Perturbation Theory of Dimensions of Comb-like Polymer Chains with Branches Randomly Spaced Along the Backbone†

Paula J. Solensky and Edward F. Casassa*

Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213.

Received December 3, 1979

ABSTRACT: A first-order perturbation calculation is given of the effect of the intramolecular segment–segment excluded volume β on the mean-square molecular radius of gyration $\langle s^2\rangle$ of "random-comb" branched polymer chains in solution. In this model system the chains are chemically homologous and of uniform mass with a fixed number of identical branches attached at random along identical backbones. The calculated average expansion of the chains beyond the random-flight mean-square dimension $\langle s^2\rangle_0$ is similar to that obtained by Berry and Orofino for "regular" combs in which the branches are spaced at uniform intervals along the backbone. However, averaging over the population of all comb isomers in the "random" model simplifies the mathematics so that the coefficient of the linear term of the series expression for $\langle s^2\rangle/\langle s^2\rangle_0$ in powers of β is obtained in closed analytic form as a function of the total number of segments in a chain and of a parameter for their apportionment between backbone and branches. The analysis is also extended to the case of a comb population with a random distribution of number of branches per molecule as well as of their placement on the backbone.

The behavior of branched-chain polymers in solution is of major interest both in respect to technological problems and to basic theoretical questions. In particular, the admission of branching as a parameter of a homologous polymer system makes it possible to vary the averaged chain segment density in the domain of the molecule in solution independently of the molecular weight.[1,2] For this reason, among others, theoretical studies of branched chains and testing of their predictions against experiment afford a potential for deeper insight into the validity of statistical mechanical theories of conformational, thermodynamic, and hydrodynamic properties of polymers in solution.[2-4] The circumstance that chain branching is often an unavoidable concomitant of polymer synthesis has motivated some theoretical developments, but a more significant factor has perhaps been the achievement of controlled synthesis of branched species, such as "star" and "comb" chains, with well-defined architecture.[4-6] For combs, statistical treatments typically were initially devised for model structures with branches disposed at regular intervals along the chain backbone,[7,8] even though the polymers available for study were generally characterized by random attachment of the branches. This caused little concern as the randomization of branch placements could plausibly be supposed to have only minor effects. However, it was then proposed that introduction of this more realistic feature into the theoretical comb model would simplify results, and such was found to be the case when this modification was made in statistical treatments of three properties: the angular intensity distribution of light scattering for unperturbed random-flight combs,[9] the second virial coefficient,[10] and the translational friction factor[11] for the random-flight case.

In this paper we work out the first-order perturbation theory of the mean-square radius of gyration for combs with randomized branch placements. Although this problem is considerably more intricate than those dealt with previously, the results in this instance too prove to be more tractable than those for the regular-comb model.

Irregular Combs

We begin the development, as we did previously,[9,10] by considering an "irregular" comb model in which a backbone of n_0 identical statistical segments, numbered 1, 2, . . ., i, . . ., n_0 from one end, has attached to it branches each consisting of n_b segments identical with those that make up the backbone. The branches, numbered 1, 2, · · ·, μ, . . ., ν, . . ., f are attached to f different, arbitrarily chosen segments $i_1, i_2, \ldots, i_\mu, \ldots, i_\nu, \ldots, i_f$ of the backbone. Thus any comb structure is completely specified by n_0, n_b, and the f designated branching nodes, or an equivalent set of parameters. Furthermore, we adopt the basic assumptions of the conventional "two-parameter" statistical theories: a chain segment is described by a root-mean-square step-length b and a mutual volume of exclusion β between a pair of segments. When $\beta = 0$ (i.e., at the Flory temperature Θ in solution) the chain conformation obeys random-flight statistics. Given the random-flight distribution of intersegmental displacements, the various averaged statistical dimensions of the chain can be calculated in standard fashion, save for the necessity of taking into account the complicated topology of chain contours produced by branching.

The effect of volume exclusion between chain segments on the mean-square molecular radius of gyration $\langle s^2\rangle$ with respect to the center of mass is obtained by the perturbation method in the series form[12]

$$\langle s^2\rangle/\langle s^2\rangle_0 = 1 + a_1 z + 0(z^2) \qquad (1)$$

where $\langle s^2\rangle_0$ is the unperturbed value of $\langle s^2\rangle$,

$$z = (3/2\pi b^2)^{3/2}\beta n^{1/2} \qquad (2)$$

and

$$n = n_0 + f n_b \qquad (3)$$

We shall limit our consideration to the first-order perturbation and thus require only the coefficient a_1 of the linear term of eq 1. For an unbranched chain, a_1 is just the well-known numerical constant 134/105; for the general comb chain it must be a function of the number of branches, their placement, and the relative lengths of branches and backbone. There is no need to recount here all the calculations leading to a_1 since Fixman[13] has obtained an expression that is formally applicable to any flexible-chain architecture:

$$a_1 = \frac{6}{gn^{7/2}} \sum_i\sum_j\sum_k\sum_l C^2{}_2/C_1{}^{5/2} \qquad (4)$$

The quadruple sum runs over all distinguishable choices of a quartet of chain segments i, j, k, l. The quantity C_1 is the number of segments, counted along the chain contour, separating two of the index segments, say k and l in

---

† Dedicated to Paul J. Flory on the occasion of his 70th birthday.

0024-9297/80/2213-0500$01.00/0

a particular configuration; C_2 is the number of segments common to this path and to the path connecting the other pair of segments i and j. Thus, unless the paths overlap, the relevant term in the quadruple sum disappears. The factor g is defined by

$$g = 6\langle s^2\rangle_0/nb^2 \qquad (5)$$

i.e., the ratio of the unperturbed mean-square radius of the branched chain to that of the linear chain of the same mass (the same total number n of segments).

To express a_1 specifically in terms of the chain-structure parameters of the comb molecule, we must address the task of cataloging and evaluating the terms of the sum in eq 4. Berry and Orofino[8] accomplished this for the "regular symmetrical" comb in which the backbone is divided into $f + 1$ sequences of equal length by the f branching nodes. Fortunately their treatment is easily adapted to deal with the present problem.

Three classifications of chain structural elements include all topologies of chain segment sequences that simultaneously contain four index segments.

