A Monte Carlo Simulation Study on Long-Chain Combs

J. E. G. Lipson

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755

Received August 2, 1990; Revised Manuscript Received September 11, 1990

ABSTRACT: This study concerns long-chain combs in which the branch lengths are fixed, the branches are placed evenly along the backbone, and the number of branches increases linearly with molecular weight. Results have been obtained for three cases, reflecting three values of the number of segments in a branch relative to the number in the backbone between branch points. Estimates of the ratios g ($=\langle S^2\rangle_{comb}/\langle S^2\rangle_{linear}$, where $\langle S^2\rangle$ represents the mean-square radius of gyration) and h ($=f_{comb}/f_{linear}$, where f represents the friction coefficient) are compared with the predictions of a Gaussian model and with experimental data. In addition, the ratio $\langle R^2\rangle/\langle S^2\rangle$ (where $\langle R^2\rangle$ represents the mean-square end-to-end distance of the backbone) is examined, in order to make a connection with some earlier Monte Carlo results.

Introduction

In recent years there has been a sustained interest in branched polymers having specialized structures. In their oft-cited paper[1] of 1949, Zimm and Stockmayer developed expressions that relate the dimensions of branched molecules without excluded volume to the number and placement of branches. Lately, attention has mainly focused on two particular topologies: In the case of regular *stars f* branches, each having the same number of segments, meet at a single branch point. An increase in the molecular weight of the molecule is mirrored in that of each branch. Recent work on regular H-combs has tackled the case in which there are two branch points with a single branch at each, in addition to the backbone. As with stars, the notation "regular" implies that all branches have the same number of segments. When one or both of the branch points are of a degree higher than 3, the structure has been called a "brush". Although the number of branch points in this kind of comb/brush is fixed, the branch lengths increase as the backbone does; hence, there is a nonzero fraction of material in the branches, even in the asymptotic limit of infinite molecular weight.

In many practical cases where the polymer of interest is branched, the structure does not have such a simple topology. However, there is a class of structures intermediate between these and the examples described above, in which the number of branch points increases as a function of molecular weight, with the branch lengths fixed. This paper deals in particular with simulation results on long-chain combs having branch points of degree 3, with the branches arranged along the backbone in an evenly spaced fashion. One variable of interest will be N_{br}/N_{bs}, the ratio of the number of segments in the branch (N_{br}) to that between the branch points along the backbone (N_{bs}). Figure 1 illustrates how a change in this ratio affects the comb structure. Applications involving these kinds of systems are varied. One can imagine the backbone chain functioning as a sort of "clothesline" off of which different reactive groups are "hung" at various intervals along and/or distances away from the backbone. Recently, well-defined comb-shaped polysaccharides have been synthesized to act as model compounds for physicochemical studies.[2] Other new variations involve grafting hydrophilic branches to a hydrophobic backbone[3] and synthetic branches onto a backbone that is a copolymer of cellulose and starch.[4] Finally, this topology is found in many examples of liquid crystal polymers. While such systems are usually studied in the melt or in nematic solvents, there has been some characterization of dilute solutions in good solvents for the purpose of molecular weight determination.[5] When a technique like size-exclusion chromatography (SEC) is used, calibration is needed, and the data for this have typically been collected by using linear analogues; there is interest in how the relationship between dimension and molecular weight is affected by the length and arrangements of the branches.

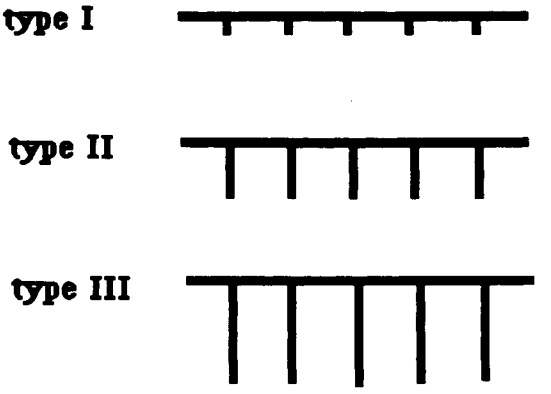

Figure 1. Three kinds of long-chain combs studied, where each segment represents a self-avoiding chain. The ratio of number of segments in the branch to the number in the backbone between branch points (N_{br}/N_{bs}) = 3/10 (type I), 6/6 (type II), and 9/4 (type III).

In this study we shall focus on the dimensions of the structures shown in Figure 1. The principle quantities of interest are $\langle S^2\rangle$, the mean-squared radius of gyration, $\langle R^2\rangle$, the mean-squared end-to-end length of the backbone, and $\langle 1/R\rangle$, the average of the inverse intermonomer separation. The latter quantity is related to the friction coefficient and, hence, to the sedimentation and diffusion coefficients. The numerical value of a quantity such as $\langle S^2\rangle$ will depend on the particular system being studied (its topology, its molecular weight) and on the lattice used in the simulation. However, ratios such as

$$g = \langle S^2\rangle_{comb}/\langle S^2\rangle_{linear} \quad (1)$$

can be formed, where $\langle S^2\rangle_{linear}$ is the value for the linear chain having the same degree of polymerization as the comb. With data collected on the same lattice for both the linear chain and the comb structures, the value of the ratio is lattice independent.[6] Ratios such as g and h are commonly quoted in experimental work as well, where

$$h = f_{comb}/f_{linear} \quad (2)$$

with f being the friction coefficient. In all cases we shall be interested in the asymptotic limit of high molecular

0024-9297/91/2224-1327$02.50/0

weight, which means that local details, such as bond angles, are considered to be unimportant.

