$\langle R^{-1}\rangle$ for them is given by eq A1 with eq A2–A4 of ref 9, where A_1 in eq A4 of ref 9 is given by eq A5 of ref 9 and the values of A_k (k = 2–7) are given in Table II.

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Expansion of Perturbed Rotational Isomeric State Polymethylene Stars

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ABSTRACT: Expansion is considered for finite, regular polymethylene stars perturbed by the excluded volume effect. A rotational isomeric state model is used for the chain statistics. The number of bonds in each branch ranges up to 10 240, and the functionality of the branch point ranges up to 20. The form of the calculation employed here provides a lower bound for the expansion. If the number, n, of bonds in the polymers is held constant, expansion is found to decrease with increasing branch point functionality. Two factors dictate the manner in which finite stars approach the limiting behavior expected for very large stars. These two factors are the chain length dependence at small n of the characteristic ratio and of $(\alpha^5 - \alpha^3)/n^{1/2}$. In very good solvents these two factors reinforce one another, but they tend to cancel in solvents in which polymer expansion is small.

Rotational isomeric state theory permits construction of realistic models for polymer chains.[1] These models incorporate expected values for bond lengths, angles between bonds, and short-range contributions to energy barriers to rotation about bonds. Matrix methods provide the formalism required for rigorous evaluation of statistical mechanical averages of configuration-dependent physical properties for the unperturbed chain. Generator matrix calculations require negligible computer time even in the case of long chains. The theorem on direct products permits rigorous extension to branched polymers.[2-4] Unperturbed tri- and tetrafunctional polymethylene stars

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have been studied by using rotational isomeric state calculations, which retain a detailed treatment of the geometry and short-range interactions at the branch point.[5-8]

Matrix methods can be adapted so that they can be applied to simple linear chains, which are perturbed by the intramolecular excluded volume effect.[9] This approach retains bond lengths, angles between bonds, short-range interactions, and first-order a priori rotational state occupancy probabilities that are appropriate for the unperturbed chain. The perturbation is introduced through correlated alteration in a priori probabilities of higher order. Conceptually it would be desirable to design the perturbation so that there would be a small difference in its effects on j-order and $(j + 1)$-order probabilities. In principle (but not in practice), this objective could be obtained via an enormous expansion in dimensions of the statistical weight matrices. If emphasis is placed instead on properly correlated changes in certain second-order a priori probabilities, the perturbed chain can be handled with matrices of dimensions identical with those required for the unperturbed chain. Any limitations imposed by adoption of this enormous computational simplification can be brought out by comparing the behavior of expanded generator matrix chains with properties deduced by other methods, such as Monte Carlo studies of molecules in which chain atoms behave as hard spheres.[10,11]

A nonzero asymptotic limit at large n is achieved for $(\alpha^5 - \alpha^3)/n^{1/2}$, where n is the number of bonds and α^2 is the ratio of perturbed and unperturbed mean square radii of gyration. The model contains an adjustable parameter that can be related to the thermodynamics of polymer–solvent interaction. For polymethylene chains this parameter, K is

$$K = [10C_M\psi_1(1 - \Theta/T)M_0^{1/2}]^{2/5} \quad (1)$$

These results can be obtained with several variations of the basic model. The variations arise because the model can be parameterized so that the perturbation is felt uniformly throughout the chain, preferentially at chain ends, or preferentially in the middle of the chain.

Subsequent studies convincingly demonstrate that the basic model should be parameterized so that the perturbation is felt preferentially in the middle of the chain. Expansion of the rotational isomeric state chains then serves to enhance the asymmetry of individual configurations,[10] a result that is in harmony with that obtained in various other studies.[12-16] A perturbation felt preferentially in the middle of the chain is also supported by comparison of the behavior of subchains in the generator matrix calculations[11] and in Monte Carlo calculations in which interacting atoms behave as hard spheres.[11,17]