I. The four index segments lie on a single linear sequence of x segments. The contribution to the sum in eq 4 from all permutations of the index segments over the x segments is

$$\Gamma_{\rm I}(x) = \int\int\int\int (C_2{}^2/C_1{}^{5/2})\ {\rm d}i\ {\rm d}j\ {\rm d}k\ {\rm d}l = (67/315)x^{7/2} \qquad (6)$$

which is just Fixman's result for a linear chain. Replacement of the summations by integrations is justified by requiring that $x \gg 1$. For a comb the linear sequence may be (a) the backbone, (b) any branch, (c) a sequence formed by a branch and all or part of the backbone section on one side of its node (e.g., $x = n_b + i_\mu$ or $x = n_b + n_0 - i_\mu$), or (d) a sequence formed by two branches and the portion of the backbone between them ($x = 2n_b + i_\nu - i_\mu$).

II. The four index segments are distributed over three linear sequences of lengths x_1, x_2, and x_3 joined together at a common point. This contribution to the quadruple sum is

$$\Gamma_{\rm II}(x_1,x_2,x_3) = {}^4\!/\!_{45}[h(x_1,x_2,x_3) + h(x_2,x_3,x_1) + h(x_3,x_1,x_2)] \qquad (7)$$

where the function h is given by

$$h(\alpha,\beta,\gamma) = \alpha(\beta + \gamma)^{-1/2}[29(\beta^3 + \gamma^3) + 72(\beta^2\gamma + {\rm B}\gamma^2)] - 29\alpha^{5/2}(\beta + \gamma) - 80\alpha^{3/2}\beta\gamma$$

III. The four index segments lie on four different linear sequences (lengths x_1, x_2, x_3, and x_4) connected to an unoccupied fifth linear sequence (length y) by a trifunctional branch point at each end of the latter. The contribution to the sum in eq 4 is

$$\Gamma_{\rm III}(x_1,x_2,y,x_3,x_4) = {}^4\!/\!_3\, y^2[x_2x_4q(x_1,x_3) + x_2x_3q(x_1,x_4) + x_1x_4q(x_2,x_3) + x_1x_3q(x_2,x_4)] \qquad (8)$$

where

$$q(\alpha,\beta) = y^{-1/2} - (\alpha + y)^{-1/2} - (\beta + y)^{-1/2} + (\alpha + \beta + y)^{-1/2}$$

We see that even the simplest contributions to eq 4, those given by eq 6, involve finite single and double sums of terms like $(n_b + i_\mu)^{5/2}$ and $(2n_b + i_\nu - i_\mu)^{5/2}$ over the set of branch loci $i_1, \ldots, i_f$. The branched topologies contributing to $\Gamma_{\rm II}$ and $\Gamma_{\rm III}$ produce triple and quadruple sums of much more complicated terms, as indicated by eq 7 and 8.

With the use of the configurational *classes* described above it is useful to divide the configurations to be enumerated for the entire comb into five *groups* according to the comb elements bearing the index segments; i.e., configurations involving no branches (group 0), one branch (group 1), two branches (group 2), three branches (group 3), and four branches (group 4).[14] In group 4 configurations, the chain backbone cannot be the locus of an index segment. The configurational classes included in each group are: group 0, class I; group 1, classes I and II; group 2, classes I, II, and III; group 3, classes II and III; and group 4, class III.

Finally, eq 4 is rewritten as

$$a_1 = \frac{6}{gn^{7/2}}\sum_{m=0}^{4} S_m \qquad (9)$$

where S_m denotes the contribution from the mth group to the quadruple sum in eq 4. The quantities S_m are given by

$$S_0 = \Gamma_{\rm I}(n_0) \qquad (10)$$

$$S_1 = \sum_{\mu=1}^{f}[\Gamma_{\rm I}(n_b + i_\mu) - \Gamma_{\rm I}(i_\mu) + \Gamma_{\rm I}(n_b + n_0 - i_\mu) - \Gamma_{\rm I}(n_0 - i_\mu) + \Gamma_{\rm II}(i_\mu,n_b,n_0 - i_\mu)] - f\Gamma_{\rm I}(n_b) \qquad (11)$$

$$S_2 = \sum_{\nu=2}^{f}\sum_{\mu=1}^{\nu-1}[\Gamma_{\rm I}(2n_{\rm b} + i_\nu - i_\mu) - 2\Gamma_{\rm I}(n_b + i_\nu - i_\mu) + \Gamma_{\rm I}(i_\nu - i_\mu) + \Gamma_{\rm II}(i_\mu,n_b,n_b + i_\nu - i_\mu) - \Gamma_{\rm II}(i_\mu,n_b,i_\nu - i_\mu) + \Gamma_{\rm II}(n_b + i_\nu - i_\mu,n_b,n_0 - i_\mu) - \Gamma_{\rm II}(i_\nu - i_\mu,n_b,n_0 - i_\nu) + \Gamma_{\rm III}(i_\mu,n_b,i_\nu - i_\mu,n_b,n_0 - i_\nu)] \qquad (12)$$

$$S_3 = \sum_{\lambda=3}^{f}\sum_{\nu=2}^{\lambda-1}\sum_{\mu=1}^{\nu-1}[\Gamma_{\rm II}(n_b + i_\nu - i_\mu,n_b,n_b + i_\lambda - i_\nu) - \Gamma_{\rm II}(i_\nu - i_\mu,n_b,n_b + i_\lambda - i_\nu) - \Gamma_{\rm II}(n_b + i_\nu - i_\mu,n_b,i_\lambda - i_\nu) + \Gamma_{\rm II}(i_\nu - i_\mu,n_b,i_\lambda - i_\nu) + \Gamma_{\rm III}(i_\mu,n_b,i_\nu - i_\mu,n_b,n_b + i_\lambda - i_\nu) + \Gamma_{\rm III}(n_b + i_\nu - i_\mu,n_b,i_\lambda - i_\nu,n_b,n_0 - i_\lambda) - \Gamma_{\rm III}(i_\mu,n_b,i_\nu - i_\mu,n_b,i_\lambda - i_\nu) - \Gamma_{\rm III}(i_\nu - i_\mu,n_b,i_\lambda - i_\nu,n_b,n_0 - i_\lambda)] \qquad (13)$$