In discussing work that has appeared on combs, it is convenient to consider three categories: other Monte Carlo (MC) results, experimental results, and calculations involving analytic expressions for the quantities of interest. There have been few Monte Carlo studies on systems like the ones being studied here. Indeed, the only relevant study was done by Gallacher and Windwer in 1966,[7] and even in this case not many connections can be made, for reasons which will be discussed below. Other studies[8] have yielded information on systems that are more closely related to the H-combs mentioned above, in that data for each kind of comb are extrapolated to the infinite molecular weight limit by allowing all sections to increase in molecular weight simultaneously rather than by keeping the branch lengths fixed and extrapolating to an infinite number of branches, as is done here.

With respect to synthetic work, the efforts in producing combs with fixed branch lengths and *evenly spaced* branches have mainly been associated with liquid crystal polymers,[9] and characterization of these systems has not been extensive. One exception to this was a study by Strazielle and Herz,[10] who synthesized a series of combs and reported g values in several good and Θ solvents (the criterion for the latter being established via viscosity–molecular weight measurements). Unfortunately, there seemed to be a large variation in the g values obtained in, say, one good (or Θ) solvent as opposed to another, making comparison with other studies difficult. More work has appeared on combs in which the branch lengths are fixed, and the branches are randomly placed along the backbone. In early studies[11] the systems were typically characterized through viscosity measurements. However, Roovers,[12,13] collaborating in part with Toporowski,[14] has synthesized a series of such combs and has characterized them relative to linear chains of the same molecular weight using several techniques. Some of these results will appear in the discussion that follows.

Finally, with respect to analytic results, quantities of interest have only been obtained for the case in which the segments in each subchain obey Gaussian statistics. Casassa and Berry[15] worked out expressions for $P(\Theta)$, the particle scattering factor, for both evenly and randomly branched combs, leading to expressions for g. Expressions for g (evenly spaced combs) have also been developed by Kurata and Fukatsu[16] (whose paper deals with several other kinds of branched systems, as well), by Galina[17a] (who considers both combs and rings), and by Forsman.[17b] In addition, Berry[18] has derived an expression for h^{-1} for the randomly branched case, and Kurata and Fukatsu[16] give an expression for h for evenly branched combs of type II (see Figure 1). Other papers have appeared[19] that deal with the effects of excluded volume on the comb dimensions; these are interesting but not directly related to the results of this study.

Calculational Details

The simulation studies were done by using an inversely restricted Monte Carlo algorithm on the tetrahedral lattice.[20] As mentioned above, it has been shown that ratios of lattice-dependent quantities, such as g, are themselves lattice-independent.[6] For previous work on stars and short combs the simulation results using this kind of algorithm have been checked against exact enumeration data for small values of N.[20b] For each kind of long-chain comb one self-avoiding structure was generated at a time, and only single occupancy of sites was allowed: thus, the simulations are meant to correspond to experimental results for these kinds of polymers in dilute solution in a good solvent. The analogous model for the linear chain is called a self-avoiding walk (SAW). In making a connection with real systems, one would imagine the branch points, represented here by a single lattice site, to be composed of some trifunctional branching unit, and the segments, represented here by a single lattice bond, to correspond to a statistical segment length.

Three values of the ratio N_{bl}/N_{bs} were chosen, and these are illustrated in Figure 1. In each case, configurations were generated for a series of molecular weights, where successive choices of N, the total number of segments, are identified with growth of the backbone such that there is an increase by 1 in the number of branches. For each value of N, which ranged between about 20 and 210 segments, an entirely new set of configurations was generated so that there would be no built-in correlation between the configurations for successive values of N. With N very much larger than about 200 the size of configuration space becomes too great for this technique to sample efficiently. The number of configurations generated depended on N and on the system being studied. For each value of N less than 100, about 100 000–200 000 configurations were typically generated, while for N greater than 100, 300 000–400 000 configurations were usually run. These were generated in batches in 10 000–20 000 so that standard deviations about the mean could be calculated for each quantity of interest; these ranged from 2 to 5%. The confidence limits associated with the data in the tables reflect uncertainty in the graphical fits.

Of the dimensional properties discussed in this paper, the mean-square radius of gyration is the most experimentally accessible. In the asymptotic limit the N-dependence of $\langle S^2 \rangle$ for self-avoiding walks can be described by the functional form[21]

$$\langle S^2 \rangle \sim AN^{2\nu}[1 + (B/N^{\Delta}) + (C/N)] \qquad (3)$$

where A, B, and C are amplitudes, and ν and Δ are scaling exponents. It is perhaps more common to see this expression with only the first term on the right-hand side, which represents the dominant scaling behavior. Although this functional form was developed to describe the asymptotic behavior of linear chains, it has also been used for other topologies; the evidence is compelling that for structures having a fixed number of branch points (e.g., regular stars and H-combs) the critical exponents retain their SAW values.[22,23] The best current estimates for these exponents are $\nu = 0.588$ and $\Delta = 0.47$.[21] Note that for the case of a linear chain obeying Gaussian statistics $\langle S^2 \rangle$ is given by using only the first term on the right-hand side, with $\nu = 0.5$. The functional form for $\langle R^2 \rangle$ is strictly analogous to that of eq 3; the critical exponents are unchanged, but the amplitudes have different values. A related expression can also be written for $\langle 1/R \rangle$.