The simplest extension of the matrix treatment to perturbed stars is to treat each chain in the star in the manner appropriate for a linear chain containing the same number of bonds. This approach is likely to produce an underestimate of the total expansion of the star. It does, however, cause the perturbation to be felt preferentially at bonds near the branch point. Interest is in the behavior of α^2 and g as functions of n, K, and f. Here f denotes the functionality of the branch point and g is the ratio of mean square radii of gyration for unperturbed branched and linear chains containing the same number of bonds.[18] Geometry and short-range interactions at the branch point in polymethylene stars become somewhat arbitrary when f rises above four. Since this study includes stars of functionality as high as 20, detailed geometry and short-range interactions at the branch point are ignored. This approach has been shown to be appropriate when major interest is in stars of large n.[19,20]

Calculations

The rotational isomeric state model adopted for the unperturbed polymethylene chains is that described by Flory and co-workers.[21] The value of g for an f-functional star containing n bonds, or $n_b = n/f$ bonds per branch, was estimated as

$$g = [(f - 1)(2n_b + 1)^2C_{c,0} - (f - 2) \times (n_b + 1)^2C_{b,0}]/[(n + 1)^2C_{l,0}] \quad (2)$$

Here $C_{i,0}$ denotes the characteristic ratio, $\langle s^2\rangle_{i,0}/n_il^2$, where $\langle s^2\rangle_{i,0}$ is the mean square unperturbed radius of gyration and l is the bond length. For $C_{l,0}$ we have the linear chain in which n_b is n. By $C_{c,0}$ we mean the characteristic ratio for a main chain of $2n/f$ bonds within the branched molecule. Its mean square radius of gyration is calculated by using the matrix expression appropriate for a linear chain containing $2n/f$ bonds. The characteristic ratio of one of the branches containing n/f bonds is denoted by $C_{b,0}$. The pertinent mean square radius of gyration is that for a subchain of n/f bonds, located at one end of a main chain of $2n/f$ bonds. Expansion factors, α^2, were calculated as

$$\alpha^2 = [(f - 1)(2n_b + 1)^2C_c - (f - 2)(n_b + 1)^2C_b][(f - 1) \times (2n_b + 1)^2C_{c,0} - (f - 2)(n_b + 1)^2C_{b,0}] \quad (3)$$

where C_c and C_b are calculated in the same manner as $C_{c,0}$ and $C_{b,0}$ except that the configuration partition function used is that for the perturbed chain. The range for n_b was 20–10 240. Branch point functionalities were 3, 4, 6, 12, and 20.

The three $C_{i,0}$ can be evaluated for the unperturbed case[1,21] and the C_i for the perturbed case[9,16] by using matrix methods. The configuration partition function, Z, is

$$Z = \mathbf{J}^*\mathbf{U}_2\mathbf{U}_3...\mathbf{U}_{n-1}\mathbf{J} \quad (4)$$

where $\mathbf{J}^*$ = row (1, 0), $\mathbf{J}$ = col (1, 1), and the statistical weight matrix for bond i is

$$\mathrm{U}_i = \begin{bmatrix} \tau & 2\sigma \\ 1 & \sigma(\psi + \omega) \end{bmatrix}_i \quad (5)$$

The statistical weight for an isolated gauche placement relative to a trans placement is denoted by σ, and $\sigma^2\omega$ is the statistical weight for an isolated pair of consecutive gauche placements of opposite sign relative to a pair of trans placements. Calculations were performed with $\sigma = \exp(-E_\sigma/RT)$ and $\omega = \exp(-E_\omega/RT)$, with E_σ = 500 cal mol^{-1}, E_ω = 2000 cal mol^{-1}, and T = 300 K. All τ_i and ψ_i are unity for the unperturbed chain.[1,21] For perturbed chains,[9-11] bonds for which i lies in the range $2 < i < n$ have τ_i and ψ_i given by

$$\sigma\psi_i = \tau_i - \sigma\omega - 2(2p_t - 1)\{2\sigma[1 - (2p_t - 1)^2]\}^{1/2} \quad (6)$$

$$\tau_i = 1 + [1 - 0.36(n + 1 - 2i)^2(n - 3)^{-2}]Kn^{1/5} \quad (7)$$

where p_t is the a priori probability for a trans placement in a long unperturbed chain. The mean square radius of gyration for the subchain comprised of bonds indexed from $j - (i - 1)/2$ through $j + (i + 1)/2$ is

$$\langle s_{ij}^2\rangle = Z^{-1}(i + 1)^{-2}\mathbf{J}^*\mathbf{U}_2\mathbf{U}_3...\mathbf{U}_{j-(i+1)/2}\mathbf{G}_{j-(i-1)/2}...\mathbf{G}_{j+(i-1)/2}\mathbf{U}_{j+(i+1)/2}...\mathbf{U}_{n-1}\mathbf{J} \quad (8)$$

