Lattice Models of Branched Polymers: Dimensions of Uniform Stars

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ABSTRACT: The dimensions of uniform star-branched polymers in a good solvent are studied by exact enumeration and Monte Carlo techniques. The mean-square radius of gyration, $\langle S_N^2(f)\rangle$, is calculated as a function of the number, f, of branches and the degree of polymerization, N. Assuming that $\langle S_N^2(f)\rangle \sim A(f)N^{2\nu(f)}$, our results indicate that $\nu(f) = \nu$, where ν is the corresponding exponent for a linear chain. Of particular interest is the ratio $g(f)$ of the mean-square radius of gyration of a uniform star polymer to that of a linear polymer of the same degree of polymerization. In the large-N limit, $g(f) = A(f)/A(1)$, and our estimates of this amplitude ratio are compared with experimental and theoretical results in the literature. Other metrical properties, including the end-to-end length and internal dimensions of a branch, are studied and the results compared with the renormalization group predictions of Miyake and Freed (*Macromolecules* **1983**, *16*, 1228).

1. Introduction

A *uniform* star-branched polymer has the same number of monomers in each of its branches. Synthetic routes[1] are now available for the preparation of such molecules, and the dimensions of these structures have been measured by light scattering.[2] In a classic paper, Zimm and Stockmayer[3] gave a theoretical treatment of such systems in the absence of excluded-volume effects, but it is only recently that theories have appeared which are relevant to the good-solvent regime.[4-7] Daoud and Cotton[4] have developed a scaling theory for the dimensions of uniform stars with f branches in which they propose that there are three concentration regimes dependent on the distance from the branch point: an inner core region in which the chains are very extended due to interchain repulsions, an intermediate region in which interchain interactions effectively screen out the excluded-volume effects, and an outer swollen region in which intrachain excluded-volume effects dominate. They predict that the ratio

$$g(f) = \lim_{N\to\infty} \langle S_N^2(f)\rangle / \langle S_N^2(1)\rangle \tag{1.1}$$

where $\langle S_N^2(f)\rangle$ is the mean-square radius of gyration of a uniform star having a total of N monomers and f branches, decreases as $f^{-4/5}$.

Miyake and Freed[5] have developed a chain conformation space renormalization group treatment and predict, in the limit of fully developed excluded volume, that

$$g(f) = \frac{3f-2}{f^2}\left\{1 - \frac{\epsilon}{8}\left[\frac{13(f-1)(f-2)}{2(3f-2)} - \frac{4(f-1)(3f-5)\ln 2}{3f-2} + \ln f\right] + \mathcal{O}(\epsilon^2)\right\} \tag{1.2}$$

where $\epsilon = 4 - d$, d being the spatial dimension. We note that when $d = 4$, eq 1.2 reduces to the result of Zimm and Stockmayer.[3] Both results for $g(f)$ imply that the exponent $\nu(f)$ defined through

$$\langle S_N^2(f)\rangle \sim A(f)N^{2\nu(f)} \tag{1.3}$$

is independent of f and equal to the exponent ν for linear polymers. In both treatments, $g(f)$ is predicted to decrease as f increases, and this is in qualitative agreement with experimental results.[1,2,8]

Miyake and Freed[5] have also studied the f dependence of the mean-square end-to-end length and internal dimensions of a branch.

Mazur and McCrackin,[9] in a paper that has not received the attention it deserves, initiated Monte Carlo studies of the excluded-volume effects in a lattice model of star-branched polymers. Since then there have been few simulation studies of stars that incorporate excluded-volume effects,[10-13] and much of the published Monte Carlo data are not in a form that allows easy comparison with the theoretical predictions.

In a preliminary publication,[12] we used exact enumeration and Monte Carlo techniques to investigate the f dependence of the number of configurations and the mean-square end-to-end length of a branch. More recently,[13] we carried out a detailed study of the number of configurations, for f = 3, 4, 5, and 6, on a variety of two- and three-dimensional lattices and compared our results with the $\mathcal{O}(\epsilon)$ predictions of Miyake and Freed.[5] In the present paper, we extend our preliminary results[12] on dimensions to include the mean-square radius of gyration and the internal dimensions of a branch for stars with a larger number of branches ($f \le 6$) on a wider variety of lattices in two and three dimensions.

2. Mean-Square Radius of Gyration

The mean-square radius of gyration of uniform star polymers is a quantity that has been investigated both experimentally[1,2,8] and theoretically.[4-7] Exact enumeration and Monte Carlo techniques provide an important bridge between experiment and theory, and in this section we use these techniques to study the mean-square radius of gyration of a lattice model of uniform stars with various values of f.

