Configurational Properties of Star-Branched Polymers

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ABSTRACT: Mean-square radii of gyration were computed for star-branched polymers simulated by a lattice model that incorporated both excluded volume and attractive energies between nonbonded segments of the polymer. The ratios, g, of the radius of gyration of a star polymer to that of a linear polymer of the same molecular weight were 6 to 15% (for star polymers of 3 to 9 branches) greater at the theta point than the corresponding ratios calculated by the unrestricted random-walk model of the polymer. The g ratios were smaller in good solvents than in theta solvents. The expansion factors, the ratios of the radius of gyration of a molecule in a good solvent to its radius of gyration in a theta solvent, were also calculated. The expansion factor decreased with the degree of branching, which is at variance with perturbation theory applied to the random walk model of star-branched polymers.

The most common method[1] of determining the degree of branching of a branched polymer involves the mean-square radius of gyration, $\langle s^2\rangle_b$, of the polymer in solution, which will be called simply the squared radius of the molecule in this paper. The squared radius $\langle s^2\rangle_b$ is either measured by light scattering or inferred from measurements of the limiting viscosity numbers of solutions of the polymer. The ratio

$$g = \langle s^2\rangle_b/\langle s^2\rangle_l \qquad (1)$$

is then calculated, where $\langle s^2\rangle_l$ is the squared radius of a linear polymer of the same molecular weight. For an assumed type of branching (e.g. star, comb, or random), the number of branches per molecule is then computed according to the theory of Zimm and Stockmayer.[2] However, the theory of Zimm and Stockmayer is based on the random walk model of the polymer, which does not allow for the excluded volume effects of a real molecule.

For linear polymers dissolved in poor solvents, a theta temperature[3] exists at which the swelling of the molecule due to excluded volume is compensated by the contraction due to attractive forces between the nonbonded segments of the molecule so that the properties of the polymer are the same as those of a random walk. Calculations based on a random walk model are customarily applied to solutions of real polymers at the theta temperature. However, volume exclusion may affect the dimensions of branched polymer differently than the dimensions of linear polymer, so that, even at the theta temperature, the Zimm–Stockmayer theory may not apply to real polymer solutions. Certainly, it would not be expected to apply at temperatures other than the theta temperature.

The definition of the theta temperature is ambiguous because it depends on the property of the polymer that is required to have the same value as the equivalent random walk model of the polymer. The definition of the theta temperature which is employed in this paper is based on the observation that the squared radius of a star-branched polymer is given by a simple exponential law,

$$\langle s^2\rangle_b = BN^\gamma$$

provided that N, the number of segments in the polymer, is sufficiently large. The theta temperature is defined as the temperature at which $\gamma = 1$, its value for the random walk model.

The relationship between g and the degree of branching is computed in this paper for a model of a polymer that is physically more realistic than the random walk model. This model incorporates both the hard-core repulsive energy exemplified by the excluded volume and the attractive energy between the nonbonded segments of the polymers. Only star-branched polymers with equal-length branches will be treated here. For these polymers, the Zimm–Stockmayer theory[2] leads to the following relation between the g ratio and f, the number of branches in the star:

$$g = (3f - 2)/f^2 \qquad (2)$$

The polymers were simulated by non-self-intersecting random walks on the simple-cubic and face-centered cubic lattice by the method of Rosenbluth and Rosenbluth.[4] Stars of three, four, and six branches connected at a single point were generated on the simple cubic lattice and stars of four, six, eight, and nine branches connected at a single point were generated on the face-centered cubic lattice. In addition, eight-branch stars were generated on the simple cubic lattice with four branches emanating from both ends of the single segment.

Two nonbonded segments of a walk separated by a distance equal to one lattice spacing were said to form a contact in the walk. Many walks simulating a star-branched polymer molecule were generated. The squared radius, s^2, the squared dimension of a single branch, r^2, and the number of contacts, n, in each walk were calculated. The walks simulated a configuration of star-branched polymer with attractive energy between nonbonded segments. The energy between segments was assumed to be ϵ for segments forming a contact, i.e., separated by one lattice distance, and to be zero for segments separated by more than one lattice distance. The internal energy of a single configuration is therefore $n\epsilon$ and its Boltzmann factor is $\exp(n/\phi)$ where

$$\phi = -\epsilon/kT \qquad (3)$$

k is the Boltzmann's constant and T is the temperature. The mean squared radius of the molecule is then estimated for various values of ϕ by averaging the squared radii of the calculated configurations weighted by their Boltzmann factors, that is,

$$\langle s^2\rangle_b = \sum_i s^2{}_i \exp(n_i\phi) \Big/ \sum_i \exp(n_i\phi) \qquad (4)$$

where i is the number of the configuration. The mean fourth power of the radius, $\langle s^4\rangle$, and the mean end-to-end distance of a single branch, $\langle r^2\rangle$, of star-branched molecules were also computed. All results with a relative error greater than 5% were rejected.

The squared radii and other properties of linear chains have been previously calculated by the same Monte-Carlo method[5,6] employed in this paper, where the computational details and analysis of error have been given.