Here, $\mathbf{G}_i$ is the 14 × 14 generator matrix containing the bond length, bond angle supplement, dihedral angles for trans and gauche states, and elements of $\mathbf{U}_i$.[1] The unperturbed mean square radius of gyration is obtained when

Table I
Expansion (α^2) of f-Functional Stars Containing 30 000 Bonds

K	$f = 3$	$f = 4$	$f = 6$	$f = 12$	$f = 20$
0.1	1.16	1.14	1.13	1.10	1.08
0.2	1.46	1.42	1.39	1.31	1.27
0.3	1.80	1.74	1.67	1.56	1.48
0.5	2.52	2.41	2.30	2.09	1.94
1.0	4.37	4.15	3.91	3.48	3.18
2.0	8.10	7.64	7.17	6.29	5.66
3.0	11.82	11.13	10.41	9.07	8.10

all τ_i and ψ_i are unity, which is achieved when K is zero. Expanded chains are obtained when τ_i and ψ_i, $2 < i < n$, are given by eq 5 and 6, K being positive.[16] While the rotational isomeric state character of the chain is retained, no attention is given to the actual structure of the branch point itself.

Results and Discussion

Reduced Expansion of Stars of High Branch Point Functionality. In Table I are collected expansion factors as functions of f and K for stars containing 30 000 bonds. For a given value of the polymer–solvent interaction parameter, K, the expansion produced by the excluded volume effect becomes smaller with an increase in branch point functionality. A similar effect has been found with first-order perturbation theory[22] and observed with stars confined to lattices of various types.[23] With lattice stars, this effect was attributed to an expansion of the stars at the Θ condition. The stars therefore had less opportunity than a linear chain for further expansion in a good solvent. While the present study finds a qualitatively similar dependence of α^2 on f, the origin of this effect is different. With our generator matrix model, linear chains and stars have α^2 equal to unity when $K = 0$, which is the unperturbed state. When $K > 0$, expansion increases with decreasing f because subchain expansion increases with an increase in $2n_b = 2n/f$. At constant n, subchains contain fewer bonds as the functionality of the star increases. Since long subchains experience a greater expansion for a specified value of K, stars are found to be come more highly expanded as their functionality decreases. Essentially the same conclusion was reached in the study using perturbation theory.[22]

Solvent and n Dependence of the Expansion. The bulk of our results are presented in the manner used by Candau et al.[24] in their investigation of the expansion of branched macromolecules. They represent the branched polymer by a spherically symmetric, Gaussian distribution of chain segments. They obtain

$$(\alpha^8 - \alpha^6)g^3 = 2C_{M,l}(1 - \Theta/T)\alpha^3 M^{1/2} g^{3/2} + (2/3)C'_{M,l} \quad (9)$$

where the last term is negligible in a good solvent. If this term is neglected, and parameters employed in the generator matrix model are substituted, eq 9 becomes

$$(\alpha^8 - \alpha^6)g^3 = (1/5)n^{1/2}\alpha^3 g^{3/2} K^{5/2} \quad (10)$$

Equation 10 suggests data for expanded stars should describe a straight line if that data is depicted as $(\alpha^8 - \alpha^6)g^3$ vs. $n^{1/2}\alpha^3 g^{3/2} K^{5/2}$. The first six figures examine adherence to this expectation for expanded trifunctional rotational isomeric state stars. Figure 1 depicts data for highly expanded trifunctional stars containing a large number of bonds. When examined on the scale of Figure 1, data for $K = 2$ describe a straight line. Points obtained with $K = 3$ nearly described a straight line. The dotted straight line in Figure 1 is drawn through the four points for $K = 2$ and the last two points for $K = 3$. Comparison with this line reveals that data depicted for $K = 3$ actually describe a sigmoid curve.