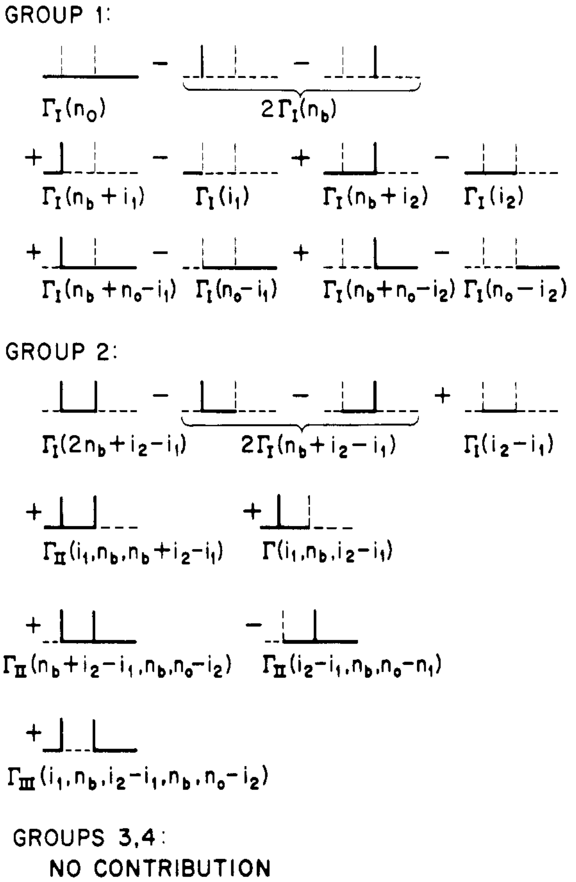
$$S_4 = \sum_{\kappa=4}^{f}\sum_{\lambda=3}^{\kappa-1}\sum_{\nu=2}^{\lambda-1}\sum_{\mu=1}^{\nu-1}[\Gamma_{\rm III}(n_b + i_\nu - i_\mu,n_b,i_\lambda - i_\nu,n_b,n_b + i_\kappa - i_\lambda) - \Gamma_{\rm III}(i_\nu - i_\mu,n_b,i_\lambda - i_\nu,n_b,n_b + i_\kappa - i_\lambda) - \Gamma_{\rm III}(n_b + i_\nu - i_\mu, n_b,i_\lambda - i_\nu,n_b,i_\kappa - i_\lambda) + \Gamma_{\rm III}(i_\nu - i_\mu,n_b,i_\lambda - i_\nu,n_b,i_\kappa - i_\lambda)] \qquad (14)$$

Although we first considered a different accounting with every contribution positive, efforts in this direction showed that there would be no gain in simplicity or convenience, and we decided to adapt the scheme of Berry and Orofino to our purpose, correcting redundant counting of configurations by introducing subtractive terms. This bookkeeping is illustrated schematically in Table I for the simple case $f = 2$. Equations 9–14 are a generalization of eq 17–21 of Berry and Orofino;[8] their final results for the regular comb are recovered from the above expressions by letting the branch node indices i_μ, i_ν, etc., assume only values that are multiples of $n_0/(f + 1)$ up to $n_0f/(f + 1)$. Although this specification effects some simplification, the S_m still contain single, double, triple, and quadruple sums that cannot be resolved further.

Random Combs

A particular irregular comb is described by a set of f numbers $i_1, i_2, \ldots, i_\mu, \ldots, i_f \le n_0$. Hence there are $n_0!/(n_0 - f)!f!$ comb isomers with the same number of segments ($n_0 + fn_b$). (If it does not matter from which end of the backbone its segments are indexed, the number of physically distinguishable isomers is half this value.) These isomers constitute the population of "random" combs, which we can define as the product of coupling f identical

Table I
Configurational Group Contributions to $C_2^2/C_1^{5/2}$ for an Irregular Comb with $f = 2$



branches without bias to each of many backbones of n_0 units. In a large system of random combs, every possible comb isomer will have an equal expectation of occurrence, which is both its mole fraction and its weight fraction since the combs are homogeneous in mass.

We now apply eq 1 to each isomeric comb species and compute the mean-square radius of gyration $\langle s^2\rangle_{\text{random}}$ averaged over the entire random-comb population

$$\langle s^2\rangle_{\text{random}} = \sum\langle s^2\rangle_J w_J = \sum_J \langle s^2\rangle_{0J}(1 + a_{1J}z + \ldots)w_J = [\langle s^2\rangle_0]_{\text{random}} + \sum_J \langle s^2\rangle_{0J} a_{1J} z w_J + \ldots \quad (15)$$

where w_j is the weight fraction (or mole fraction) of the Jth isomer. The subscript J is added to other quantities likewise to designate the Jth species. Further defining a coefficient $(a_1)_{\text{random}}$ for the first-order perturbation averaged over the random comb population by

$$\langle s^2\rangle_{\text{random}}/[\langle s^2\rangle_0]_{\text{random}} = 1 + (a_1)_{\text{random}}z + \ldots \quad (16)$$

we obtain from eq 15 and from eq 4 and 5 for the individual irregular comb species,

$$(a_1)_{\text{random}} = \frac{6\sum\limits_J[\sum\limits_i\sum\limits_j\sum\limits_h\sum\limits_l(C_2^2/C_1^{5/2})_J]w_J}{n^{7/2}\sum\limits_J g_J w_J} = \frac{6\sum\limits_J[\sum\limits_m S_{mJ}]w_J}{n^{7/2}\sum\limits_J g_J w_J} \quad (17)$$

The circumstance that in a large random-comb system the complete spectrum of branch placements occurs makes it possible to execute the sums in the numerator of eq 17 completely, and thus obtain simple (though unwieldy) analytic results in which the branch-node indices $i_1, i_2, \ldots$, etc., no longer appear as parameters. In effect the order of summation indicated can be reversed to average each term within the brackets over the entire comb population.

