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Configurational Statistics of Unperturbed Wormlike and Rotational Isomeric State Stars of Finite Size

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ABSTRACT: A comparison is presented between the behavior of unperturbed stars of finite size whose configurational statistics are evaluated by rotational isomeric state theory and the Kratky–Porod wormlike chain. Emphasis is placed on the initial slopes of the characteristic ratio, C, or g when plotted as a function of the reciprocal of the number of bonds, n. The wormlike chain treatment has its greatest success in providing a quantitative relationship between the initial slopes of C vs. $1/n$ for stars and the linear chain when the macromolecules have a reasonably high characteristic ratio. In general, the wormlike chain treatment does not provide a good description of the manner in which the initial slope of C vs. $1/n$ or g vs. $1/n$ for stars depends on C for an infinitely long unbranched chain. An exception is provided by polymethylene stars, for which the wormlike model is quite successful. Finite stars of low characteristic ratio are, without exception, poorly described by the wormlike model.

Characterization of branched homopolymers usually includes an assessment of the effect of branching on macromolecular dimensions. The conventional parameter is denoted by g and defined as the ratio of the mean-square radii of gyration for branched and unbranched polymers having the same number of bonds.[1] This parameter is susceptible to numerical evaluation using a variety of models for the configurational statistics of the polymer. A theoretical value is most easily obtained if the macromolecules are unperturbed by long-range interactions. The amount of attention given to the actual molecular structure dictates the complexity of the final working equations. These equations are of quite simple form if they are based on random-flight statistics, but they can become rather complicated if rotational isomeric state theory is used.[2–4] Numerical evaluation of the former equations can frequently be accomplished even in the absence of a hand-held calculator, but evaluation of the latter requires access to a digital computer. Recently[5] equations for g have been developed for unperturbed branched molecules whose rays are Kratky–Porod[6] wormlike chains. These equations are susceptible to numerical evaluation using a hand-held calculator, placing them intermediate in complexity between those based on random-flight statistics and rotational isomeric state theory.

A common feature of the behavior of the different models is brought out by examination of the limiting value for g at infinite molecular weight for molecules with a specified branching pattern and ratio of ray contour lengths. Illustrative examples are provided by molecules having a single trifunctional or tetrafunctional branch point and the same number of bonds in each branch. All three models of the configurational statistics yield precisely the same value of g in the limit of infinite molecular weight.[1,5,7,8] For the specific examples cited, g approaches $^7/_9$ if the branch point is trifunctional, and it approaches $^5/_8$ if the branch point is tetrafunctional.[1,5,7,8] Clearly the simple equations obtained with random-flight statistics are to be preferred if the sole objective is computation of g at infinite molecular weight.

A different situation arises if the objective is a value for g for a branched molecule of finite size. Equations based on random-flight statistics are of no assistance in this endeavor. For example, random-flight statistics yields $g = {}^7/_9$ for all trifunctional stars in which the branches contain the same number of bonds, regardless of whether the number of bonds in a branch is one, infinite, or anywhere in between! In contrast, both the rotational isomeric state and Kratky–Porod wormlike chain treatments predict g should depend on the number of bonds in the branched molecule.[5,7–9] A question quite naturally arises as to when the rotational isomeric state and Kratky–Porod chain treatments yield essentially identical g for branched polymers of finite size. The objective here is to present and discuss pertinent data for the cases of trifunctional and tetrafunctional stars in which each branch contains the same number of bonds. We do so by comparing the behavior predicted by the Kratky–Porod wormlike chain treatment[5] with previously published results of rotational isomeric state calculations for polymers having short-range interactions represented by a symmetric threefold rotation potential[7,8,10] and for cross-linked homopolypeptides and sequential copolypeptides.[9]

Predictions for Wormlike Stars

Two different definitions will be adopted for the characteristic ratio, C. They share the features of being directly proportional to the mean-square unperturbed radius of gyration, $\langle s^2\rangle_0$, and inversely proportional to the number of bonds in the molecule. For wormlike chains or stars, C is defined as $\langle s^2\rangle_0/L$, where L denotes the total contour length. When rotational isomeric state theory is used, C will be defined as $\langle s^2\rangle_0/nl^2$ for simple homopolymers and as $\langle s^2\rangle_0/n_\mathrm{p}l_\mathrm{p}{}^2$ for polypeptides. Here n denotes the number of bonds of length l, and n_p is the number of virtual bonds of length l_p (3.80 Å).[11] Differences in definitions for C will be of no consequence for comparisons made in this work.