In this paper, the dependence of the squared radii on the number of segments, N, the interaction parameter, ϕ, and the number of branches of the star molecule is studied. The ratio g, eq 1, is calculated and compared with g ratios calculated by

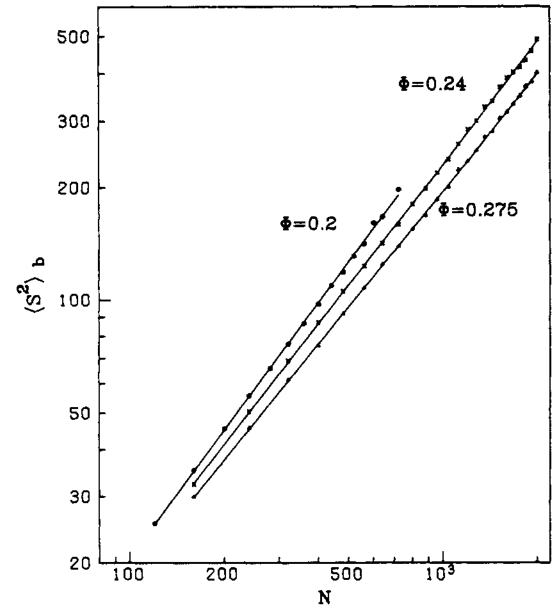

Figure 1. Squared radius, $\langle s^2 \rangle_b$, vs. chain length, N, for four-branch stars on the simple cubic lattice for ϕ = 0.20, 0.24, and 0.275. The points are fitted by straight lines.

the Zimm–Stockmayer theory, eq 2. The expansion factors of the stars are computed and compared with the expansion factors calculated by analytical theories based on the unrestricted random walk model of the star polymers. Finally, the mean-square end-to-end distances of a single branch and the mean fourth power of the radius are computed. While these last two quantities are not directly related to experimental measurements, they nevertheless lead to a better understanding of the conformation of star-branched polymers.

Variation of Squared Radius with Number of Segments. Figure 1 shows $\langle s^2 \rangle_b$ vs. the total number of segments, N, in the star molecule on a log–log scale for four-branch stars generated on the simple cubic lattice for values of ϕ from 0.2 to 0.275. The values of $\langle s^2 \rangle_b$ are seen to lie on straight lines for large numbers of segments in the star. Similar curves were obtained for stars from three to nine branches generated on the simple and face-centered lattices. Thus, the squared radii of stars for large N can be given by the relationship

$$\langle s^2 \rangle_b = BN^\gamma \tag{5}$$

which was previously found[5] to hold in the case of linear chains. The value of B of eq 5 depends on ϕ and the degree of branching.

For linear chains, values of γ for various lattices have been shown to be represented[5] by a single master curve by plotting γ vs. $\sigma\phi$, where σ is one less than the coordination number of the lattice, i.e., σ = 5 and 11 for the simple and face-centered cubic lattices, respectively. The master curve for γ vs. $\sigma\phi$ for linear chains given in Figure 17 of ref 5 is reproduced in Figure 2 by a solid line. In Figure 2 the values of γ for star-branched molecules with three, four, six, and eight branches on the simple cubic lattice are shown by the filled symbols and for three, four, and six branches on the face-centered cubic lattice are shown by open symbols. All the symbols are seen to fall on the master curve for linear chains within their expected scatter for values of $\sigma\phi$ in the range of 1 to 1.4. Thus, to a reasonable approximation, a single curve can give values of γ as a function of $\sigma\phi$ for both linear and star-branched molecules on simple and on face-centered cubic lattices and presumably on other lattices as well.

In particular, the theta point, defined here as the point for which γ = 1, is seen in Figure 2 to be given by $\sigma\phi$ = 1.375 for both the linear and branched polymers, which is the value reported in ref 5. Therefore, the theta points of linear and star-branched molecules of up to eight branches are approximately the same.

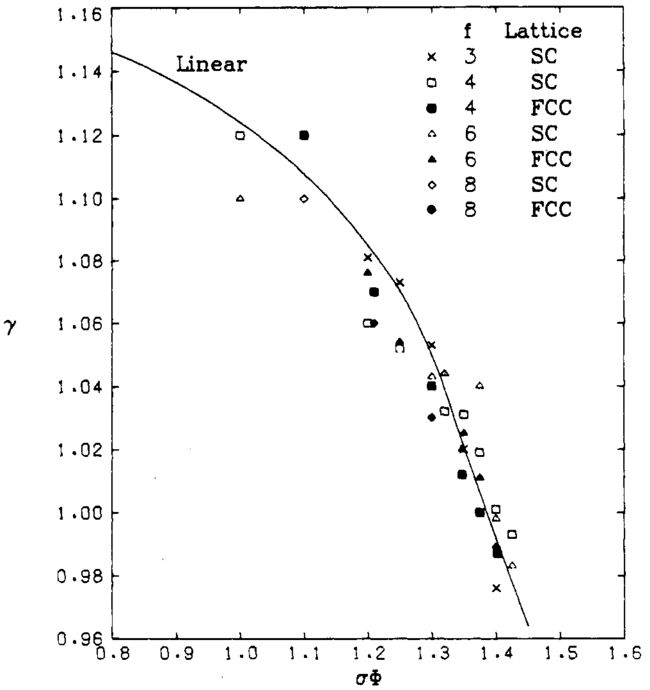

Figure 2. The values of γ for star molecules with three, four, six, and eight branches on the simple and face-centered cubic lattices vs. $\sigma\phi$. The values of γ for linear molecules from Figure 17 of ref 5 are given by the solid curve.