Results and Discussion

Mean-Square Radius of Gyration. In previous work, simulation results for SAWs, stars, and regular H-combs have been analyzed to show that the exponent ν remains unchanged upon the inclusion of a small, finite number of branch points. One piece of evidence for this comes from a plot of ln $\langle S^2 \rangle$ versus ln N for a series of regular stars, which shows a set of straight lines parallel to that for a SAW.[22] In such a case the amplitudes associated with the correction terms ($N^{-0.47}$, N^{-1}) must be small. Figure

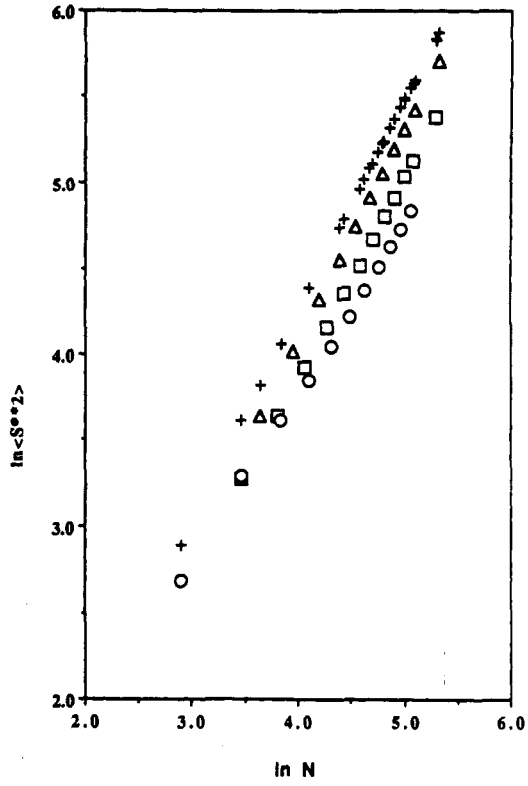

Figure 2. log–log plot of the mean-square radius of gyration versus molecular weight (=number of segments, N). (+) = SAW, (△) = type I, (□) = type II, (○) = type III.

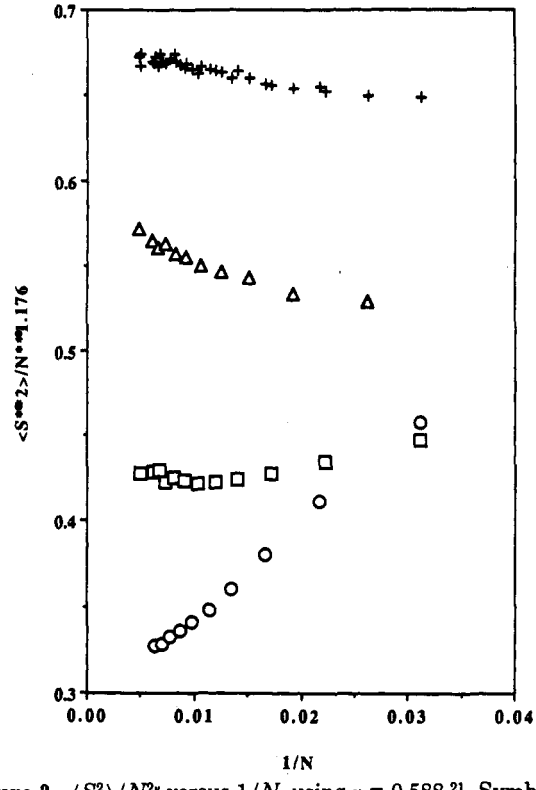

Figure 3. $\langle S^2\rangle/N^{2\nu}$ versus $1/N$, using $\nu = 0.588$.[21] Symbols as in the caption for Figure 2.

2 shows an analogous plot for the three kinds of combs being studied here, along with SAW data that have been generated for each value of N associated with the combs. While each set of data points can be connected to form a straight line, none of the comb lines are exactly parallel with that for the SAW. The small deviation from the SAW behavior implies that, although the dominant critical exponent is very likely given by the SAW value (i.e., that $\nu = 0.588$ for self-avoiding combs), the correction-to-scaling terms are nonnegligible. Thus, in order to get estimates for the amplitude A in eq 3, the simulation data should be fit to the full equation. Recall that the goal is to study lattice-independent ratios such as g, defined through eq 1. In the case of regular stars ν was taken to be independent of the number of branches, and g could be found by taking the ratio of the amplitudes $A(\text{star})/A(\text{SAW})$. This procedure worked well for cases in which the corrections-to-scaling were small, the amplitudes being obtained by extrapolation to $N \to \infty$ of the data for $\langle S^2\rangle$ plotted against N^{-1} (or $N^{-0.47}$). For the long-chain combs being studied here, estimates of the amplitude depend on whether one or both correction terms are included. Figure 3 shows a plot of $\langle S^2\rangle/N^{1.176}$ plotted against N^{-1} for the comb and the SAW data; the inclusion of branches results in a contraction in the dimension of the structure, relative to that of a SAW having the same number of segments. As N_{br} increases, relative to N_{bs}, the contraction becomes more pronounced; clearly the data for the SAW and each of the three combs are heading toward different asymptotic limits. The need to use eq 3 in its entirety in order to estimate the amplitudes A is illustrated in Figure 4, where $\langle S^2\rangle/N^{1.176}$ is plotted against $N^{-0.47}$ for the type III case. The data points are the simulation results, the solid curve is a fit to eq 3 using the method of differential corrections,[24] and the other two curves are linear least-square fits obtained by using only one of the correction-to-scaling terms in each case. The differences between the fits shown here are exaggerated, in the sense that if a linear fit (to

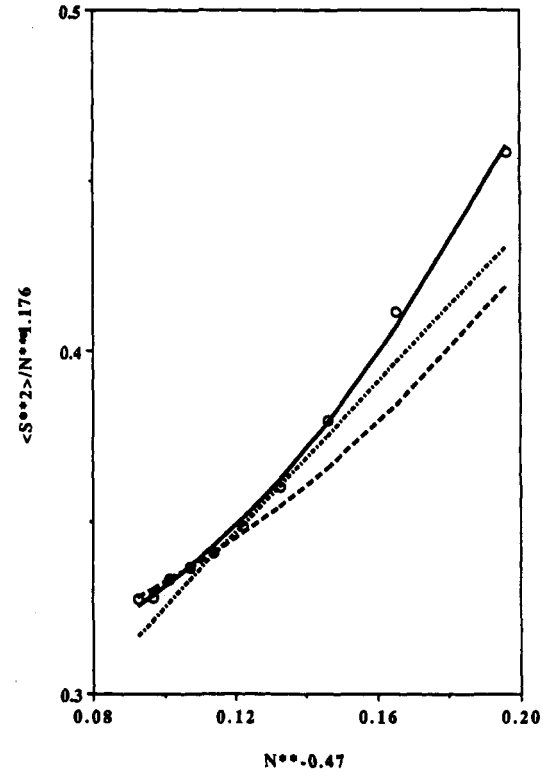

Figure 4. $\langle S^2\rangle/N^{2\nu}$ versus $N^{-0.47}$ for the type III combs. The curves represent fits done using (—) eq 3 with both correction terms, (– · –) eq 3 with the $N^{-0.47}$ correction only, and (– –) eq 3 with the $1/N$ correction only.