The first requirement for a treatment of finite chains is to be able to properly account for the departures from the asymptotic behavior as the molecular weight becomes infinite. For this reason, attention is directed to $\mathrm{d}C/\mathrm{d}(1/L)$, $\mathrm{d}C/\mathrm{d}(1/n)$, $\mathrm{d}g/\mathrm{d}(1/L)$, and $\mathrm{d}g/\mathrm{d}(1/n)$ as $1/L$ or $1/n$ goes to zero. Comparatively simple closed expressions can be obtained for $\mathrm{d}C/\mathrm{d}(1/L)$ and $\mathrm{d}g/\mathrm{d}(1/L)$ for wormlike chains and stars in the limit where $1/L$ approaches zero. Behavior predicted by these expressions can be compared with that obtained from numerical calculations in which the unperturbed dimensions were evaluated by rotational isomeric state theory.

Behavior of the Characteristic Ratio. The Kratky–Porod wormlike chain treatment predicts the asymptotic value of C at infinite L is

$$C_{1/L\to 0} = ga/3 \tag{1}$$

where a denotes the persistence length and g is unity for unbranched chains,[12] $^7/_9$ for trifunctional stars,[1,5] and $^5/_8$ for tetrafunctional stars.[1,5] Since C is always positive, the limiting behavior at infinite contour length demands the

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persistence length also be positive.

Starting from eq 10 of ref 5, the wormlike chain treatment yields

$$[\mathrm{d}C/\mathrm{d}(1/L)]_{1/L\to 0} = -a^2(2f - 1 + 2F/f)/f = -a^2\alpha \qquad (2)$$

where f denotes the number of rays in the star and F is determined by the initial directions of the rays as they leave the branch point.[5]

$$F = \sum_{i<j} \cos(\pi - \theta_{ij}) \qquad (3)$$

The supplement of the angle between rays i and j at the branch point is denoted by θ_{ij}. The minimum value for F is $-f/2$, and this value is obtained when the initial directions of all rays cancel.[5] Thus a tetrafunctional star with tetrahedral geometry at the branch point has $f = 4$ and $F = -2$. Appearance of F in eq 2 demonstrates that the wormlike chain treatment predicts the *initial* direction of the rays retains an influence on C even as $1/L$ approaches zero.

The right-hand side of eq 2 can be written more compactly as $-a^2\alpha$, where α is a positive constant whose value depends solely on branch-point functionality and initial directions of the rays as they leave the branch point. The value of α is unity for an unbranched chain. If the initial directions of all rays cancel, α is $^4/_3$ for a trifunctional star, is $^3/_2$ for a tetrafunctional star, and approaches 2 as the functionality becomes infinite. The increase in α with increasing branch-point functionality indicates departures from the limiting behavior should be more severe in stars than in the unbranched chain.

Since physically meaningful values for f and F demand that α be positive, the wormlike chain treatment predicts

$$[\mathrm{d}C/\mathrm{d}(1/L)]_{1/L\to 0} < 0 \qquad (4)$$

Furthermore, since α is independent of chain stiffness as represented by the persistence length

$$\frac{[\mathrm{d}C_{\mathrm{star}}/\mathrm{d}(1/L)]_{1/L\to 0}}{[\mathrm{d}C_{\mathrm{linear}}/\mathrm{d}(1/L)]_{1/L\to 0}} = (2f - 1 + 2F/f)/f \qquad (5)$$

where the f and F are those appropriate for the star. The numerical value of the ratio in eq 5 should be the same for all stars of a given functionality and branch-point geometry. If the initial directions of the rays cancel, this ratio is $^4/_3$ for trifunctional stars and $^3/_2$ for tetrafunctional stars. It increases to $^{13}/_9$ for trifunctional stars if the branch-point geometry is tetrahedral.

Elimination of a from eq 1 and 2 yields

$$[\mathrm{d}C/\mathrm{d}(1/L)]_{1/L\to 0} = -(9\alpha/g^2)(C_{1/L\to 0})^2 \qquad (6)$$

If the limiting characteristic ratio on the right-hand side is understood to be that of the unbranched chain, then

$$[\mathrm{d}C/\mathrm{d}(1/L)]_{1/L\to 0} = -9\alpha(C_{\mathrm{linear},1/L\to 0})^2 \qquad (7)$$

This equation indicates the initial departure from the asymptotic behavior for stars of specified functionality and branch-point geometry should be directly proportional to the square of the limiting characteristic ratio for the linear chain.