Candau et al.[7] found that in the case of polystyrene in cyclohexane the theta temperature θ_α and θ_{A_2}, defined as the temperatures at which α = 1 and the second virial coefficients are zero, respectively, were lower for star-branched than for linear polymer. However, the differences in theta temperatures were small: less than 1% for stars of 4 to 8.7 branches to 3.6% for stars of up to 15.5 branches.

Zilliox[8] likewise found that θ_{A_2} was lower for star-branched than for linear polystyrene in cyclohexane. He also found that the differences in theta temperatures decrease with increasing molecular weight of the polymer. However, these differences are less than the accuracy inherent in our determination of the theta point by Monte-Carlo calculations (see Figure 2). Thus, the present calculations of the dependence of the theta point on branching are not in disagreement with those of Candau et al.[7] and Zilliox.[8]

Ratio of Squared Radii. The squared radii of both branched and linear chains for a given value of $\sigma\phi$ and large values of N are given by an equation of the form of eq 5 with the same value of γ. Their ratio g, defined by eq 1, is therefore expected to be independent of N for large values of N. The g ratios are shown in Figures 3 to 5 for values of ϕ of 0, 0.2, and 0.275 for the simple cubic lattice. These ratios are plotted vs. N^{-1} to facilitate extrapolation to determine their limiting value for infinite N. Data are shown for three-, four-, six-, and eight-branch stars on the simple cubic lattice. For ϕ = 0 in Figure 3, the lines show considerable curvature at large values of N, so they were not extrapolated to infinite chains. Because the values of g for large N and low ϕ are the least accurate, it is uncertain if the curvature of the curves in Figure 3 is real. However, for the values of ϕ near the theta point value of 0.275, shown in Figures 4 and 5, the g ratios vary very slightly with N so that the limiting values of g are accurately determined. While there is always a risk in extrapolation to infinite

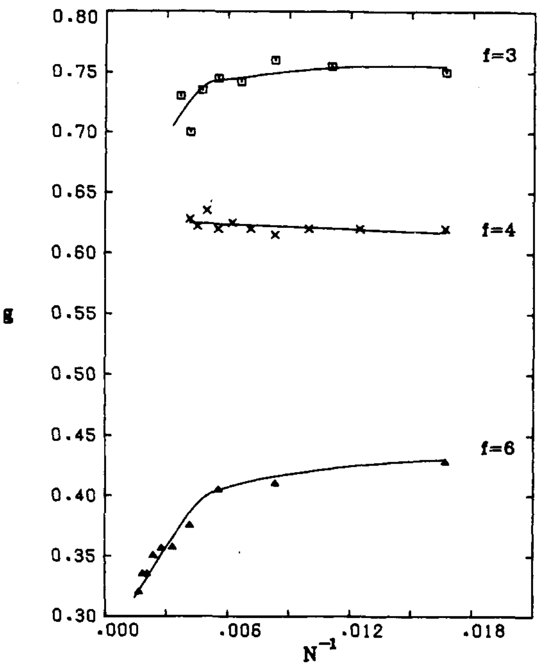

Figure 3. The g ratios for three-, four-, and six-branch star molecules on the simple cubic lattice vs. N^{-1} for $\phi = 0$. Because the curves show curvature for large values of N, they cannot be extrapolated to infinite N.

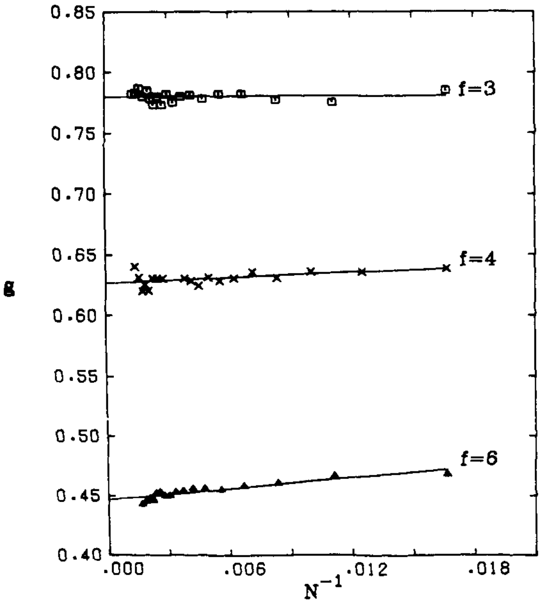

Figure 4. The g ratios for three-, four-, and six-branch star molecules on the simple cubic lattice vs. N^{-1} for $\phi = 0.2$. The ratios are extrapolated to infinite N ($N^{-1} = 0$).

chain length, the possibility of a break in the curves in Figures 4 and 5 for large values of N seems unlikely. Values of g were also calculated and extrapolated to infinite N ($N^{-1} = 0$) for $\phi = 0.24$, 0.25, and 0.26 for three-, four-, six-, and eight-branch stars on the simple cubic lattice and for four-, six-, eight-, and nine-branch stars for a range of ϕ values on the face-centered cubic lattice. Figure 6 shows the limiting values of g for infinite chains vs. $\sigma\phi$. By employing the variable $\sigma\phi$ instead of ϕ, it is seen that the curves of g for star molecules for each value of f, determined in different lattices, may be represented by a single curve. Therefore, the curves in Figure 6 are independent of the lattice.