To illustrate this, we examine the first term in S_1. The random-comb system contains N_J molecules of a species J for which there are f quantities $\Gamma_I(n_b + i_\mu)_J$. If there are N molecules of all kinds in the system, the sum

$$\sum_J N_J \sum_{\mu=1}^{f} \Gamma_I(n_b + i_\mu)_J$$

over all the i_μ of all species must contain Nf terms distributed uniformly among the n_0 possible values of i_μ. Hence, there are Nf/n_0 identical terms in the sum for any i_μ. Dividing by N and introducing for convenience the scaled quantities $n_b/n_0 = \rho$ and $i_\mu/n_0 = u$, we have

$$\sum_J w_J \sum_{\mu=1}^{f} \Gamma_I(n_b + i_\mu)_J = \frac{f}{n_0}\sum_{i=1}^{n_0}\Gamma_I(n_b + i) = n_0^{7/2}\int_0^1 \Gamma_I(\rho + u)\,\mathrm{d}u \quad (18)$$

Since the reordering of terms in the double sum gives a single sum running over all values $1 < i < n_0$, no sensible error is caused by replacing that sum by an integral. Averaging over the random-comb system also leads to a corresponding reduction of the multiple sums in the S_m. For example, noting that there are $f(f - 1)$ pairs of indices i_μ, i_ν for a species J, we have

$$\sum_J w_J \sum_{\nu=2}^{f}\sum_{\mu=1}^{\nu-1} \Gamma_I(i_\nu - i_\mu)_J = f(f - 1)n_0^{7/2}\int_0^1\int_0^v \Gamma_I(v - u)\,\mathrm{d}u\,\mathrm{d}v \quad (19)$$

All the integrals generated in this fashion from the terms contributing to the partial sums S_m can be expressed in a common form. At each level of integration $L = 1, 2, 3$, and 4, we must evaluate

$$I_L = \rho^{p/2}\int_0^{x_{L+1}} (A + B\rho + bx_L)^{q/2}x_L^m\,\mathrm{d}x_L \quad (20)$$

with parameters that can assume values as follows: $p = 0, 1, 2, \ldots, 7$; $m = 0, 1, 2, 3, 4$; $A = 0, 1$; $B = 0, 1, 2$; $b = -1, 0, 1$; and $q = -1, 0, 1, 3, 5, 7$. The upper limit x_{L+1} of the variable x_L is the variable of integration at the next level. At the final level the upper limit is always unity.

Although it is straightforward to evaluate all the integrals of the form of eq 20 analytically, there are many of them: more than 300 integrations are encountered at the first level and the number rapidly proliferates at successive levels of the multiple integrations. Preliminary efforts soon demonstrated that an error-free manual computation would hardly be accomplished without enormous effort. However, the repetitive character of the integrations suggested the utility of devising the computer algorithm that was finally used to perform the integrations and compile the results. The appropriate numerical quantities in each function Γ and the branch-length parameter ρ constitute the input for the calculation. The program utilizes the rules for integration by parts to carry out each integration, and for the multiple integrals the procedure is repeated until the final result is obtained. All results are expressed by terms of the form

$$I = (A' + B'\rho)^{1/2}[c_0 + c_1\rho + c_2\rho^2 + \ldots c_7\rho^7] \quad (21)$$

with $A' = 0, 1$; $B' = 0, 1, 2$. The coefficients $c_0, c_1, \ldots$, etc., are all rational fractions. Essentially, the product of the

Table II
Numerical Coefficients for Formulating $\tilde{S}_m$ in Equation 22

$\tilde{S}_m$	$(A' + B'\rho)^{1/2}$	c_0	c_1	c_2	c_3	c_4	c_5	c_6	c_7
$\tilde{S}_1$	1	$\frac{-1196}{2835}$	$\frac{-78}{105}$						
	$(\rho)^{1/2}$		$\frac{-32}{27}$	$\frac{-116}{45}$	$\frac{-151}{63}$	$\frac{-2348}{2835}$			
	$(1 + \rho)^{1/2}$	$\frac{1196}{2835}$	$\frac{112}{81}$	$\frac{440}{189}$	$\frac{6224}{2835}$	$\frac{2348}{2835}$			
$\tilde{S}_2$	1	$\frac{772}{10395}$	$\frac{-1912}{2835}$	$\frac{-509}{315}$					
	$(\rho)^{1/2}$			$\frac{-256}{135}$	$\frac{1492}{315}$	$\frac{6052}{945}$	$\frac{2536}{891}$		
	$(1 + \rho)^{1/2}$	$\frac{-1544}{10395}$	$\frac{80}{891}$	$\frac{-2752}{6237}$	$\frac{-9752}{3465}$	$\frac{-155336}{31185}$	$\frac{-2536}{891}$		
	$(2\rho)^{1/2}$			$\frac{-128}{135}$	$\frac{-656}{63}$	$\frac{-2848}{189}$	$\frac{-248704}{31185}$		
	$(1 + 2\rho)^{1/2}$	$\frac{772}{10395}$	$\frac{18232}{31185}$	$\frac{84896}{31185}$	$\frac{85696}{10395}$	$\frac{407744}{31185}$	$\frac{248704}{31185}$		
$\tilde{S}_3$	1		$\frac{5528}{31185}$	$\frac{1076}{2835}$					
	$(\rho)^{1/2}$				$\frac{-32}{135}$	$\frac{2432}{315}$	$\frac{3040}{567}$	$\frac{40448}{31185}$	
	$(1 + \rho)^{1/2}$		$\frac{-11056}{31185}$	$\frac{-428}{297}$	$\frac{-113552}{31185}$	$\frac{-172336}{31185}$	$\frac{-48992}{10395}$	$\frac{-40448}{31185}$	
	$(2\rho)^{1/2}$				$\frac{-256}{135}$	$\frac{-1264}{105}$	$\frac{-25408}{2835}$	$\frac{-16384}{31185}$	
	$(1 + 2\rho)^{1/2}$		$\frac{5528}{31185}$	$\frac{33104}{31185}$	$\frac{30832}{31185}$	$\frac{307072}{31185}$	$\frac{275392}{31185}$	$\frac{16384}{31185}$	
$\tilde{S}_4$	1	$\frac{652}{31185}$							
	$(\rho)^{1/2}$					$\frac{64}{135}$	$\frac{128}{315}$	$\frac{-512}{2835}$	$\frac{-1024}{6237}$
	$(1 + \rho)^{1/2}$			$\frac{-1304}{31185}$	$\frac{152}{2079}$	$\frac{-7936}{31185}$	$\frac{-13568}{31185}$	$\frac{1024}{10395}$	$\frac{1024}{6237}$
	$(2\rho)^{1/2}$					$\frac{-128}{135}$	$\frac{-512}{315}$	$\frac{4096}{2835}$	$\frac{16384}{6237}$
	$(1 + 2\rho)^{1/2}$			$\frac{652}{31185}$	$\frac{-152}{2079}$	$\frac{15872}{31185}$	$\frac{54272}{31185}$	$\frac{-8192}{10395}$	$\frac{-16384}{6237}$

calculation is just the set of all these coefficients for the various expressions of the form of eq 21. It is important to note that exact analytical results are obtained; no numerical quadratures or other approximation procedures are involved.