$N^{-0.47}$ or N^{-1}) were to be done, it would make sense to ignore some of the low-N data. However, use of both correction terms leads to an excellent fit over the whole data set in all cases. The amplitudes obtained in this fashion are then used to form estimates of the ratio g, and these are listed in Table I.

Table I

	type I	type II	type III
g from fit to full eq 3	0.90 ± 0.02	0.68 ± 0.02	0.43 ± 0.02
g from extrapolation of $g(N)$	0.86 ± 0.02	0.64 ± 0.02	0.43 ± 0.02
h from extrapolation of $h(N)$	0.94 ± 0.01	0.86 ± 0.01	0.78 ± 0.02
weight fraction material in branches	0.23	0.50	0.69

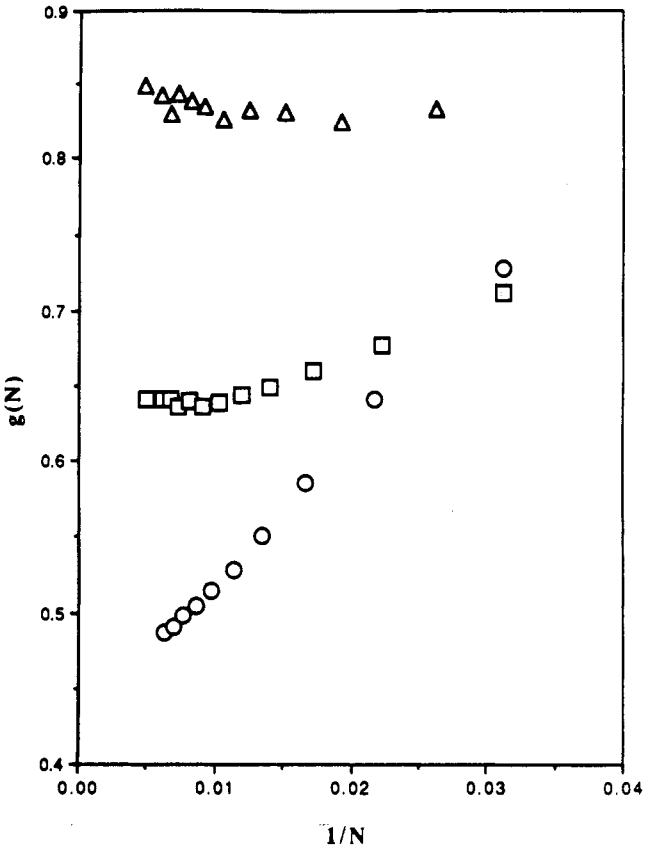

Figure 5. $g(N)$ versus $1/N$; symbols as described in the caption to Figure 2.

An alternative route to g is to form the ratio of $\langle S^2\rangle_{comb}/\langle S^2\rangle_{SAW}$ ($=g(N)$) for each value of N and to extrapolate to the limit of $1/N \rightarrow 0$. Figure 5 shows how $g(N)$ approaches its limiting value for each case. Since the set of amplitudes for each comb will differ from those for the SAW, the N-dependence of $g(N)$ might be complicated. Without having a functional form, it is not feasible to use the method of differential corrections, so in this case estimates of g are obtained via extrapolation by ruler. Resulting values for g are included in Table I. These estimates are comparable to those obtained from the extrapolation using eq 3, within the confidence limits quoted.

Although no experimental data are as yet available for combs that exactly parallel those studied here, these results can be put in context with respect to work on related systems. For two specialized cases, analytic expressions have been developed that relate $g(N)$ to the number of branches and the weight fraction of material in the backbone of the comb.[15,19] Both involve branches of fixed length attached to the backbone; the branches are randomly placed in one model and regularly placed in the other. Neither model incorporates the effects of excluded volume, whereas the structures studied here model the fully developed limit of excluded volume. However, a comparison of results for g with and without excluded

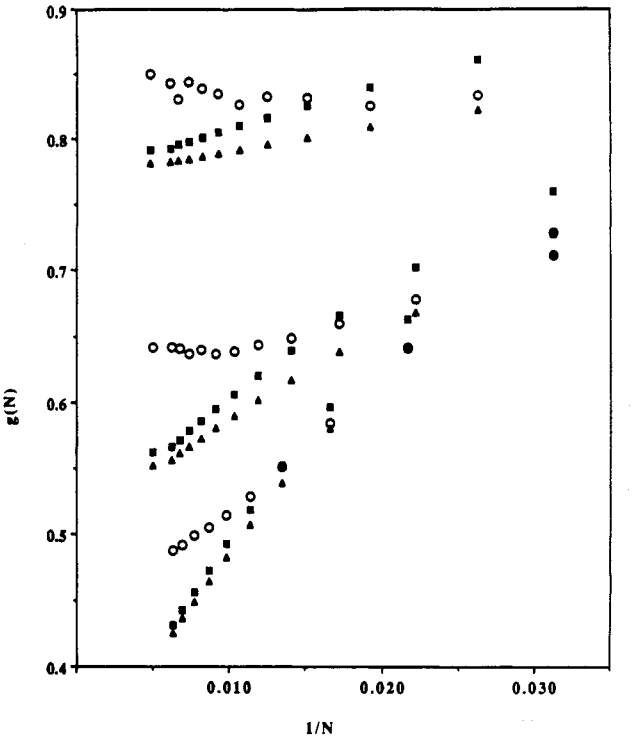

Figure 6. $g(N)$ versus $1/N$; a comparison of the data from this study with the predictions of the Gaussian model.[15,19] There are three data sets shown, representing results for type I, II, and III combs from top to bottom, respectively. Within *each* data set the notation is (○) Monte Carlo data; (■) Gaussian model, random-branch placement; (▲) Gaussian model, even-branch placement.