An inversely restricted Monte Carlo approach[14] has been used to study stars on the simple cubic lattice with $f \le 6$. We have generated data for stars with $n \le 50$ monomers per branch and averaged our results over, typically, 40 000 configurations. For small N, we have calculated $\langle S_N^2(f)\rangle$ exactly[15] and the Monte Carlo estimates are in excellent agreement with these results.

In Figure 1, we show the radius of gyration depends on the degree of polymerization, N, for structures ranging from a linear chain to a uniform star with six branches. At fixed degree of polymerization, it is clear that the radius of gyration decreases, that is, the stars become more compact, as f increases. Since we expect the functional form eq 1.3 for $\langle S_N^2(f)\rangle$, the exponent $\nu(f)$ is estimated through a log–log plot such as that shown in Figure 2. The data are linear for each value of f and the resulting lines are essentially parallel, indicating that the exponent $\nu(f)$ is independent of f. Indeed the widely used value $\nu = 0.6$ is consistent with these data for all f, and this value is

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Table I
Estimates of the Amplitudes $A(f)$ and the Amplitude Ratios $g(f)$ for the Mean-Square Radius of Gyration of Uniform Stars on the Simple Cubic Lattice

	$2\nu = 1.2$		$2\nu = 1.176$		
f	$A(f)$	$g(f)$	$A(f)$	$g(f)$	$g(f)_{MF}$[a]
1, 2	0.166 ± 0.001	1	0.1936 ± 0.0008	1	1
3	0.126 ± 0.001	0.76 ± 0.01	0.146 ± 0.001	0.75 ± 0.01	0.798
4	0.100 ± 0.001	0.60 ± 0.01	0.115 ± 0.001	0.59 ± 0.01	0.667
5	0.084 ± 0.001	0.51 ± 0.01	0.098 ± 0.002	0.51 ± 0.01	0.580
6	0.071 ± 0.001	0.43 ± 0.01	0.082 ± 0.002	0.42 ± 0.01	0.519

[a] From Miyake and Freed.

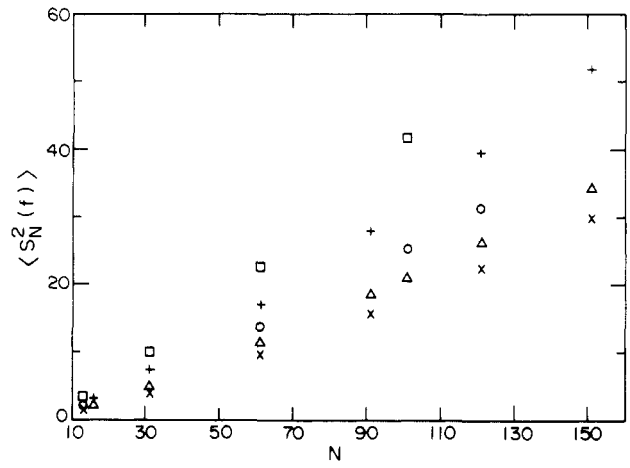

Figure 1. Dependence of the mean-square radius of gyration $\langle S_N^2(f) \rangle$ on the degree of polymerization (N) and on the number (f) of branches for the simple cubic lattice: (□) $f = 1, 2$; (+) $f = 3$; (○) $f = 4$; (△) $f = 5$; (×) $f = 6$.