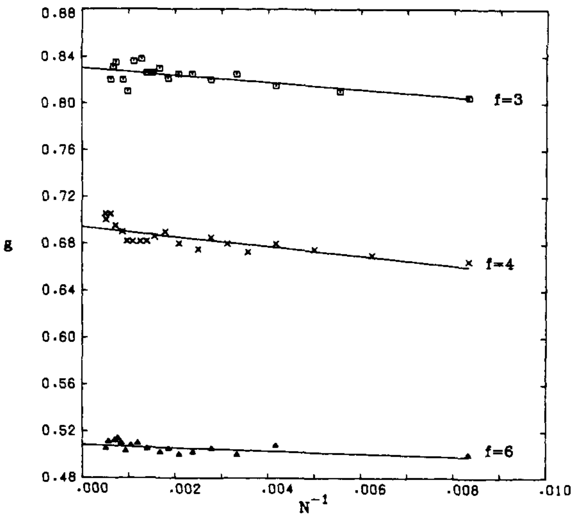

Figure 5. The g ratios for three-, four-, and six-branch star molecules on the simple cubic lattice vs. N^{-1} at the theta point ($\phi = 0.275$). The ratios are extrapolated to infinite N.

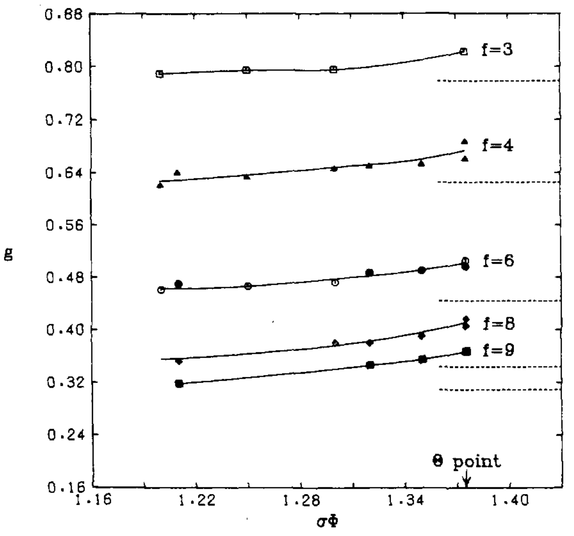

Figure 6. The g ratios extrapolated to infinite N for three-, four-, six-, eight-, and nine-branch star molecules vs. $\sigma\phi$ on both the simple and face-centered cubic lattices. The filled symbols are for the face-centered cubic lattice and the open symbols are for the simple cubic lattice. The g ratios for random-walk star molecules (eq 2) are shown by dashed lines for, from top to bottom, three-, four-, six-, eight-, and nine-branch stars. The value of $\sigma\phi$ at the theta point is indicated.

The g values for the random walk model of the polymer calculated from eq 2 are shown by dotted lines for three-, four-, six-, eight-, and nine-branched stars in Figure 6. As previously mentioned, the random walk model values of g are expected to agree with our values of g at the theta point, which occurs at $\sigma\phi = 1.375$. However, our g values at the theta point are seen in Figure 6 to be larger than the random walk values for all the star molecules. Our g values at the theta point are 6% greater than the random walk values for three-branch star molecules. This deviation from the random walk values increases with increasing number of branches. For a nine-branch star molecule this increase amounts to 15%.

Expansion Factors. The squared radius $\langle s^2\rangle_\phi$ of a polymer for a value of ϕ less than its theta value, i.e., in a good solvent, is greater than the squared radius, $\langle s^2\rangle_\theta$, of the polymer in a theta solvent. Their ratio

$$\alpha^2 = \langle s^2\rangle_\phi / \langle s^2\rangle_\theta \qquad (6)$$

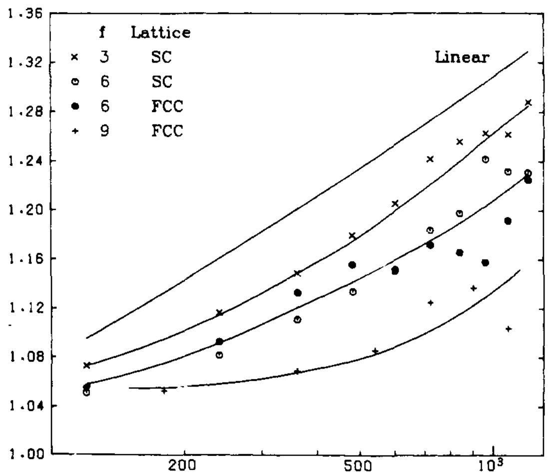

Figure 7. The expansion factors for $\sigma\phi$ = 1.20 of linear and star molecules with number of branches, f, of three, six, and nine on the simple cubic (SC) and face-centered cubic (FCC) lattices.

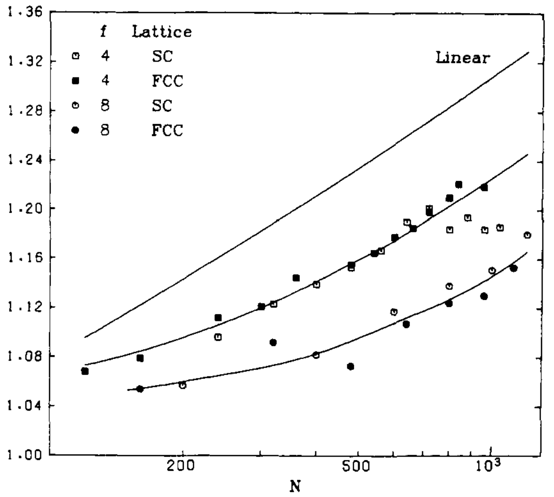

Figure 8. The expansion factors for $\sigma\phi$ = 1.2 of linear and star molecules with four and eight branches.

measures the expansion of the polymer in good solvent and is called the expansion factor of the polymer.