Behavior of *g*. From eq 4, 6, 7, and 10 of ref 5, wormlike stars are predicted to exhibit the behavior shown in eq 8 The right-hand side of this equation can be written

$$[\mathrm{d}g/\mathrm{d}(1/L)]_{1/L\to 0} = -a[6(1 - 2f + f^2 + F)/f^2] = -a\beta \qquad (8)$$

as $-a\beta$, where β is a positive constant whose value depends solely on branch-point functionality and initial directions of the rays as they leave the branch point. If initial directions of the rays cancel, $\beta = {^5/_3}$ for trifunctional stars, $^{21}/_8$ for tetrafunctional stars, and approaches 6 as the functionality becomes infinite. Since the persistence length is positive

$$[\mathrm{d}g/\mathrm{d}(1/L)]_{1/L\to 0} < 0 \qquad (9)$$

and elimination of the persistence length from eq 1 and 8 yields

$$[\mathrm{d}g/\mathrm{d}(1/L)]_{1/L\to 0} = -3\beta C_{\mathrm{linear},1/L\to 0} \qquad (10)$$

The last equation indicates the initial departure of g from its asymptotic value is directly proportional to the limiting characteristic ratio of the linear chain.

Rotational Isomeric State Computations

Behavior predicted by several of the above equations can be tested by using numerical results obtained from rotational isomeric state calculation. For this purpose, it is only necessary to replace $1/L$ by $1/n$ in eq 4, 5, 7, 9, and 10. Use will be made here of results obtained in two sets of rotational isomeric state calculations performed by using generator matrices[7,8] and also of results obtained in another study in which the Monte Carlo method was employed.[10] The Monte Carlo method was used in a study of tri- and tetrafunctional stars having three equally probable rotational states for each internal bond and bond angle supplements of 60, 70, 80, 90, and 100°. In these studies tetrafunctional branch points always had tetrahedral geometry ($F = -2$), but the trifunctional branch points had bond angle supplements of 60–100°, corresponding to F ranging from $-^3/_2$ to 0.52.

The generator matrix study of simple stars included molecules in which first- and second-order interactions were those appropriate for unperturbed polyethylene,[13] as well as cases where these interactions were a reasonable approximation to those encountered in unperturbed poly(oxymethylene).[14] Branch-point geometry in these cases dictates $F = -2$ for tetrafunctional stars and $F = -1.03$ for trifunctional stars.

Results are also presented for unperturbed cross-linked polypeptides. The central amino acid residue in each polypeptide chain is L-cysteinyl, and two L-cysteinyl residues participate in formation of the interchain disulfide cross-link. These cross-linked polypeptides can be viewed as tetrafunctional stars with rays of equal contour length emanating from the L-cystinyl residue. Initial directions of the rays are not fixed, however, because the L-cystinyl residue is flexible.[15] Therefore the appropriate value for F is probably somewhat larger than -2.

Results and Discussion

Sign of the Approach to the Asymptotic Limits for *C* and *g*. Equation 4 demands $[\mathrm{d}C/\mathrm{d}(1/n)]_{1/n\to 0}$ be negative for both linear chains and stars, while eq 9 demands $[\mathrm{d}g/\mathrm{d}(1/n)]_{1/n\to 0}$ be negative for stars. These predictions are easily tested by using rotational isomeric state theory. Pertinent results, based on mean-square unperturbed radii of gyration reported in ref 10, are depicted in Figures 1 and 2. Chains in question have three equally probable rotational states ($\phi = 0, \pm 120°$) for each internal bond. Tetrafunctional branch points have tetrahedral geometry. All other bond angle supplements are in the range 60–100°, as noted on the figures.