volume is worthwhile based on analogy with studies on regular stars. For those systems much evidence, both experimental and simulation, has led to the conclusion that the ratio g appears to be insensitive[6] to the effects of solvent quality or excluded volume. However, the analysis of Barrett and Tremain[23] suggests that the Gaussian model should be less accurate in predicting g for regular stars as f increases. In Figure 6 the Monte Carlo results for $g(N)$ are plotted against $1/N$ along with the estimates for Gaussian combs with the branches randomly and evenly placed (calculated for each value of N for which there are simulation data). It has been noted indirectly[18] that, for the Gaussian case in the asymptotic limit, the different branch placement should not affect the ratio g, and this is confirmed in Figure 6. In studying the case of evenly branched Gaussian combs, Galina[17] noted that in the asymptotic limit g is given by the weight fraction of units in the backbone; for the three cases studied here, these values are 0.77 (type I), 0.50 (type II), and 0.31 (type III), and all three are consistent with the trends observed in Figure 6. In each case, the limiting value of g for the self-avoiding combs (as predicted using MC data) is distinctly above the prediction using the Gaussian model. How do the Gaussian predictions compare with experimental data? In Figure 7 are shown g values plotted against the weight fraction material in the branches for a series of experimental systems, along with the simulation data and theoretical predictions. The two limits along the abscissa correspond to the linear chain (weight fraction in branches goes to zero) and a star having an infinite number of branches (weight fraction goes to 1). The experimental data, all taken from the work of Roovers,[12,13] are for combs having different molecular weights, with different branches lengths (fixed for any one sample), and different numbers of branches; results for both good and Θ solvents are plotted.[25] It is striking how the data for many different

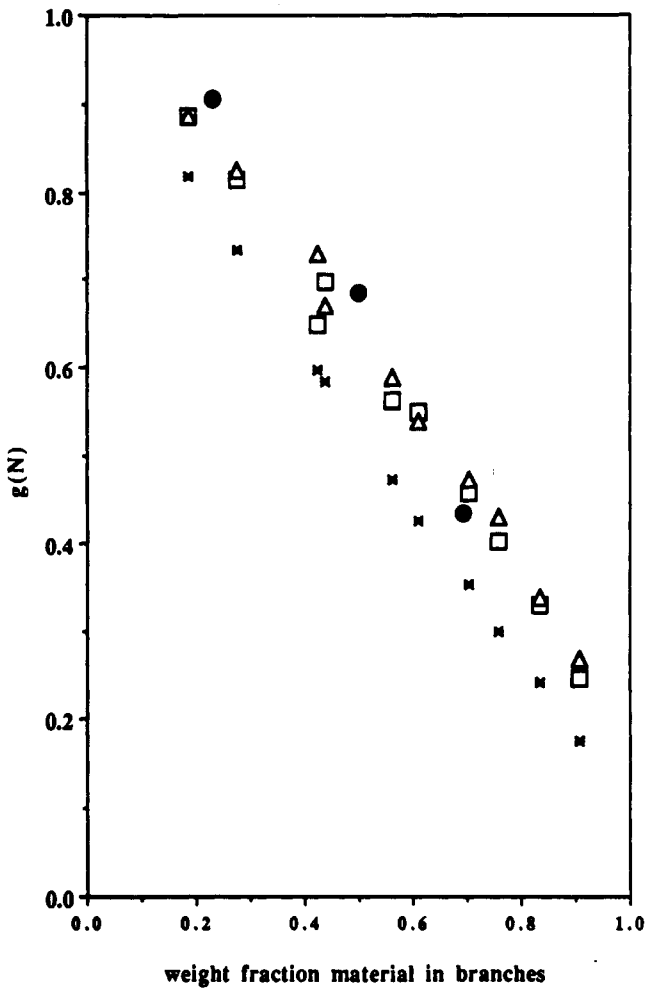

Figure 7. $g(N)$ versus weight fraction of material in the branches. (●) Monte Carlo data; (⋊)Gaussian model;[15,19] (□) experimental data, good solvent; (△) experimental data, Θ solvent.[13]