The expansion factors for star molecules for $\sigma\phi$ = 1.20 are plotted in Figures 7 and 8 vs. the number, N, of segments in the molecules. The expansion factors for star molecules of three, six, and nine branches are shown in Figure 7, and for star molecules of four and eight branches are shown in Figure 8. Also, the expansion factors for linear molecules on both the simple and face-centered cubic lattices were recomputed from the results given in Tables I and II of ref 5 for $\sigma\phi$ = 1.20. The same values for the expansion factors were obtained for molecules on both lattices and are shown by the curves labeled "linear" on Figures 7 and 8.

The expansion factors in good solvents (characterized by low values of $\sigma\phi$) are shown in Figure 9 ($\sigma\phi$ = 1.1) and in Figure 10 ($\sigma\phi$ = 0).

The expansion factor is seen from Figures 7 to 10 to be less for star molecules than for linear molecules and to decrease with increasing f, the number of branches in the star. The expansion factor for the same values of f, $\sigma\phi$, and N is also seen to be independent of the lattice. Also, the expansion factor is seen to increase as $\sigma\phi$ decreases, i.e., as the attractive energy between segments of the molecule decreases.

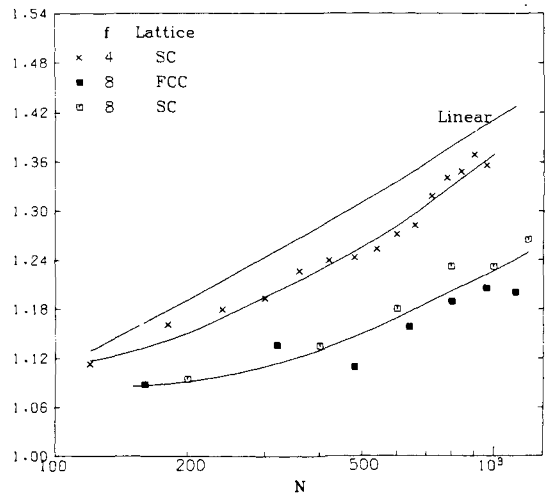

Figure 9. The expansion factors for $\sigma\phi$ = 1.1 of linear and star molecules with four and eight branches.

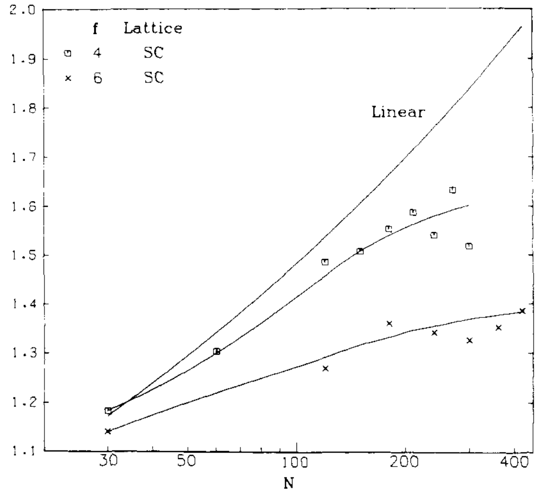

Figure 10. The expansion factors for $\sigma\phi$ = 0 (no attractive energies between segments) of linear and star molecules with four and six branches.

Table I
Effect of Volume Exclusion and Number of Branches, f, on $\langle r^2 \rangle$ of Branches of Star Molecules at the Theta Point ($\langle r^2 \rangle = AN$)

	Lattice	
	Simple cubic A	Face-centered cubic A
Linear (ref)	1.69	1.4
$f = 3$	1.75	
$f = 4$	1.82	1.45
$f = 6$	1.90	
$f = 8$	1.93	1.56

Mean-Square End-to-End Distances of Branches. The mean-square end-to-end distance of a single branch of a star, $\langle r^2 \rangle$, that is, the mean-square distance from the center of a star to the end of a branch, was also calculated. The values of $\langle r^2 \rangle$ at the theta point for large values of N fit the equation

$$\langle r^2 \rangle = AN \tag{7}$$

The fitted values of A are shown in Table I for the simple and face-centered cubic lattices and compared with $\langle r^2 \rangle$ for a linear chain at the theta temperature. The value of A is seen