Figure 1 shows that the expected negative values for $[\mathrm{d}C/\mathrm{d}(1/n)]_{1/n\to 0}$ are obtained if the bond angle supplement is small. However, $[\mathrm{d}C/\mathrm{d}(1/n)]_{1/n\to 0}$ becomes *positive* if the bond angle supplement is sufficiently large. The

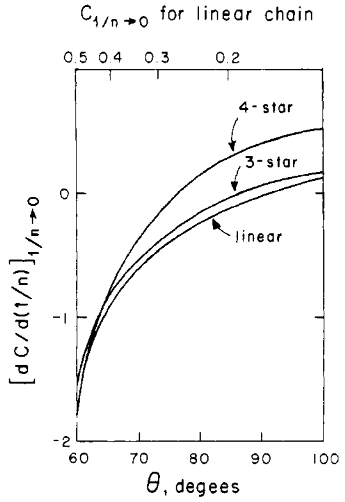

Figure 1. Initial slope of $\langle s_2\rangle_0/nl^2$ vs. $1/n$ for linear chains and for trifunctional and tetrafunctional stars having the same number of bonds in each branch. Tetrafunctional stars have tetrahedral bond angles at the branch point. All other bond angles have the supplement θ. Each internal bond has three equally probable rotational states ($\phi = 0, \pm 120°$). The asymptotic limit for $\langle s^2\rangle_0/nl^2$ for the linear chains is also shown.

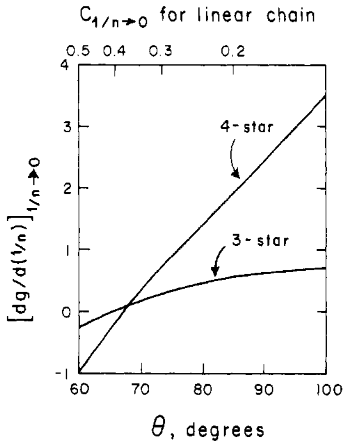

Figure 2. Initial slope of g vs. $1/n$ for stars considered in Figure 1.

change in sign occurs at smaller bond angle supplements as the functionality of the branch point increases. The sign of $[dg/d(1/n)]_{1/n\to0}$ also depends on the bond angle supplement, as shown in Figure 2. This derivative becomes positive at smaller bond angle supplements than does $[dC/d(1/n)]_{1/n\to0}$.

The results depicted in Figures 1 and 2 can lead to rather bizarre behavior of the persistence length if this parameter is obtained from eq 2 and 8. Consider, for example, chains in which θ is 80°. Figure 1 and eq 2 yield a *positive* persistence length for the linear chain. The trifunctional star also has a positive persistence length if it is determined in this manner. However, Figure 2 and eq 8 require a *negative* persistence length for the trifunctional star. The persistence length determined in this manner is also negative for the tetrafunctional star. If, however, the persistence length for the tetrafunctional star were to be determined from eq 2 and Figure 1, it would be found to be *imaginary*!

An alternative way of looking at the data presented in Figures 1 and 2 is as a function of the limiting characteristic ratio of the linear chain, rather than as a function of θ. When examined in this fashion, it quickly becomes apparent that the bizarre behavior of the persistence length

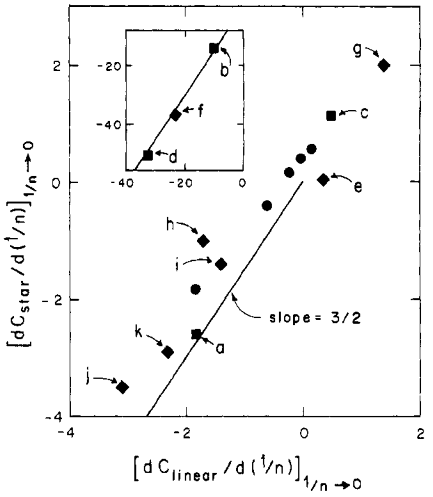

Figure 3. Correlation between the initial slope of $\langle s^2\rangle_0/nl^2$ vs. $1/n$ for tetrafunctional stars and the initial slope of $\langle s^2\rangle_0/nl^2$ vs. $1/n$ for the corresponding linear chains. The solid line of slope $^3/_2$ denotes behavior expected for wormlike stars with tetrahedral geometry at the branch point. This line terminates at the point 0,0. Circles denote points for molecules considered in Figures 1 and 2. Squares denote molecules in which statistical weights for gauche states differ from those for trans states. Values of the statistical weights σ and ω,[13] respectively, are (a) 0.54,1, (b) 0.54,0.088, (c) 10,1, and (d) 10,0. Diamonds denote results for the following polypeptides: (e) polyglycine; (f) poly(L-alanine); (g) poly(L-alanyl-D-alanine); (h) poly(L-prolyl-L-prolylglycine); (i) poly(L-prolyl-L-alanylglycine); (j) poly(glycyl-L-alanyl-L-proline); (k) poly(L-alanyl-L-alanylglycine).