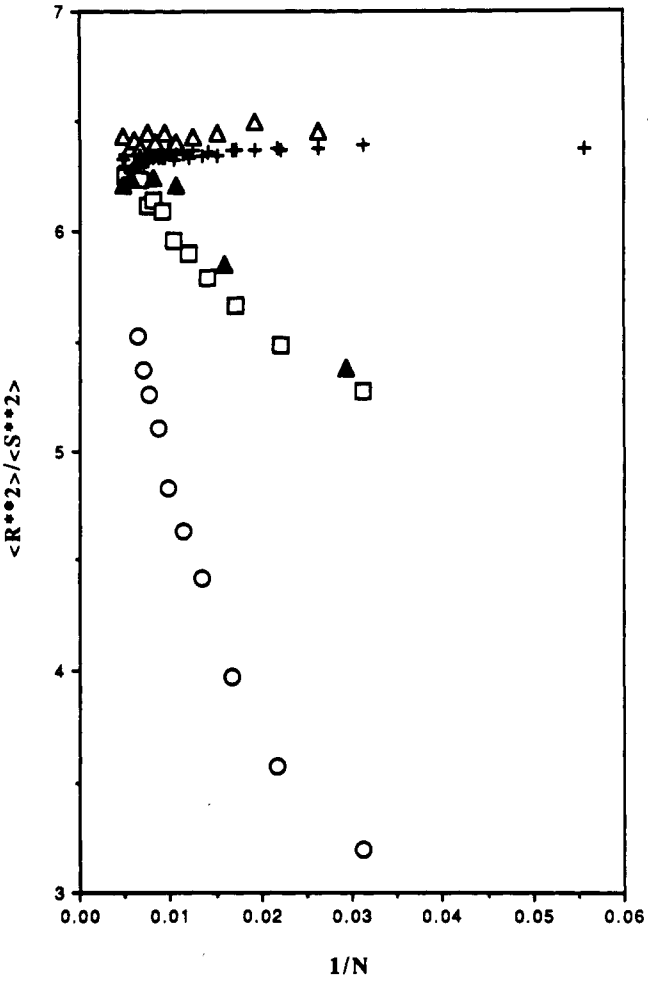

Figure 8. Checking the prediction that the ratio $\langle R^2\rangle/S^2\rangle$ approaches 6.37 in the asymptotic limit. (▲) from Gallacher and Windwer;[7] other symbols as described in the caption to Figure 2.

experimental systems fall together on a relatively narrow band. Just as noteworthy is the appearance of the simulation results within this band, considering that they are for combs having regularly spaced branches. The predictions based on the Gaussian model for combs having fixed branch lengths randomly spaced along the backbone are well below the experimental results.

Mean-Square End-to-End Length and Radius of Gyration of the Backbone. In principle, the mean-square radius of gyration of the backbone of a comb ($\langle S_2\rangle_{bb}$) could be measured through labeling studies. In practice, this has been considered but has never been done.[26] However, although there are no experimental results for this quantity, or for the mean-square end-to-end length of the backbone ($\langle R^2\rangle$), there is a prediction in the literature for the ratio $\langle R^2\rangle/\langle S^2\rangle$. Recall that for a linear chain obeying Gaussian statistics this would be exactly equal to 6. In a paper published in 1966 Gallacher and Windwer[7] presented Monte Carlo data for regular combs on the tetrahedral lattice. Their analysis came before the current notions of scaling and corrections to scaling; hence, it is not possible to relate much of their work to the results presented here. In addition, although estimates for what is equivalent in their paper to the exponent ν show they are modeling chains in the good solvent regime (i.e., excluded-volume effects are incorporated), the configurational averages involve a weighting factor that reflects several choices of (nonbonded) nearest-neighbor interaction energies. Therefore, their results do not exactly correspond to the results in this work. However, they did investigate whether the N-dependence of the ratio $\langle R^2\rangle/\langle S^2\rangle$ supported the conjecture[27] that this quantity is a universal constant, equal to 6.37, for polymers with excluded volume, in three dimensions. In Figure 8 $\langle R^2\rangle/\langle S^2\rangle$ is plotted against $1/N$ for the three kinds of combs studied here, along with the SAW results; also included is the one related data set that could be extracted from the paper of Gallacher and Windwer. Their results and those for the SAW and type I and II combs do appear to be converging to a limiting value between 6.3 and 6.6; the trend for the type III combs is not inconsistent with this limiting value, but the approach to the limit is rather steep. Shanes and Nickel[28] have recently used perturbation theory to calculate $\langle S^2\rangle$ for a flexible linear chain with excluded-volume interaction and, combining their result with previous work[29] for $\langle R^2\rangle$, give the result $6\langle S^2\rangle/\langle R^2\rangle = 0.9602 \pm 0.0002$ in the limit of large N. This would correspond to an intercept of about 6.25 in Figure 7, which is somewhat lower than the simulation results.

Effect of Branching on the Friction Coefficient. The hydrodynamic contribution to the friction coefficient can be expressed in the Kirkwood approximation, in the non-free-draining limit, as [30]

$$1/f = (1/3\pi\eta_0 N^2)\sum_i\sum_j\langle 1/R_{ij}\rangle \qquad (4)$$

where η_0 is the viscosity coefficient of the solvent. An estimate of the ratio h can therefore be obtained by analyzing the Monte Carlo data using eq 4 and taking the

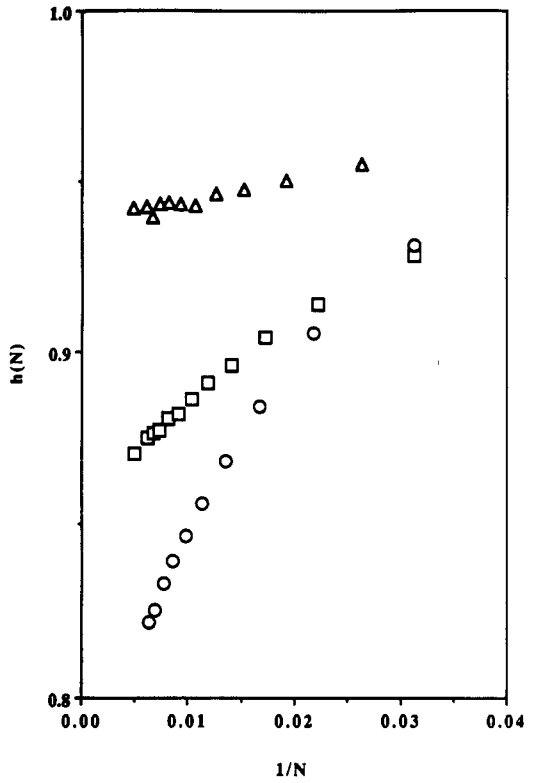

Figure 9. $h(N)$ versus $1/N$; symbols as described in the caption to Figure 2.