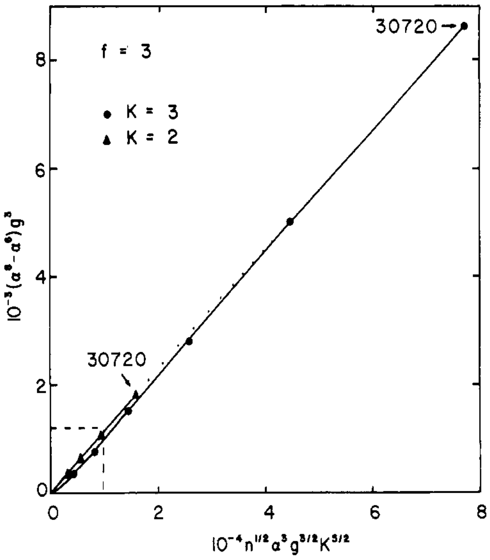

Figure 1. Perturbed trifunctional polymethylene stars in media where K is 2 or 3. Arrows denote points for the largest stars, which contain 30 720 bonds. Upon moving toward the origin, points describe stars in which the number of bonds falls successively by a factor of 2. The dotted straight line is an extension of the line through the triangular points to the last point depicted by a filled circle. The rectangle outlined by the dashed line near the origin denotes the part of this figure that is presented in expanded form as Figure 2.

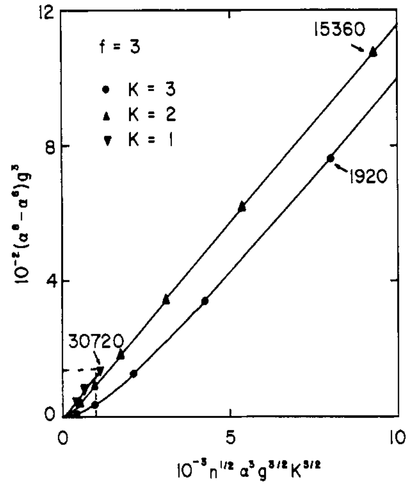

Figure 2. Expansion of that portion of Figure 1 near the origin. The number of bonds in the largest star for each value of K is indicated on the figure. The portion of the figure outlined by the rectangle near the origin is shown in expanded form in Figure 3.

That portion of Figure 1 that lies near the origin is depicted in greater detail in Figure 2. Curvature in the data obtained with $K = 3$ becomes readily apparent in Figure 2. It becomes especially marked when the number of bonds in the trifunctional star falls below 10^3. Data depicted for $K = 2$ in Figure 2 appear to describe a straight line, with a hint of curvature near the origin. The points depicted for $K = 1$ also describe a straight line. Many of the qualitative changes seen upon going from Figure 1 to Figure 2 are also evident as attention is directed to behavior closer and closer to the origin (Figures 3–6). For each K examined, the behavior is nearly linear if the number of bonds is on the order of 10^4, but curvature becomes readily apparent when the number of bonds falls to 10^3.

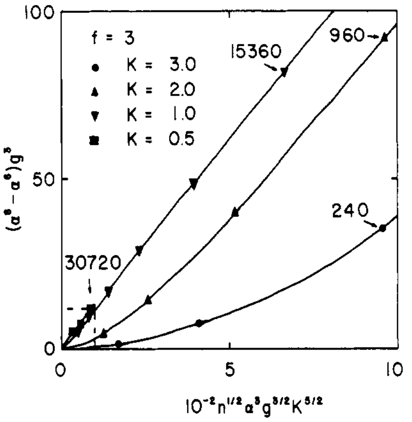

Figure 3. Expansion of that portion of Figure 2 near the origin. The number of bonds in the largest star for each value of K is indicated on the figure. The portion of the figure outlined by the rectangle near the origin is shown in expanded form in Figure 4.

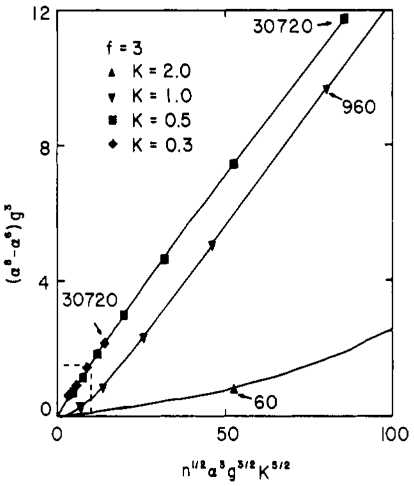

Figure 4. Expansion of that portion of Figure 3 near the origin. The number of bonds in the largest star for each value of K is indicated on the figure. The portion of the figure outlined by the rectangle near the origin is shown in expanded form in Figure 5.