occurs with molecules having low characteristic ratios. If $C_{1/n\to0}$ for the linear chain is larger than about 0.4, the predictions embodied in eq 4 and 9 are in harmony with results obtained from rotational isomeric state calculations. This conclusion is supported by results of other calculations for simple chains with interdependent rotational potentials[7] and for cross-linked polypeptides.[8] For example, cross-linked poly(L-alanyl-D-alanine) and polyglycine have positive values for $[dC/d(1/n)]_{1/n\to0}$ and $[dg/d(1/n)]_{1/n\to0}$. Limiting characteristic ratios for their linear chains are 0.137 and 0.36, respectively. In contrast, six other polypeptides, for which the asymptotic characteristic ratio of the linear chain ranges upward from 0.436,[8] yield results in harmony with eq 4 and 9. Hence we conclude the asymptotic $\langle s^2\rangle/nl^2$ for the linear chain must exceed 0.4 if the wormlike chain treatment of stars is to produce even qualitative agreement with actual results for molecules of finite size.

Correlation between Slopes for Stars and Linear Chains. In the preceding section attention was focused only on signs of the derivatives. A more severe test of the wormlike model for stars occurs when data are plotted in the manner shown in Figure 3. Equation 5 predicts points for all tetrafunctional stars with tetrahedral branch-point geometry should fall on a line of slope $^3/_2$. This line commences at the origin and is confined to the quadrant where both derivatives are negative. The inset in Figure 3 shows that rotational isomeric state chains conform closely to this behavior when the derivatives are strongly negative. Macromolecules represented in the inset are unperturbed poly(L-alanine) and rotational isomeric state models for unperturbed polymethylene and poly(oxymethylene). Their linear chains have asymptotic limits for C which are 0.94 or higher.

Less satisfactory agreement is obtained for macromolecules whose points lie close to the origin. If the derivatives are negative, but within the range covered by the main

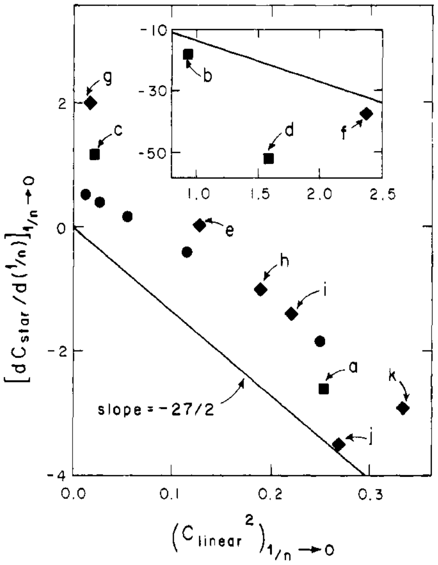

Figure 4. Correlation between the initial slope of $\langle s^2\rangle_0/nl^2$ vs. $1/n$ for tetrafunctional stars and the square of the characteristic ratio for the infinitely long linear chain. Points are identified in the legend for Figure 3.

body of Figure 3, there is a pronounced tendency for the points to lie above the line. This situation is seen with the four glycine-containing sequential copolypeptides related to collagen. Linear chains of macromolecules whose points lie in the main body of Figure 3 have limiting C ranging downward from 0.58.

An extrapolation of the straight line carries it through the point for poly(L-alanyl-D-alanine), which has the most positive derivatives of the macromolecules studied. The success of this extrapolation is somewhat surprising in view of the fact that the wormlike chain treatment demands these derivatives always be negative.