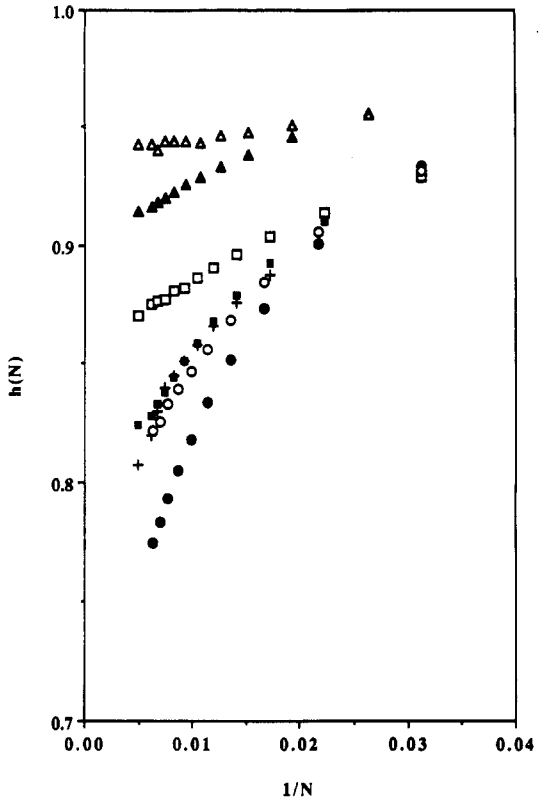

Figure 10. $h(N)$ versus $1/N$; a comparison of the data from this study with the predictions of the Gaussian model.[18] Open symbols as described in Figure 2; filled symbols represent the predictions of the Gaussian model with random-branch placement[18] for (▲) type I, (■) type II, and (●) type III. (+) is for the Gaussian model with even-branch placement,[16] type II only.

ratio described by eq 2. Just as for g, however, there are two routes that can be followed. One possibility is to fit the data for $\langle 1/R \rangle$ to an equation that is analogous to eq 3 for $\langle S^2 \rangle$, obtain the amplitudes for each type of comb and the SAW, and form h. Alternatively, $h(N)$ can be extrapolated to the asymptotic limit; these data are shown in Figure 9, in which $h(N)$ is plotted against $1/N$ for the three types of combs. As with the results for g, h values obtained by extrapolating $h(N)$ are representative of the results from fitting to the scaling equation, so only one set of values is given in Table I.

Berry[18] derived an analytic expression for $1/h$ for combs with randomly placed branches in which the subchains obey Gaussian statistics; for the analogous model with evenly placed branches, Kurata and Fukatsu[16] worked out an expression for the type II case, only, i.e., each subchain has the same number of segments. In Figure 10 the predictions of the Gaussian model are compared with the simulation results of this study. Once again, the Gaussian model yields values that are lower than the simulation results; here the differences are even greater than those found for the g values. Comparison with some experimental results[14] is illustrated in Figure 11, which shows the data for the same series of combs (in good solvent)[31] used to make comparison with g values. The results of this study are in excellent agreement with the experimental results, just as they were in the comparison of g values. Given that the Gaussian model underestimates both g and h values, it is expected that forming a ratio of ratios, for example, $h/g^{1/2}$, would result in some cancellation of error.[32] Thus, if one is determined to use the Gaussian model, a more reliable route in predicting g for a comb of given structure would be to measure h and obtain an estimate of g through the Gaussian prediction for $h/g^{1/2}$.

Summary and Conclusions

Monte Carlo data have been collected and analyzed for long-chain combs in which the branch lengths are fixed, the branches are placed evenly along the backbone, and the number of branches increases linearly with molecular weight. Three particular cases have been studied here, associated with different values of the ratio of branch length to interbranch spacing.

The dimensional properties of these systems are amenable to analysis using the same formalism as is used for linear chains, and the evidence is that the critical exponent, ν, remains unchanged from its value for a self-avoiding walk. However, in analyzing the combs data, it was found that correction-to-scaling terms made significant contributions. In all cases, extrapolation to the asymptotic limit was entirely straightforward, with the results for the three categories studied being well-separated.

Comparison with the predictions of the Gaussian model indicates that the latter is not as effective in modeling the dimensions of these combs as it was in the case of stars. The underestimates for g and h in using this model were emphasized by comparison with experimental data. On the other hand, the predictions from this study showed excellent agreement with experimental results, indicating that the choice of random versus regular placement of branches along the backbone has very little effect on the dimensions, for a given weight fraction of material in the branches. In addition, the comparison of experimental results for what were believed to be good and Θ conditions suggests that g and h values for these kinds of combs are no more sensitive to solvent quality than those for stars; this reaffirms that the Gaussian model does not provide as useful a model of Θ conditions for these systems as it has for regular stars.

Acknowledgment. I am grateful to the donors of the Petroleum Research Fund, administered by the American

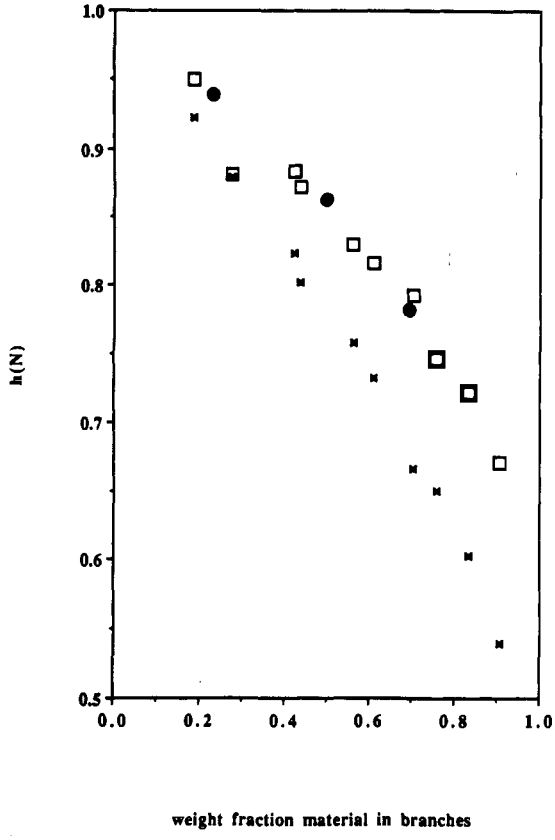

Figure 11. $h(N)$ versus weight fraction of material in the branches. (●) Monte Carlo data; (⊗) Gaussian model;[18] (□) experimental data, good solvent.[14]