To systematize our results, we write the averaged linear perturbation coefficient $(a_1)_{\text{random}}$ as

$$(a_1)_{\text{random}} = \frac{6}{(1 + \rho f)^{7/2} \sum_J g_J w_J} \left[\frac{67}{315} + f\tilde{S}_1 + f(f - 1)\tilde{S}_2 + f(f - 1)(f - 2)\tilde{S}_3 + f(f - 1)(f - 2)(f - 3)\tilde{S}_4 \right] \quad (22)$$

The quantities $\tilde{S}_1$, $\tilde{S}_2$, $\tilde{S}_3$, and $\tilde{S}_4$ are sums of terms, each in the form of eq 21, which are to be constructed from the entries in Table II. For example, the first two rows of the table give the following contributions to $\tilde{S}_1$:

$$-\frac{1196}{2835} - \frac{78}{105}\rho - \left[\frac{32}{27} + \frac{116}{45}\rho + \frac{151}{63}\rho^2 + \frac{2348}{2835}\rho^3 \right] \rho^{3/2}$$

It is thus a simple matter to calculate the $\tilde{S}_m$ for a chosen value of ρ. These results and the number of branches f are then substituted into eq 22. The $\tilde{S}_m$ are plotted in Figure 1 to indicate the relative importance of the contributions of the configurational groups enumerated above with changing ρ. To calculate $(a_1)_{\text{random}}$ from eq 22 the averaged g factor is also needed, but this has been given previously[9] as:

$$g_{\text{random}} \equiv \sum_J g_J w_J = \frac{(1 + f\rho)^2 + 2f\rho^2 + (3f - 2)f\rho^3}{(1 + f\rho)^3} \quad (23)$$

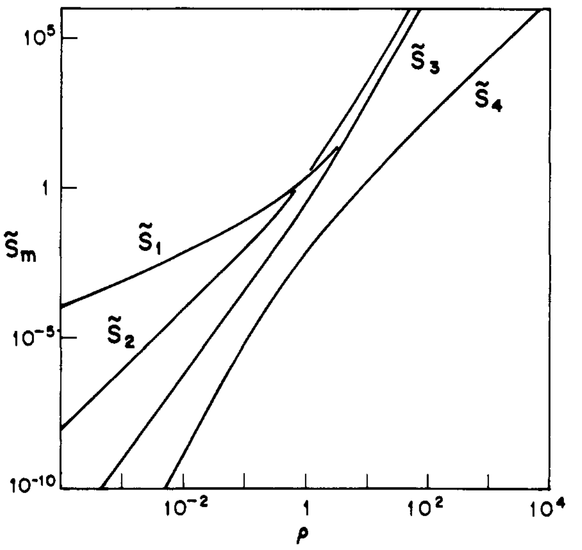


Figure 1. Dependence of the $\tilde{S}_m$ in eq 22 on relative branch length. Beyond $\rho \approx 10$, $\tilde{S}_1$ and $\tilde{S}_3$ tend to merge asymptotically.

It is easily verified that as $\rho \rightarrow 0$ or $f = 0$, $(a_1)_{\text{random}}$ assumes the value for a linear chain. Expanding $(1 + \rho)^{1/2}$ in series we see that

$$\tilde{S}_1 = (268/315)\rho + 0(\rho^{3/2}) \tag{24}$$

and that $\tilde{S}_2$, $\tilde{S}_3$, and $\tilde{S}_4$ contribute nothing of first order in ρ. (Figure 1 shows that the initial contributions from $\tilde{S}_2$, $\tilde{S}_3$, and $\tilde{S}_4$ are respectively of order ρ^2, ρ^3, ρ^4.) Then noting that

$$g_{\text{random}} = 1 - \rho f + 0(\rho^2) \tag{25}$$

and using eq 22, we obtain the initial dependence for small ρ

$$(a_1)_{\text{random}} = \frac{134}{105}\left[1 + \frac{3}{2}\rho f + \ldots\right] \tag{26}$$

This is consistent with the result given by Berry and Orofino

$$\lim_{\substack{\rho \to 0 \\ f \to \infty}} a_1 = (134/105)(1 + f\rho)^{3/2} \tag{27}$$

for the regular comb with many short branches, in which the unperturbed size is determined only by the length of the backbone.

The asymptotic behavior of $(a_1)_{\text{random}}$ for large ρ can be obtained by expanding the factors $(1 + B'\rho)^{1/2} = (B'\rho)^{1/2}(1 + 1/B'\rho)^{1/2}$ in the $\tilde{S}_m$ in powers of $1/\rho$ and combining terms in like powers. In the limit $\rho \rightarrow \infty$, the results for f-branch "regular stars" are recovered. From the slopes of the curves in Figure 1 it can be seen that $\tilde{S}_1$, $\tilde{S}_2$, and $\tilde{S}_3$ increase asymptotically as $\rho^{7/2}$ while $\tilde{S}_4$ increases only as ρ^2. Therefore, in the limit, $\tilde{S}_4$ contributes nothing to a_1. This is expected since group 4 configurations contain only contributions of class III, which are all zero for star molecules. (When the four index segments are all on different arms of the star, the paths connecting the segments in pairs share no sequence of segments.) It is noteworthy that the asymptotic behavior of the $\tilde{S}_m$ is essentially established when ρ is on the order of 10.