Correlations with the Asymptotic Characteristic Ratio of the Linear Chain. The wormlike chain model for tetrafunctional stars provides a quite accurate correlation between the initial slopes of C vs. $1/n$ for stars and linear chains, provided these slopes are sufficiently negative (Figure 3). Now we inquire into this model's success in relating $[dC_{star}/d(1/n)]_{1/n\to 0}$ to the limiting characteristic ratio for the linear chain. According to eq 7, if data for the macromolecules considered in Figure 3 are replotted as shown in Figure 4, all points should fall on a straight line emanating from the origin and having a slope of $-{}^{27}/_{2}$. The main body of Figure 4 demonstrates the actual points lie above this line if the characteristic ratio of the linear chain has an asymptotic limit smaller than 0.6. For these macromolecules, a large, but still finite, star has a characteristic ratio somewhat greater than that estimated from eq 7 and the asymptotic limit of C for the linear chain. The reverse situation holds for more extended chains, as is shown by the inset in Figure 4. Comparison of the insets for Figures 3 and 4 shows that the wormlike chain treatment for stars of large characteristic ratio can adequately relate certain properties of these molecules (Figure 3) but provides only a poor relationship between other properties (Figure 4). The best agreement is obtained when similar types of properties are compared, as is the case in Figure 3, which is concerned with the initial slopes when C is plotted as a function of $1/n$. Poor agreement is obtained if an *initial slope* of C vs. $1/n$ is compared with an *intercept* in a plot of C vs. $1/n$ (Figure 4).

Correlation between *g* and the Asymptotic Characteristic Ratio of the Linear Chain. The above generalization bodes ill for the ability of the wormlike chain treatment to relate the initial slope of g vs. $1/n$ to the asymptotic characteristic ratio of the linear chain. The prediction, eq 10, is that data for the tetrafunctional stars, plotted as shown in Figure 5 should yield a straight line emanating from the origin and having a slope of $-{}^{63}/_{8}$. Clearly the points in Figure 5 are poorly described by a straight line. If a straight line were drawn through the collection of points, its slope would be substantially more negative than $-{}^{63}/_{8}$ and its intercept on the vertical axis would be positive.

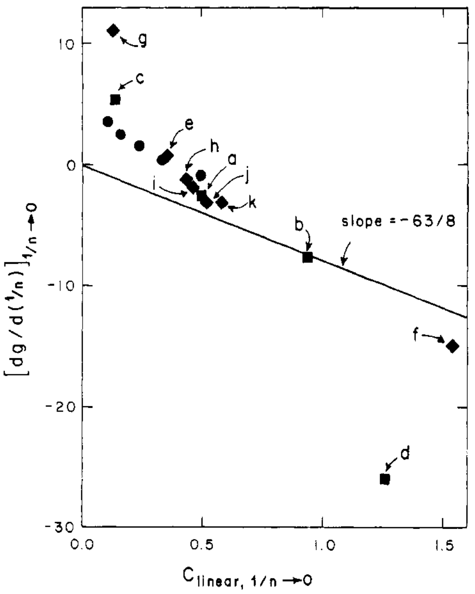

Figure 5. Correlation between the initial slope of g vs. $1/n$ for tetrafunctional stars and the characteristic ratio for the infinitely long linear chain. Points are identified in the legend for Figure 3.

The point which lies closest to the line predicted by the wormlike chain treatment in Figure 5 is that for polymethylene. The result is in accord with the observation that the wormlike chain treatment provides a reasonably good description of g for polymethylene stars down to macromolecules containing a small number of bonds.[5] Figure 5 demonstrates that agreement will not be as good for most other macromolecules. The wormlike chain treatment badly underestimates the dependence of g on $1/n$ for certain macromolecules having high characteristic ratios.

Conclusions

Poor agreement is noted between predictions for wormlike stars and numerical results obtained from rotational isomeric state calculations for molecules of low characteristic ratio. A chain of constant curvature is apparently a poor model for a molecule having a low characteristic ratio. It should be emphasized that, for present purposes, a low characteristic ratio is not to be equated with high chain flexibility. All molecules considered in Figures 1 and 2 have the same flexibility, there being three equally probable rotational states for each internal bond. Yet these molecules differ significantly in their characteristic ratios and in their adherence to eq 4 and 9.

The wormlike chain treatment of stars provides a reasonably good account of certain properties of macromolecules with large characteristic ratios. Greatest success is seen in providing a quantitative relationship between the initial slopes of C vs. $1/n$ for stars and the corresponding linear chains. In contrast, rather poor agreement is obtained when the initial slope of C_{star} vs. $1/n$ or g vs. $1/n$

is related to the limiting characteristic ratio of the linear chain. Exceptions do occur, with the initial slope of g vs. $1/n$ for polymethylene being a noteworthy example.

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Improved Blob Hypothesis in Single-Chain Statistics

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ABSTRACT: An improved version of the blob hypothesis is proposed in which the local swelling is modeled by a formula similar to Flory's for the end-to-end distance. The improved version leads to smoother transitions from Θ- to good-solvent behavior of polymer solution properties such as α_s, α_H, and $S(q)$ but preserves all the qualitative aspects of the original blob hypothesis.