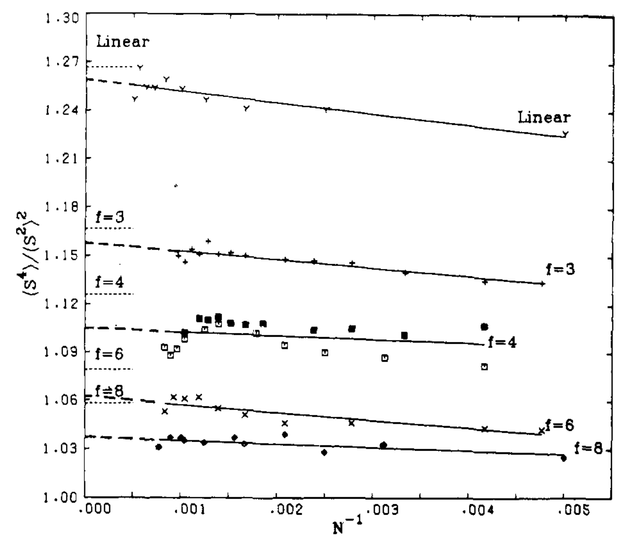

Figure 11. Fourth reduced moments of linear and of star molecules of three to eight branches at the theta condition. The reduced moments for unrestricted random walk stars of infinite length are shown by dotted lines. The fourth reduced moments of linear chains are taken from ref 5. All points are for molecules on the simple cubic lattice except for the filled squares and diamonds which are for molecules on the face-centered cubic lattice.

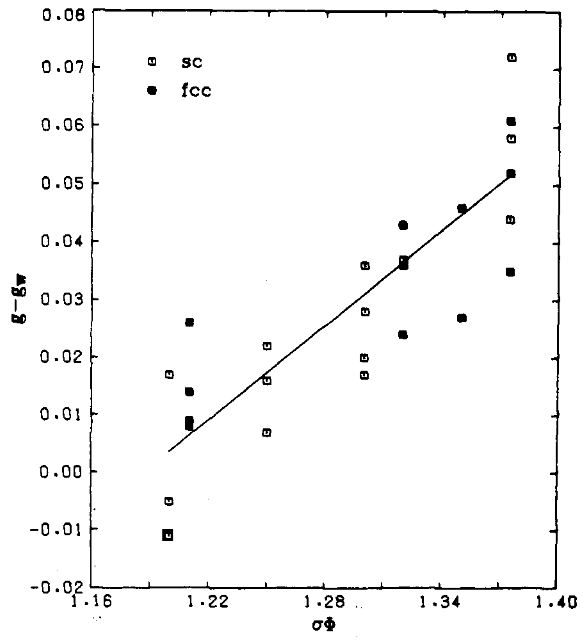

Figure 12. The g ratio for star molecules of three to nine branches minus their g ratio for the random walk model vs. $\sigma\phi$. The difference is shown for star molecules on both the simple cubic (SC) and face-centered cubic (FCC) lattices.

to increase with the number of branches in the star, indicating that the chains become more extended as the number of branches in a star increases.

Induction Length. As previously mentioned the radius of a linear or of a branched chain varies with the number of segments in the chain according to eq 5 for sufficiently large values of N but deviates from eq 5 for small values of N. We define the induction length as the smallest value of N for which $\langle s^2\rangle$ is given by eq 5 to within a relative error of about 5%. In ref 5, the induction length for linear chains may be seen from the figures to be less than 10 for $\phi = 0$ but to increase with ϕ to the order of 100 for ϕ equal to its theta value. Similar induction effects for the mean-square end-to-end distances of linear chains were also observed (see p 656 of ref 6).

However, for branched molecules, the opposite behavior of the induction length with ϕ was observed, i.e., the induction length is large for $\phi = 0$ and greatly decreases as ϕ approaches its theta value.

Reduced Moments. The fourth reduced moments, $\langle s^4\rangle/\langle s^2\rangle^2$, of the radius measure the sharpness of the distribution of the radii of the molecules. Figure 11 shows the calculated fourth reduced moments for star molecules of three, four, six, and eight branches at theta condition ($\sigma\phi = 1.375$) on the simple cubic and face-centered cubic lattices. The reduced moments are seen to be independent of the lattice. The fourth reduced moments for linear chains on the simple cubic lattice (from ref 5) are also shown. The curves are extrapolated to infinite chain lengths ($N^{-1} = 0$).

An expression for the fourth reduced moment for stars of f branches consisting of infinitely long unrestricted random walks can be obtained from eq 18 given by Šolc.[9] It is given below by eq 8

$$\frac{\langle s^4\rangle}{\langle s^2\rangle^2} = \frac{135 - 120/f + 4/f^2}{15(3 - 2/f)^2} \qquad (8)$$

Reduced moments for random linear chains ($f = 1$ or 2), and for stars of three, four, six, and eight branches were calculated by eq 8 and are shown by dashed lines on Figure 11. The reduced moments of linear molecules and three-branch stars at the theta point extrapolated to infinite chain length are close to the corresponding values of the unrestricted random walks. However, the reduced moments of four-, six-, and eight-branch stars at the theta point extrapolated to infinite chain lengths are smaller than the corresponding values of the unrestricted random walks.

The fourth reduced moment of the radius of star molecules of infinite length at the theta point is seen by both our Monte-Carlo calculations and the random walk calculations of Šolc[9] to be less than that of a linear molecule and to decrease with increased branching. Therefore, the distribution of the radii of star molecules at the theta point is sharper than that of linear molecules, and the sharpness increases with increasing degree of branching. This is in agreement with the theory of Šolc according to which all reduced moments approach unity for infinite f, so that the distribution of the reduced radii of star molecules approaches a delta function as the number of branches in the star molecules approaches infinity.