The common initial slope of the plots of $(a_1)_{\text{random}}$ vs. $f\rho$ in Figure 2 is prescribed by eq 26. The plots also show that for some range of ρ, $(a_1)_{\text{random}}$ is greater than the corresponding coefficient for the star with the same number of branches. This behavior was previously found for regular combs, and there is evidently a rapid convergence of $(a_1)_{\text{random}}$ to the regular-comb results as the number of branches increases. On the scale of the plot, the two functions become virtually indistinguishable beyond $f = 15$. This behavior follows from the resemblance between combs with regular and random branch placements when the branching is dense.

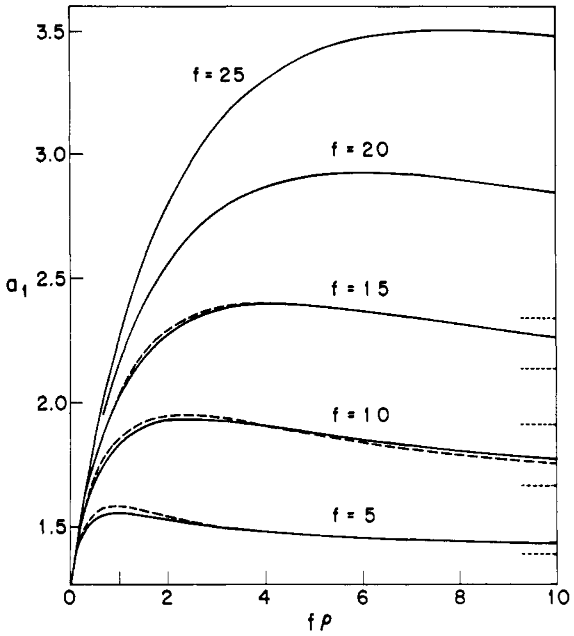


Figure 2. Plots of a_1 vs. $f\rho$ for random (solid curves) and regular (dashes) combs with the number of branches indicated. Where the regular-comb function is not shown, it is indistinguishable from $(a_1)_{\text{random}}$ on the scale of the plot. Values of a_1 for the corresponding regular stars are marked at the right.

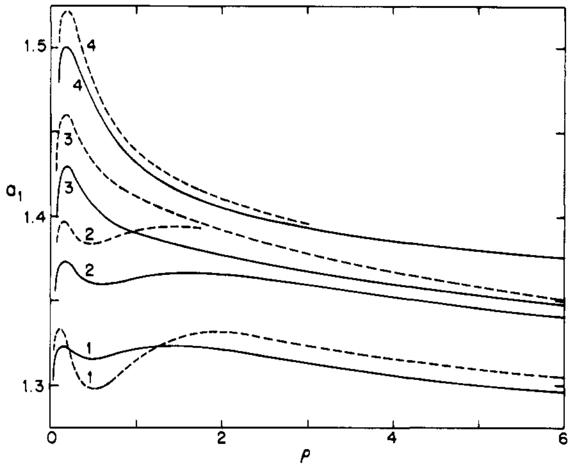


Figure 3. Dependence of a_1 on ρ for random (solid curves) and regular (dashes) combs with few branches.

For small numbers of branches, there are greater differences between random and regular combs. As shown in Figure 3, $(a_1)_{\text{random}}$ and the regular-comb function exhibit maxima at about the same ρ (ca. 0.2), but the maximum a_1 for the regular comb is greater than the maximum $(a_1)_{\text{random}}$. A peculiar feature for the regular combs with $f = 1$ and 2 is a minimum and second maximum in a_1 before the decrease to 134/105 as $\rho \rightarrow \infty$ for these pathologic "stars". Interestingly, although this oscillatory character of a_1 is modified by the averaging over all branch placements in the random-comb calculation, it is not obliterated.

Using their numerical data, Berry and Orofino have quite extensively mapped the behavior of a_1 for regular combs with variation of f, ρ, and g. Since their results are quantitatively similar to ours, their discussion is applicable as well to $(a_1)_{\text{random}}$, and we can dispense with further elaboration here. In summary, we confirm the supposition that the randomization of branch placements has only a secondary effect on a_1, but our analytic relations are easier to work with than the regular-comb results. Numerical calculation of $(a_1)_{\text{random}}$ from eq 22 has a large advantage in ease (and computation time) as compared with the regular-comb case.

Heterogeneous Combs

Although the random-comb model is proposed as more realistic than the regular comb, a further gain in realism can be made by introducing a distribution in numbers of branches per molecule as well as of their placement on the backbone. The random-comb population with f branches per molecule can be regarded as an "f-mer species" in the entire sample of combs, and the preceding calculations can then be applied to this more complicated case for a distribution of f-mers. Here we consider only one particularly simple case: the probability x_f that a molecule has f branches is given by the binomial distribution

$$x_f = \binom{n_0}{f} p^f (1 - p)^{n_0 - f} \qquad (28)$$

where $p = \bar{f}/n_0$ is the probability that a backbone segment chosen at random will be found to bear a branch. We have called systems so distributed "heterogeneous" combs.[9,16] The probability x_f is obviously the mole fraction of chains with f branches. The binomial distribution is realized when a large number of identical backbones and identical branches are made to couple at random. Thus, heterogeneous combs could result from a synthetic procedure and random combs might be approximated by a fractionation of the product. The parameter $\bar{f}$, the mean number of branches per chain, is in principle known from the number of branches and backbones used in making up the system.

In calculating a mean-square radius of gyration averaged over all structures in the heterogeneous-comb system, the pertinent average is the one determined by diffraction measurements on a collection of molecules chemically homologous (alike in electron density) but otherwise heterogeneous in mass and/or structure:

$$\langle s^2 \rangle_{\text{hetero}} = \sum_f M_f w_f \langle s^2 \rangle_f \Big/ \sum_f M_f w_f \qquad (29)$$

where M_f is the molecular weight of the f-mer random combs and w_f is their weight fraction in the comb population. Similarly, $\langle s^2 \rangle_f$ is the mean-square radius $\langle s^2 \rangle_{\text{random}}$ for f-mers given by eq 15. Henceforth, the subscript f is used in this way to indicate quantities referring to random combs with f branches.