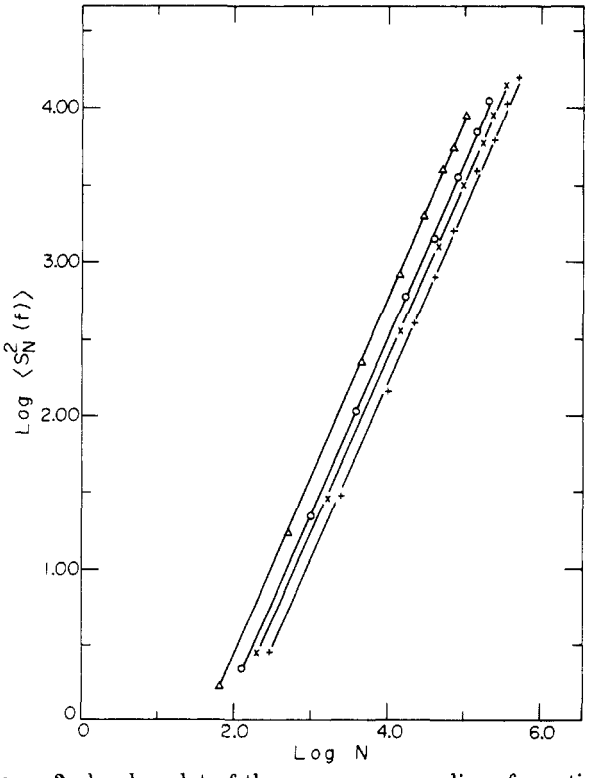

Figure 2. log–log plot of the mean-square radius of gyration $\langle S_N^2(f) \rangle$ against the degree of polymerization N for the simple cubic lattice: (△) $f = 3$; (○) $f = 4$; (×) $f = 5$; (+) $f = 6$.

adopted in estimating the amplitudes $A(f)$. Thus, in Figure 3 $\langle S_N^2(f) \rangle / N^{1.2}$ is plotted against n. Clearly, the amplitudes decrease as f increases. We have carried out a detailed numerical analysis of these results, and our estimates

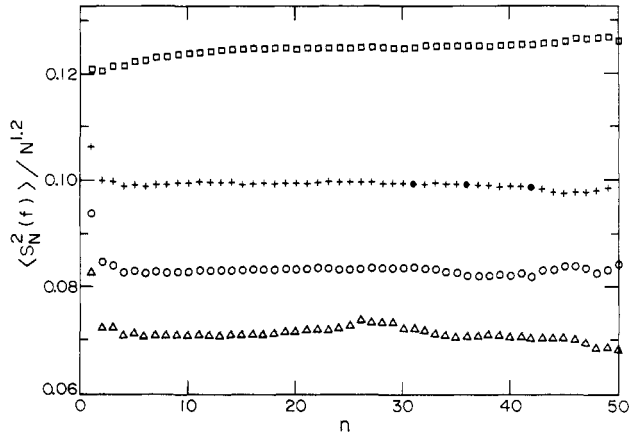

Figure 3. Mean-square radius of gyration scaled by $N^{1.2}$ as a function of the branch length (n) and the number of branches (f) for the simple cubic lattice: (□) $f = 3$; (+) $f = 4$; (○) $f = 5$; (△) $f = 6$.

Table II
Comparison of Values of the Amplitude Ratios $g(f)$ for Various Values of the Number of Branches, f

	f			
	3	4	5	6
this work	0.76 ± 0.01	0.60 ± 0.01	0.51 ± 0.01	0.43 ± 0.01
Zimm (Monte Carlo)		0.63 ± 0.01		0.45 ± 0.01
Bauer et al. (exptl)		0.633, 0.65		0.458, 0.46
Huber et al. (exptl)	0.761[a]			
	0.69[b]			
Zimm and Stockmayer	0.778	0.625	0.520	0.444
Miyake and Freed	0.798	0.667	0.580	0.519

[a] Θ solvent. [b] Good solvent.

of the amplitudes are given in Table I. We also give the amplitude ratios[16] $g(f) = A(f)/A(1)$, which are expected to be lattice-independent quantities and which can therefore be compared with experimental results.

The exact value of the exponent ν is controversial. Using a renormalization group approach, Le Guillou and Zinn-Justin[17] have estimated that $\nu = 0.588 \pm 0.0015$. In Table I, we also give estimates of $A(f)$ and $g(f)$ using this value for ν. Although the values of $A(f)$ are sensitive to ν, the ratios $g(f)$ are relatively insensitive.

We have also analyzed the exact values of $\langle S_N^2(f) \rangle$ that we calculated for small N. Extrapolating to large N yields estimates of $A(f)$ consistent with the Monte Carlo estimates given in Table I.