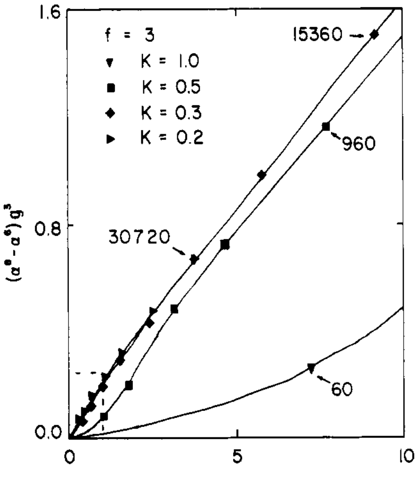

Figure 5. Expansion of that portion of Figure 4 near the origin. The number of bonds in the largest star for each value of K is indicated on the figure. The portion of the figure outlined by the rectangle near the origin is shown in expanded form in Figure 6.

Similar trends are seen with perturbed polymethylene stars of higher functionality, as is shown in Figure 7 for

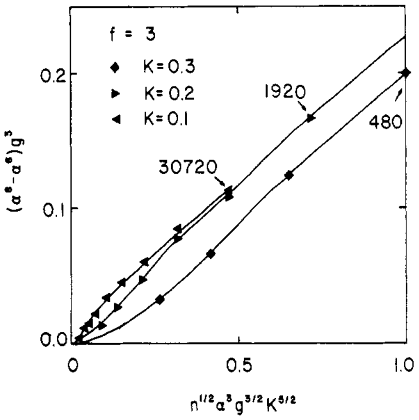

Figure 6. Expansion of that portion of Figure 5 near the origin. The number of bonds in the largest star for each value of K is indicated on the figure.

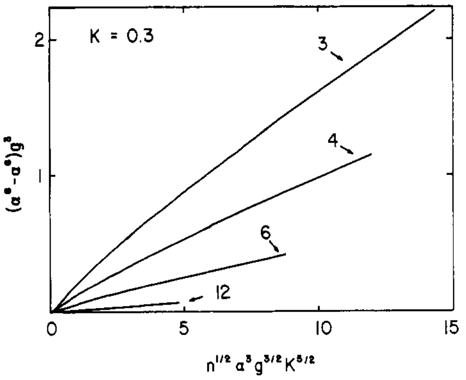

Figure 7. Perturbed polymethylene stars of the indicated functionality in media where K is 0.3. Each curve terminates when the number of bonds in the star is $10240/f$.

$K = 0.3$. While linear behavior is approached by the largest stars, curvature is readily apparent near the origin. Data depicted in Figure 7 were presented incorrectly in the preprint.[19]

Before advancing an explanation for the behavior seen in Figures 1–6, it is useful to briefly review several properties of linear rotational isomeric state polymethylene chains. While unperturbed polymethylene chains reach an asymptotic limit at large n for $\langle s^2\rangle_0/nl^2$, finite chains have a smaller value for this ratio.[21] Departure from the asymptotic limit is apparent for chains containing as many as 1000 bonds. Perturbed rotational isomeric state chains have a nonzero asymptotic limit for $(\alpha^5-\alpha^3)/n^{1/2}$ at infinitely large n.[9] However, the nature of the approach to the asymptotic limit depends on the size of the perturbation. If K is as large as 3, $(\alpha^5-\alpha^3)/n^{1/2}$ continuously increases upon the approach to the asymptotic limit.[9] Finite chains therefore experience a smaller expansion than that predicted from the limiting value for $(\alpha^5-\alpha^3)/n^{1/2}$. Different behavior is seen when K is small. There is still a nonzero asymptotic limit for $(\alpha^5-\alpha^3)/n^{1/2}$, but now this quantity passes through a maximum as one proceeds through finite chains to infinite chains. This maximum occurs when the number of bonds is on the order of 10^3 if K is 0.53.[10] The maximum is more pronounced at smaller K. Certain polymer–solvent systems such as polyisobutylene in diisobutylene at 20 °C or in cyclohexane at 30 °C[25] are known to experience a maximum in $(\alpha^5-\alpha^3)/n^{1/2}$ at finite n.