With eq 16, eq 29 gives

$$\langle s^2 \rangle_{\text{hetero}} = \sum_f M_f w_f \langle s^2 \rangle_{0f} (1 + a_{1f} z_f + \ldots) \Big/ \sum_f M_f w_f \qquad (30)$$

or

$$\frac{\langle s^2 \rangle_{\text{hetero}}}{[\langle s^2 \rangle_0]_{\text{hetero}}} = 1 + \frac{\sum_f M_f w_f \langle s^2 \rangle_{0f} a_{1f} z_f}{\sum_f M_f w_f \langle s^2 \rangle_{0f}} \qquad (31)$$

where

$$[\langle s^2 \rangle_0]_{\text{hetero}} = \sum_f M_f w_f \langle s^2 \rangle_{0f} \Big/ \sum_f M_f w_f \qquad (32)$$

To put eq 31 into useful form, we make the following substitutions: (a)

$$M_f = m_0 n_f = m_0 n_0 (1 + f\rho) \qquad (33)$$

where m_0 is the molecular weight of a segment; (b)

$$w_f = x_f \frac{1 + f\rho}{1 + \bar{f}\rho} \qquad (34)$$

which follows from the distribution function, eq 28; (c)

$$\langle s^2 \rangle_{0f} = 1/6 n_0 b^2 (1 + f\rho) g_f \qquad (35)$$

where g_f is given by eq 23; (d) a_{1f} according to eq 22; and (e)

$$z_f = \left(\frac{3}{2\pi b^2} \right)^{3/2} \beta {n_0}^{1/2} (1 + f\rho)^{1/2} \qquad (36)$$

Through cancellation of factors the numerator of the final term in eq 31 becomes

$$\sum_f M_f w_f \langle s^2 \rangle_{0f} a_{1f} z_f = \frac{m_0 {n_0}^2 b^2 \bar{z}}{(1 + \bar{f}\rho)^{3/2}} \sum_f \left[\frac{67}{315} + \sum_{\nu=1}^{4} \frac{f! \tilde{S}_\nu}{(f - \nu)!} \right] x_f \qquad (37)$$

where $\bar{z}$ is defined by

$$\bar{z} = \left(\frac{3}{2\pi b^2} \right)^{3/2} \beta {n_0}^{1/2} (1 + \bar{f}\rho)^{1/2} \qquad (38)$$

To eliminate the sum over branch numbers f in eq 37, we need four moments of the binomial distribution:[17] e.g., for the coefficient of $\tilde{S}_1$

$$\sum_f f x_f = \bar{f} \qquad (39)$$

and for the coefficient of $\tilde{S}_2$

$$\sum_f f(1 - f) x_f = \sum_f f^2 x_f - \sum_f f x_f = \bar{f}^2 \left(1 - \frac{1}{n_0} \right) \approx \bar{f}^2 \qquad (40)$$

Since we have assumed throughout that $n_0 \gg 1$, there is no loss of generality in taking the approximate equality in eq 40 as exact. The coefficients of $\tilde{S}_3$ and $\tilde{S}_4$ are similarly found to be $\bar{f}^3$ and $\bar{f}^4$, respectively. Substituting eq 35 and 23 into the denominator of the last term of eq 31, we again obtain a sum over f, but evaluation of this requires only the first two moments of the distribution.

Assembling the results outlined in the preceding paragraph, we obtain finally the averaged chain expansion for the heterogeneous comb systems

$$\langle s^2 \rangle_{\text{hetero}} / [\langle s^2 \rangle_0]_{\text{hetero}} = 1 + (a_1)_{\text{hetero}} \bar{z} + \ldots \qquad (41)$$

in which

$$(a_1)_{\text{hetero}} = \left[\frac{134}{105} + 6 \sum_\nu \bar{f}^\nu \tilde{S}_\nu \right] \Big/ (1 + \bar{f}\rho)^{7/2} g_{\text{hetero}} \qquad (42)$$

$$g_{\text{hetero}} = [1 + \bar{f}\rho(2 + 3\rho + \rho^2) + \bar{f}^2 \rho^2 (1 + 3\rho)] / (1 + \bar{f}\rho)^3 = 6[\langle s^2 \rangle_0]_{\text{hetero}} \Big/ \sum_f n_f w_f b^2 \qquad (43)$$

The averaged quantity g_{hetero} has been obtained previously.[9] If it were desired, the first-order perturbation result for stars with a random distribution of numbers of arms could be obtained from eq 42 by letting $\rho \to \infty$, but it would obviously be simpler to perform the appropriate averaging directly, using the expression for a_1 for regular stars.

Acknowledgment. This work has been supported by the Center for the Joining of Materials, Carnegie-Mellon University, through the National Science Foundation, Materials Research Section (Grant No DMR76-81561). We are indebted to Mr. Robert T. McKeever for his invaluable help in creating the computer program and to Dr.

Carolyn M. Bogan for the initial suggestion concerning the computational method.

References and Notes

(1) G. C. Berry and E. F. Casassa, *J. Polym. Sci., Part D*, **4**, 1 (1970); E. F. Casassa, *J. Polym. Sci., Part A-2*, **8**, 1651 (1970).

(2) F. Candau, P. Rempp, and H. Benoit, *Macromolecules*, **5**, 627 (1972).

(3) D. Decker, *Makromol. Chem.*, **125**, 136 (1969); I. Noda, T. Horikawa, T. Kato, T. Fujimoto, and M. Nagasawa, *Macromolecules*, **3**, 795 (1970); J.-C. Meunier and R. van Leemput, *Makromol. Chem.*, **147**, 191 (1971); J. Pannell, *Polymer*, **12**, 558 (1971); G. C. Berry, *J. Polym. Sci., Part A-2*, **9**, 687 (1971); F. Candau and P. Rempp, *Eur. Polym. J.*, **8**, 737 (1972); J.-G. Zilliox, *Makromol. Chem.*, **156**, 121 (1972).

(4) D. J. Bauer and L. J. Fetters, *Rubber Chem. Technol.*, **51**, 406 (1978).

(5) T. Altares, D. P. Wyman, V. R. Allen, and K. Meyersen, *J. Polym. Sci., Part A-2*, **3**, 4131 (1965).