In Table II, we compare our overall estimates of $g(f)$ with the Monte Carlo results of Zimm,[11] the $\mathcal{O}(\epsilon)$ calculations of Miyake and Freed,[5] the classical result of Zimm and Stockmayer,[3] and experimental results.[2,8,18,19] For $f = 3$

Table III
Estimates of the Amplitudes $B(f)$ for the Mean-Square End-to-End Branch Lengths of Uniform Stars on the Simple Cubic Lattice

	$2\nu = 1.2$		$2\nu = 1.176$		
f	$B(f)$	$B(f)/B(1)$	$B(f)$	$B(f)/B(1)$	$[B(f)/B(1)]_{MF}$[a]
1	1.067 ± 0.015	1	1.21 ± 0.01	1	1
3	1.189 ± 0.005	1.11 ± 0.02	1.35 ± 0.01	1.12 ± 0.02	1.111
4	1.240 ± 0.005	1.16 ± 0.02	1.41 ± 0.01	1.17 ± 0.02	1.166
5	1.284 ± 0.004	1.20 ± 0.02	1.456 ± 0.009	1.20 ± 0.02	1.222
6	1.325 ± 0.007	1.24 ± 0.03	1.50 ± 0.02	1.24 ± 0.03	1.277

[a] From Miyake and Freed.

and 4, the general agreement between the various results is excellent. At $f = 5$ our estimate is distinctly lower than that of Miyake and Freed, and this trend is confirmed at $f = 6$ where their result in considerably above both Monte Carlo estimates and the experimental results. Miyake and Freed themselves suggest that their use of a δ-function pseudopotential is inadequate to account for packing considerations in the "core" region when f becomes large. Their treatment seems to lead to an overestimation of the interference between branches,[20] but it is not clear whether this is due to packing considerations or whether the discrepancy between our estimates and theirs would be reduced by extending their calculation to include terms of order ϵ^2. We further note that for all f our estimates of $g(f)$ are rather close to the Zimm and Stockmayer values, which correspond to the complete absence of excluded-volume interactions. This observation supports the opinion—see section 4 for further discussion—that $g(f)$ is not sensitive to the quality of the solvent.

Finally, we have used our results in Table I to test the scaling prediction[4,6] $g(f) \sim f^{-4/5}$. We find[21] that for $f = 3$, 4, 5, and 6

$$f^{4/5}g(f) = 1.83 \tag{2.1}$$

to within about 1%. This should be compared with the experimental values[4] for uniform stars with $f = 7$–16 polystyrene branches, which lie between 1.99 and 2.41. The corresponding value of $f^{4/5}g(f)$ using the Zimm and Stockmayer theory would be 1.88 to within 1%. In contrast, the Miyake and Freed results are in less good agreement with the Daoud and Cotton predictions. The agreement between our Monte Carlo results and the Daoud and Cotton prediction supports their picture of the outer region of the star but provides no information about the two inner regimes, since our results for $g(f)$ are obtained in the $N \to \infty$ limit.

3. Dimensions of Branches of Uniform Stars

The mean-square end-to-end length of linear polymers with excluded volume has received an enormous amount of attention from theorists.[22] In the case of uniform stars, the increase in the length, over the corresponding value for a linear polymer, is a reflection of the interference between branches. Thus, in this section, we consider the mean-square end-to-end length $\langle R_n^2(f)\rangle$ of a branch of n monomers in a uniform star with f branches. We make use of the expected functional form

$$\langle R_n^2(f)\rangle \sim B(f)n^{2\nu(f)} \tag{3.1}$$

analogous to eq 1.3 for the radius of gyration.

We have estimated $\langle R_n^2(f)\rangle$ using Monte Carlo techniques for $n \leq 50$ and $f \leq 6$ on the simple cubic lattice (sample sizes typically being 500 000) and for $n \leq 30$ and $f \leq 4$ on the square lattice (sample sizes typically being 2×10^6).

One expects that the exponent $\nu(f)$ will be the same as for the radius of gyration, and our data for the cubic lattice

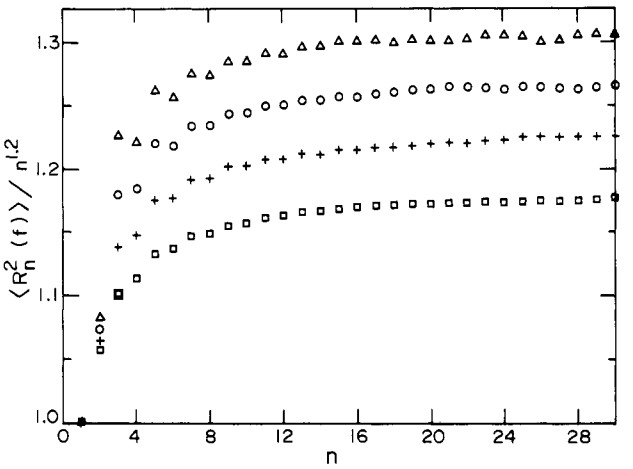

Figure 4. Mean-square end-to-end length of a branch scaled by $n^{1.2}$ as a function of the branch length (n) and the number of branches (f) for the simple cubic lattice: (□) $f = 3$; (+) $f = 4$; (○) $f = 5$; (△) $f = 6$.

