their experimental results and the theory of Kuhn is fortuitous. To complicate the interpretation of their data further, the intrinsic viscosities they reported were determined in a good solvent. Measurements of the second virial coefficient showed a steady decrease with the extent of cross-linking. In the samples investigated, a twofold variation in the virial coefficient was observed. Modern polymer theories relate a large positive value of the second virial coefficient to a large positive value of the excluded volume parameter, which is indicative of a polymer in a highly expanded state. It is clear, then, that a large portion of the collapse in dimensions observed by Longi et al. was simply due to the approach of the cross-linked polymers to the Θ state.

Allen et al.[6] chloromethylated anionic polystyrene to make a styrene/(chloromethyl)styrene random copolymer. The chloromethyl groups were reacted with n-butylamine, and the resultant secondary amine was cross-linked with diisocyanate in dilute solution. Subsequent measurements of the unperturbed dimensions of these polymers, primarily by intrinsic viscosities, revealed a large contraction relative to the linear polymer, in qualitative agreement

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† This work performed at the University of Washington.

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