(6) J. Roovers, *Polymer*, **20**, 843 (1979). See also references therein.

(7) T. A. Orofino, *Polymer*, **2**, 305 (1961); G. C. Berry, V. C. Long, and L. M. Hobbs, *ibid.*, **5**, 31 (1964); E. F. Casassa, *J. Chem. Phys.*, **41**, 3217 (1964); E. F. Casassa, *ibid.*, **45**, 2811 (1966); M. Kurata and M. Fukatsu, *ibid.*, **41**, 2934 (1964).

(8) G. C. Berry and T. A. Orofino, *J. Chem. Phys.*, **40**, 1614 (1964).

(9) E. F. Casassa and G. C. Berry, *J. Polym. Sci., Part A-2*, **4**, 881 (1966).

(10) E. F. Casassa and Y. Tagami, *J. Polym. Sci., Part A-2*, **6**, 63 (1968).

(11) G. C. Berry, *J. Polym. Sci., Part A-2*, **6**, 63 (1968).

(12) H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, 1971, Chapter 3.

(13) M. Fixman, *J. Chem. Phys.*, **23**, 1656 (1955).

(14) We have modified the categories of Berry and Orofino in two ways: our group 0 is part of their group 1, and the first three Γ_{I} terms in our group 2 (eq 12) correspond to terms in their group 1. It seems to us that our choice in the latter instance is logically preferable.

(15) This tabulation should be compared with Table I in ref 8 for regular combs. Apart from the differences in cataloging noted above, the symmetry of the regular comb renders pairs of diagrams that appear in our scheme identical. Table I in ref 8 also has errors, which have been corrected here, in the group 2 enumeration. The Berry–Orofino chain parameters y and y/r translate to n_b and $n_0/(f + 1)$ in this paper.

(16) It is obviously artificial to identify a statistical backbone segment with just one chemical unit affording a locus for attachment of a branch. However, if $\bar{f}$ is far less than n_0, this simplification has no sensible effect on the distribution of branches in the system.

(17) H. Cramér, "Mathematical Methods of Statistics", Princeton University Press, Princeton, 1946, pp 175 and 195.

Asymmetry of Flexible Chains, Macrocycles, and Stars

Wayne L. Mattice

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803.

Received October 16, 1979

ABSTRACT: Instantaneous asymmetry of the distribution of chain segments has been characterized for four types (linear chain, macrocycle, three-star, four-star) of flexible unperturbed polymers containing fixed bond angles. Stars contain the same number of atoms in each branch. Results for large polymers are in harmony with those reported by several previous investigators. Asymmetry of large polymers increases in the order four-star < macrocycle < three-star < linear chain. Development of the limiting asymmetry is characterized in each case. Individual principal components of the mean square radius for the four types of molecules considered reflect differences in both asymmetry and characteristic ratio. Almost all differences in mean square radius of gyration for these molecules can be attributed to variation in the averaged largest principal component of the mean square radius when the number of bonds is large. Thus cyclization of a long linear chain demands a major reduction in the largest principal component but only minor adjustment of the remaining principal components.

The squared radius of gyration, s^2, characterizes the extension of chain atoms about their center of mass for a specified configuration of a polymer molecule. Asymmetry of this spatial distribution can be assessed through evaluation of the principal components, $L_1^2 \geq L_2^2 \geq L_3^2$, $s^2 = L_1^2 + L_2^2 + L_3^2$. Interest is focused on departures from unity of any two independent ratios, such as L_2^2/L_1^2 and L_3^2/L_1^2.

If the polymer molecule is flexible, average extension of atoms about the center of mass is characterized in a straightforward manner by the mean square radius of gyration, $\langle s^2 \rangle$. Asymmetry of the spatial distribution, however, is subject to different definitions which yield contrasting results. The starting point in each case can be viewed as the radius of gyration tensor, $\mathbf{S}_{x2}$, for every accessible configuration, with every $\mathbf{S}_{x2}$ expressed in an internal coordinate system rigidly attached to a specified part of the molecule. This coordinate system might, for example, be defined by the orientation of two consecutive bonds.[1] One definition of asymmetry utilizes the principal components ($\langle S_{2,a} \rangle \geq \langle S_{2,b} \rangle \geq \langle S_{2,c} \rangle$, $\langle s^2 \rangle = \langle S_{2,a} \rangle + \langle S_{2,b} \rangle + \langle S_{2,c} \rangle$) of $\langle \mathbf{S}_{x2} \rangle$, where $\langle \mathbf{S}_{x2} \rangle$ denotes the average of all accessible $\mathbf{S}_{x2}$, averaging being accomplished in the internal coordinate system.[1] If this definition of asymmetry is employed, all flexible homopolymers of sufficiently high molecular weight will be found to possess spherical symmetry ($\langle S_{2,a} \rangle = \langle S_{2,b} \rangle = \langle S_{2,c} \rangle$).[1-3] Smaller polymers will not have a spherically symmetric spatial distribution. In such cases asymmetry may depend upon the precise location of the internal coordinate system in which the $\mathbf{S}_{x2}$ are expressed.[2,3]

An alternative definition of asymmetry, and the one to be employed in the remainder of this work, focuses attention on the average, $\langle L_i^2 \rangle$, $i = 1, 2, 3$, of the corresponding principal moments for all accessible $\mathbf{S}_{x2}$. This definition thus permits an assessment of the average instantaneous asymmetry of the spatial distribution. Large flexible polymer chains are definitely asymmetric when this definition,[4-6] or one based on the end-to-end vector,[7] is adopted. Furthermore, sufficiently large unperturbed flexible chain molecules have been found to all have virtually identical asymmetries, as measured by $\langle L_2^2 \rangle / \langle L_1^2 \rangle$ and $\langle L_3^2 \rangle / \langle L_1^2 \rangle$. Validity of this assertion is illustrated by results collected in Table I. Monte-Carlo calculations have been carried out for chains on a cubic lattice[4-6] as well as for rotational isomeric state models for unperturbed poly(methylene),[1] poly(oxyethylene),[8] and poly(thiaethylene).[9] Averages of these results are $\langle L_2^2 \rangle / \langle L_1^2 \rangle =$