We now return to the behavior of expanded stars. Attention is first restricted to those stars in which subchains contain enough bonds so that a linear chain with the same n is essentially at the asymptotic limit for $(\alpha^5-\alpha^3)/n^{1/2}$.

A straight line might then be expected when the data are plotted in the manner of Figures 1–6. This expectation is borne out by the data in these figures.

Now consider the behavior as one examines stars of successively smaller n. First consider the consequences of the actual behavior of the unperturbed chain. As the number of bonds falls below 10^3, $\langle s^2\rangle_0/nl^2$ for an unperturbed linear chain falls significantly below the value characteristic of infinite chains. Since the longest subchain in a star contains only $2n/f$ bonds, while the linear chain considered in evaluation of g contains n bonds, one then expects, and finds,[19,20] that g falls below its asymptotic limit. As a consequence, data for small stars in Figures 1–6 would be expected to lie below the extrapolation of the data obtained with large stars.

The effect described above can be greatly exaggerated by the manner in which expansion occurs in finite chains. At large K, $(\alpha^5 - \alpha^3)n^{1/2}$ for short chains is much smaller than the value that obtains for infinitely long chains. Consequently, small stars will experience a smaller expansion than would have been expected from the behavior of infinitely large stars. Since α^2 will therefore decline more rapidly as n decreases, there will be an exaggeration of the tendency for points in Figures 1–6 to fall below the extrapolation of the behavior of large perturbed stars. For linear perturbed chains, $(\alpha^5 - \alpha^3)/n^{1/2}$ depends more strongly on n as K increases from 1 to 3.[9] Consequently, the curvature at small n for stars in Figures 1–6 would be expected to be most pronounced at the highest K. This behavior is in fact observed. It is well illustrated by the stars with $n = 240$ in media where K is 2 and 3 (Figure 3).

At small K, $(\alpha^5 - \alpha^3)/n^{1/2}$ for perturbed linear chains passes through a maximum as one proceeds from finite to infinite chains. When such K are used, certain finite stars will experience a larger expansion than that expected based on the behavior of infinite stars. When data are then plotted as in Figures 1–6, the increment for α^2 for these finite stars may oppose the effect of the decline in g. If perfect cancellation were to occur, linear behavior could be expected down to extremely small n. In the event that the increment in α^2 were to outweigh the decline in g, one might even find points for finite stars that were higher than those predicted by the behavior of infinitely larger stars. There may be an approach to this latter type of behavior in the curve with $K = 0.1$ in Figure 6.

Equations 9 and 10 provided the motivation for plotting the data for perturbed trifunctional stars in the manner shown in Figures 1–6. Both equations predicted observation of a straight line, but they differ with regard to the presence or absence of a nonzero intercept. Figures 1–6 demonstrate that all lines become curved sufficiently close to the origin. However, if attention is restricted to the larger stars, those for which $n > 1920$, a reasonable approximation to a straight line is seen. In very good solvents, e.g., $K = 3$ (Figure 1), this straight line can be extrapolated to an intercept that is not readily distinguishable from zero. A different result is obtained in marginally good solvents. For the case where $K = 0.1$ (Figure 6), linear extrapolation of the best straight line through the four points for $n > 1920$ yields a positive intercept on the $(\alpha^8 - \alpha^6)g^3$ axis. If this positive intercept were interpreted according to eq 9, $C'_{M,l}$ would be assigned a positive value, which would signify that the star is expanded at $T = \Theta$. However, the simple model employed here yields no expansion whatsoever at the Θ temperature. The origin of the positive intercept obtained by linear extrapolation of the points for $n > 1920$ with $K = 0.1$ can be traced to the fact that $(\alpha^5 - \alpha^3)/n^{1/2}$ passes through a maximum as one proceeds from finite to infinite linear chains.

The present generator matrix model for perturbed stars results from the simplest imaginable extension of methodology used for perturbed linear polymethylene chains. Refinements can be guided by results of Monte Carlo calculations performed on stars in which interacting atoms behave as impenetrable spheres.

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