Discussion

***g* Ratios.** The g ratios calculated by our lattice model have been compared with the g ratios calculated by the random walk model of the star molecule (Figure 6). Another way of representing the g ratios is shown in Figure 12, where the differences between the g ratios calculated by our lattice model and by the random walk model are plotted vs. $\sigma\phi$. Although this method of plotting emphasizes the scatter of the points, it shows that the difference between the g values for a given value of $\sigma\phi$ is approximately independent of both the lattice and number of branches in a star molecule. Therefore, using eq 2, the g ratios may be represented as

$$g = (3f - 2)/f^2 + C \qquad (9)$$

for $f \leq 9$, $C = 0.05$ at the theta point, and it decreases with decreasing values of $\sigma\phi$, corresponding to solution in good solvents.

Expansion Factor. The expansion factor has been found to be smaller for star-branched molecules than for linear molecules of the same molecular weight and to decrease with an increasing number of branches in the molecule. This agrees with measurements of the expansion factor of four- and six-branch stars of polystyrene reported by Meunier and Leemput.[10] Berry[14] measured the expansion factor of a six-branch star polymer and found it to be greater than the expansion factor of a linear molecule at "equivalent thermodynamic conditions",[14] while Zilliox[8] found it to be the same. However, they did not compare the expansion factors at equal molecular weight and temperature, so their results are not directly comparable with ours.

Further evidence that the expansion factors of star-branched molecules are less than that of linear molecules is given by intrinsic viscosity measurements. Roovers and Bywater[11] and Hadjichristidis and Roovers[11] and others measured

$$g' = [\eta]_b/[\eta]_l \tag{10}$$

where g' is the ratio of the intrinsic viscosities of star-branched to linear molecules for four- and six-branch stars. They found it to be greater at the theta solvent than in a good solvent, i.e.,

$$g_\theta' > g_\phi' \tag{11}$$

where the subscripts θ and ϕ refer to a theta solvent and a good solvent.

The g' ratio has been related to the g ratio by Zimm and Stockmayer,[2] Zimm and Kilb,[12] and Stockmayer and Fixman.[13] While they predict different relationships between g' and g, they all predict that g increases as g' increases. Therefore, from eq 11, we have

$$g_\theta \geq g_\phi \tag{12}$$

An inequality of expansion factors is obtained from eq 12. Substituting for g by eq 1 and rearrangement gives

$$\frac{\langle s^2\rangle_{l\phi}}{\langle s^2\rangle_{l\theta}} > \frac{\langle s^2\rangle_{b\phi}}{\langle s^2\rangle_{b\theta}} \tag{13}$$

By eq 6,

$$\alpha^2{}_l > \alpha^2{}_b \tag{14}$$

so the expansion factors of star-branched molecules will be less than those of linear molecules in agreement with our findings. The evidence for eq 14 must be considered indirect due to the uncertainty in the relationship of g to g'.

This behavior of the expansion factor may be intuitively understood by comparing the configurations of a star-branched and linear molecule in a theta and in a good solvent. In the theta solvent, each branch of the star-branched molecule will have an extended configuration as compared to the linear molecule, as exemplified by the mean-square end-to-end distances of a branch, shown in Table I. If the star-branched and linear molecules are placed in a good solvent, they will both expand to more extended configurations. However, because the star-branched molecule has already been partially extended in the theta solvent, its expansion, when placed in a good solvent, is less than the expansion of the linear molecule. Thus, the expansion factors of star-branched molecules are expected to be less than the expansion factors of linear molecules, in agreement with our results.

Analytical theories of the expansion factors of linear and star molecules have been developed, among others, by Stockmayer and Fixman,[13] Berry,[14] Ptitsyn,[15] and Casassa.[16] These theories represent the polymer at the theta condition by an unrestricted random walk, that is, by a walk without long-range interactions such as excluded volume effects or attractive energies between nonbonded segments. In these theories, the repulsive energies between segments are introduced as a perturbation to the random walk to represent the polymer in a good solvent. These theories predict that the expansion factor of a star-branched molecule is greater than that of a linear molecule and that it increases with an increase in the number of branches. This is opposite to the behavior predicted by our calculations, namely that the expansion factor of a star-branched molecule is less than that of a linear molecular and that it decreases with the increase in the number of branches. We believe that the reason for this disagreement between the analytical theories and our calculations is that the random walk is not an adequate approximation for the branched molecules at the theta condition. The failure of the random walk model to represent star molecules at the theta condition is shown in Table I. By the random walk model, the mean-square end-to-end distance $\langle r^2\rangle$ of a single branch of a star molecule should be independent of the number of branches in a star. However, Table I shows that $\langle r^2\rangle$ increases with the number of branches in the star molecule.

Comparison of Real Polymers and Random Lattice Walks. The results in this paper are based on molecules constrained to a lattice. Can the results be applied to real star-branched polymer in solution? First, distances between segments of the molecules are limited to the discrete distances between lattice points while distances between segments in a real polymer may vary continuously, giving rise to a "granularity" for the results for a short molecule simulated on a lattice. However, in the case of the long molecules which are investigated in this paper, we believe that this "granularity" effect is negligible. Second, the short-range structure of lattice molecules is different from that of real polymers because the angles between segments of lattice molecules are arbitrarily taken to conform to the lattice and are not equal to the angles between segments of real polymers. However, the g value is the ratio of branched to linear chains of polymers having the same short-range structure so it is expected to be independent of the short-range structure. This is confirmed by the agreement between the g values for molecules on the simple and the face-centered cubic lattices.