The calculation of both static and dynamic properties of a single chain in solution as a function of temperature requires knowledge of the equilibrium distribution $\psi_0(\mathbf{R}_{ij})$ of the vector distance between the ith and jth monomers in the presence of excluded-volume effects.[1] This function is usually modeled[2] in two steps: first, it is assumed to be Gaussian so that its characteristic function is taken to be

$$\psi_0(q) = \exp\left(-\frac{q^2}{6}\langle|R_{ij}|^2\rangle\right) \tag{1}$$

The second step involves a simplifying assumption for the second moment $\langle|R_{ij}|^2\rangle$. Peterlin[2] assumed it to be of the form

$$\langle|\mathbf{R}_{ij}|^2\rangle = l^2|i-j|^{1+\epsilon} \tag{2}$$

where l is the statistical length and ϵ is a monotonically increasing function of z, the excluded-volume parameter, determined from $\epsilon = (^1/_2)\partial \ln \alpha_R{}^2/\partial \ln z$, where α_R is the swelling factor for the end-to-end distance; i.e., $\langle R^2\rangle = l^2N^{1+\epsilon}$. This model implies that portions of the chain with the same chemical length $n = |i-j|$ swell uniformly with the same exponent.

The "temperature blob" model by Daoud[3] modifies this aspect of Peterlin's model as

$$\langle|\mathbf{R}_n|^2\rangle = nl^2 \qquad \text{for } n \le N_\tau \tag{3a}$$

and

$$\langle|\mathbf{R}_n|^2\rangle = (n/N_\tau)^{2\nu-1}nl^2 \qquad \text{for } n \ge N_\tau \tag{3b}$$

which implies Θ-solvent behavior within the so-called "temperature blob", referring to a section of the chain for which $n \le N_\tau$, and good-solvent behavior among the blobs. The crossover occurs at $n = N_\tau$, which depends on the temperature as

$$N_\tau \sim \tau^{-2} \tag{4}$$

where τ denotes the reduced temperature $(T - \Theta)/T$. The main feature of the blob hypothesis is that the exponent of the local swelling takes on only two discrete values, namely, $\nu = 0.5$ within the blob and $\nu = 0.6$ (or any other value) among the blobs. In contrast to the previous model, where ϵ is a continuous function of temperature, the exponent ν is independent of temperature but the size of the blobs decreases with temperature. As demonstrated in earlier work,[1-4] the blob model of $\psi_0(\mathbf{R}_{ij})$ explains the qualitative features of static and dynamic quantities, such as the static form factor $S(q)$ as a function of q, the radius of gyration R_G, the first cumulant $\Omega(q)$ of the dynamic structure factor, the hydrodynamic radius R_H, and the intrinsic viscosity[5] $[\eta]$. However, the step change in the statistics of portions of the chain below and above N_τ leads to numerical inaccuracies of about 15% or less, as pointed out in ref 1, when N_τ becomes comparable to the chain length. For example, the model predicts no swelling near the Θ temperature, where $N_\tau > N$, which is not consistent with first-order perturbation theory.

In this article, we propose an improvement of these aspects of the blob model by abandoning the concept of two discrete exponents for short and long portions of the chain. We first introduce

$$\langle|\mathbf{R}_{ij}|^2\rangle = l^2|i-j|\alpha^2(i,j) \tag{5a}$$

where $\alpha(i,j)$ is the local swelling factor of the chain. It is, of course, well-known[6] that $\alpha(i,j)$ not only is a function of the chemical length $n = |i-j|$ but also depends on i, i.e., the location of the subchain relative to the ends. We first assume, as done in the previous two models,[2,3] that $\alpha(i,j) \approx \alpha(n)$. In Peterlin's model $\alpha(n) = n^\epsilon$, and in Daoud's model $\alpha(n) = 1$ for $n \le N_\tau$ and $\alpha(n) = (n/N_\tau)^{2\nu-1}$ when $n \ge N_\tau$. The main idea in our model is that $\alpha(n)$ is approximated, for all n, by a formula similar in form to Flory's formula[7]

$$\alpha^5(n) - \alpha^3(n) = \gamma_R z(n) \tag{5b}$$

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