Chemical Society, for their support of this research. Conversations with S. G. Whittington and D. S. Gaunt regarding some aspects of data analysis were useful indeed, and early feedback from A. J. Barrett was very motivating.

References and Notes

(1) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.
(2) Ichikawa, H.; Kobayashi, K.; Sumitomo, H. *Macromolecules* **1990**, *23*, 1884.
(3) Weber, M.; Stadler, R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30*, 109.
(4) Narayan, R.; Stacy, N.; Lu, Z. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30*, 105.
(5) Mattoussi, H.; Ober, R. *Macromolecules* **1990**, *23*, 1809.
(6) Whittington, S. G.; Lipson, J. E. G.; Wilkinson, M. K.; Gaunt, D. S. *Macromolecules* **1986**, *19*, 1241.
(7) Gallacher, L. V.; Windwer, S. *J. Chem. Phys.* **1966**, *44*, 1139.
(8) (a) Prats, R.; Pla, J.; Freire, J. J. *Macromolecules* **1983**, *16*, 1701. (b) Freire, J. J.; Prats, R.; Pla, J.; Garcia de la Torre, G. *Macromolecules* **1984**, *17*, 1815. (c) McCrackin, F. L.; Mazur, J. *Macromolecules* **1981**, *14*, 1214.
(9) (a) Yokota, K.; Kougo, T.; Hirabayashi, T. *Polym. J.* **1983**, *15*, 891. (b) Yokota, K.; Hirabayashi, T. *Polym. J.* **1986**, *18*, 177. (c) Leon, A.; Gargallo, L.; Horta, A.; Radic, D. *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *27*, 2337.
(10) Strazielle, C.; Herz, J. *Eur. Polym. J.* **1977**, *13*, 223.
(11) (a) Pannell, J. *Polymer* **1971**, *12*, 558. (b) Berry, G. C.; Hobbs, L. M.; Long, V. C. *Polymer* **1964**, *5*, 31, 517.
(12) Roovers, J. E. L. *Polymer* **1975**, *16*, 827.
(13) Roovers, J. *Polymer* **1979**, *20*, 843.
(14) Roovers, J.; Toporowski, P. M. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1907.
(15) Casassa, E. F.; Berry, G. C. *J. Polym. Sci., Polym. Phys. Ed.* **1966**, *4*, 881.
(16) Kurata, M.; Fukatsu, M. *J. Chem. Phys.* **1964**, *41*, 2934.
(17) (a) Galina, H. *Macromolecules* **1983**, *16*, 1479. (b) Forsman, W. C. *Macromolecules* **1968**, *1*, 343.
(18) Berry, G. C. *J. Polym. Sci., Polym. Phys. Ed.* **1968**, *6*, 1551.
(19) (a) Berry, G. C.; Orofino, T. A. *J. Chem. Phys.* **1964**, *40*, 1614. (b) Solensky, P. J.; Casassa, E. F. *Macromolecules* **1980**, *13*, 500.
(20) (a) Rosenbluth, M. N.; Rosenbluth, A. W. *J. Chem. Phys.* **1955**, *23*, 356. (b) Lipson, J. E. G.; Whittington, S. G.; Wilkinson, M. K.; Martin, J. L.; Gaunt, D. S. *J. Phys. A* **1985**, *18*, L469.
(21) Le Guillou, J. C.; Zinn-Justin, J. *J. Phys. (Les Ulis, Fr.)* **1989**, *50*, 1365.
(22) Lipson, J. E. G.; Gaunt, D. S.; Wilkinson, M. K.; Whittington, S. G. *Macromolecules* **1987**, *20*, 186.
(23) Barrett, A. J.; Tremain, D. L. *Macromolecules* **1987**, *20*, 1687.
(24) Neilsen, K. L. *Methods in Numerical Analysis*; Macmillan and Co.: Toronto, 1956.
(25) In his paper (ref 13) Roovers notes that g is determined from experimental data at the "Flory Θ-temperature". In the context of his paper this appears to mean the temperature (in cyclohexane) at which the linear analogue (PS chains) has a value of $\langle S^2 \rangle$ equal to that predicted using the Gaussian model. Good solvent conditions are taken to be the same as those for the linear chain, i.e., toluene at 35 °C.
(26) Roovers, J. E. L., private communication.
(27) Wall, F. T.; Erpenbeck, J. J. *J. Chem. Phys.* **1959**, *30*, 637.
(28) Shanes, F. C.; Nickel, B. G. *Preprint* 1990.
(29) Muthukumar, M.; Nickel, B. G. *J. Chem. Phys.* **1987**, *86*, 460.
(30) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.
(31) In ref 14 good and Θ conditions for the comb PS molecules are considered to be the same as those for the linear PS molecules. There was not as complete a data set for the Θ conditions, so this data is not shown.
(32) Complete cancellation of errors is not expected since, as Roovers and Toporowski point out in ref 14, h is related to $\langle 1/R \rangle$ and $g^{1/2}$ to $\langle S^2 \rangle^{1/2}$. Thus, the contributions from large intermonomer separations are weighted more heavily in $g^{1/2}$ than in h.