Third, the potential energy assumed between segments of the lattice chains is a crude approximation to the potential energy between segments of a real polymer. However, the assumed potential energy contains the main features of the potential energy of a real polymer: the infinite potential corresponding to volume exclusion at short distances and the range of negative potential corresponding to attraction between the segments. However, the narrow region of "soft" repulsion and the gradual "cut-off" of the attractive potential are absent. We doubt whether the inclusion of these regions in our assumed potential will alter our conclusions.

Thus, we believe that our lattice chain model of polymers in solution is sufficiently realistic to give reliable estimates of g and the expansion factors. Certainly, it is a more realistic model than the random walk model which ignores the effects of volume exclusion.

Conclusions

Mean-square radii of gyration were computed for star-branched polymers simulated by non-self-intersecting random walks on the simple and face-centered cubic lattices. Varying amounts of attractive energies were added between nonbonded segments of the walks in order to simulate polymer configurations in good and poor solvents. The radii were found to be proportional to N^γ, where N is the total number of segments in the star-branched polymer, and the exponent γ depends on the attractive energies between segments. The curve of γ vs. the quantity $\sigma\phi$ (which depends on the lattice and goodness of the solvent via the amount of attractive energy between segments) was found to coincide with the corresponding curve previously found for the case of linear polymers. Therefore, γ is independent of branching of the polymer. In particular, the point at which $\gamma = 1$, which defines the theta point, is independent of branching. From the calculated squared radii, the g ratio and expansion factors were calculated, and their values were found to disagree with the values calculated from analytical theories. At the theta conditions, the calculated g values are from 6 to 15% greater than those calculated according to the Zimm–Stockmayer theory. However, the g values for moderately good solvents ($\sigma\phi = 1.1$) agree well with the values obtained from the Zimm–Stockmayer theory for random flight model of a star.

Our calculations predict that the expansion factor is less for stars than for linear polymers and that it decreases with increasing number of branches, while analytical theories predict the opposite behavior. We believe that this disagreement is due to the use of the random walk model in analytical theories of polymers at their theta condition.

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Span of a Random-Flight Model of a Star-Branched Polymer Chain

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ABSTRACT: An expression is derived for the probability distribution function of the span of a random-flight model of a star-branched polymer molecule. The model consists of f random flight chains, each containing N steps, which emanate from a common point. Numerical results showing the form of the distribution function as a function of the number of branches are presented.

In this paper we continue our investigation of spans of random flight models of polymer chains.[2a] The spans of a polymer chain are defined to be the lengths of the sides of the smallest box with edges parallel to the coordinate axes which contain the entire chain. Daniels[2b] was the first to determine the distribution function and moments of what he called the "extent" and what we choose to call the span of a random walk (or polymer chain). Later, and independendently, Feller[3] and Kuhn[4,5] treated the same or equivalent problems. There is now an extensive literature on this subject.[6-13] Interest in these extreme dimensions arises from several directions. First, the typical or average spanning rectangular box is far from cubic.[12-14] This asymmetry must affect solution properties of polymer chains in which there is relative motion between the solvent and the polymer chain. Second, the notion of the span of polymer chains enters in theories of gel permeation chromatography in which separation of polymer chains according to molecular weight is envisaged as arising from a partition or exclusion of the chains in small pores on the basis of size or span.[15-17]

In this paper we calculate the distribution function of the span of a star-branched random-flight chain. Casassa,[17] using an observation of van Kreveld,[18] determined the first moment without explicitly finding the distribution function. Using an argument which is implicit in Daniel's paper[2b] and which was elaborated on by Rubin, Mazur, and Weiss,[2a] we obtain the distribution function of the span, show how it appears in the calculations of Casassa and Tagami,[16] and thus verify Casassa's formula[17] for the average span of a star-branched polymer chain.

Span of a Star-Branched Polymer Chain

In this paper we assume a random-flight model of a star-branched polymer chain (star) in which f random flight chains, each consisting of N steps, emanate from a common point. We derive an expression for $P(R_1,R_2,R_3,N)$, the joint probability distribution function (pdf) of the three spans of a star in the directions of the coordinate axes x_1, x_2, x_3. The pdf $P(R_1,R_2,R_3,N)$ is the probability that the star has a span in the x_i direction which lies between R_i and $R_i + \mathrm{d}R_i$, $i = 1, 2, 3$. Let $R_i > 0$, $i = 1, 2, 3$, define the lengths of the edges of a rectangular box $\Omega(R_1,R_2,R_3)$ which spans the star, has a corner located at the origin of the x_1, x_2, x_3 coordinate system, and has its edges parallel to the coordinate axes. For any configuration of the star, label the coordinates of the central point by $x_1^{(0)}$, $x_2^{(0)}$, $x_3^{(0)}$ and the coordinates of the tips of the branches by $x_1^{(k)}$, $x_2^{(k)}$, $x_3^{(k)}$ for $1 \leqslant k \leqslant f$.

In the limit of large N, the pdf for any one of the branches of the star is governed by the equation

$$\frac{\partial v}{\partial N} = \frac{1}{6}\left(\frac{\partial^2 v}{\partial x_1{}^2} + \frac{\partial^2 v}{\partial x_2{}^2} + \frac{\partial^2 v}{\partial x_3{}^2}\right) \qquad (1)$$

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