Table IV
Estimates of the Amplitudes $B(f)$ for the Mean-Square End-to-End Branch Lengths of Uniform Stars on the Square Lattice

		$B(f)/B(1)$,	
f	$B(f)$	this work	Miyake and Freed
1	0.774 ± 0.005[a]	1	1
3	0.966 ± 0.001	1.25 ± 0.01	1.222
4	1.045 ± 0.002	1.35 ± 0.01	1.332

[a] Reference 27.

are consistent with $\nu(f) = \nu \simeq 0.6$. In Figure 4 we show the n dependence of $\langle R_n^2(f)\rangle/n^{1.2}$ for various values of f. We have estimated the amplitudes $B(f)$ in eq 3.1 by assuming this value of ν and extrapolating against $1/n$ and also by assuming $\nu = 0.588$ and allowing for the presence of a confluent singularity.[17] The estimates of $B(f)$ and of the ratios $B(f)/B(1)$ are given in Table III. As expected, the values of the amplitudes are sensitive to the assumed value of the exponent but the estimates of the amplitude ratios depend only weakly on the value of ν. From the work of Miyake and Freed,[5] we find that

$$B(f)/B(1) = 1 + (1/8)(f-1)(\ln 2 - 1/4)\epsilon + \mathcal{O}(\epsilon^2) \tag{3.2}$$

and give the $\mathcal{O}(\epsilon)$ estimates in Table III.

Corresponding results for the square lattice are shown in Table IV. In this case, there is general agreement[23-27] that the exponent is $\nu = 0.75$, and we adopt Rapaport's estimate[27] for the amplitude $B(1)$, which was obtained by extrapolating $\langle R_n^2(1)\rangle/n^{3/2}$ against n^{-1}. The values for $f = 3$ and 4 were obtained in a similar way.

For small n and $f \leq 4$, we have also calculated $\langle R_n^2(f)\rangle$ exactly for the square, triangular, tetrahedral, and simple cubic lattices. The results for the simple cubic and square lattices are in excellent agreement with our Monte Carlo

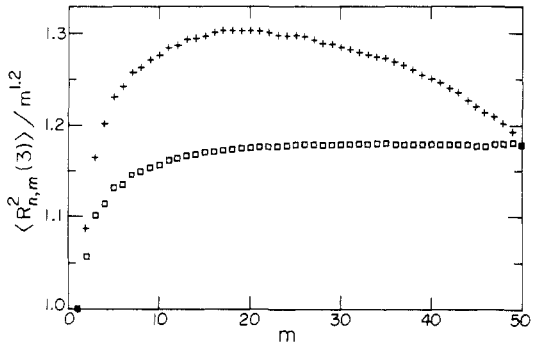

Figure 5. m dependence of $\langle R_{n,m}{}^2(3)\rangle/m^{1.2}$ for the simple cubic lattice: (□) $n = m$; (+) $n = 50$.

estimates. In three dimensions, the data are consistent with the Monte Carlo results given in Table III. For the two-dimensional lattices, we estimate

$$B(3)/B(1) = 1.24 \pm 0.03$$
$$B(4)/B(1) = 1.34 \pm 0.05 \qquad (3.3)$$

in good agreement with the Monte Carlo results in Table IV.

In three dimensions the agreement between the Monte Carlo estimates and those of Miyake and Freed is extremely good, especially for $f = 3$ and 4. However, in two dimensions our ratios are greater than theirs. The source of this discrepancy is not clear but may be attributable to the relatively higher importance of ϵ^2 terms in two dimensions than in three. It is interesting that this effect works in the opposite direction for $B(f)/B(1)$ compared to $A(f)/A(1)$.

We have also examined the "internal dimensions" of a branch of a star. Specifically, we have calculated $\langle R_{n,m}{}^2(f)\rangle$, the mean-square distance between the branch point and the mth monomer in a branch containing a total of n monomers, in a star with f branches. Of course, $\langle R_{n,n}{}^2(f)\rangle \equiv \langle R_n{}^2(f)\rangle$. We have compared $\langle R_{n,m}{}^2(f)\rangle$ with $\langle R_m{}^2(f)\rangle$, with n fixed at 50 monomers, to investigate the expansion of the inner part of a branch by the outer part. In Figure 5, we compare $\langle R_{n,m}{}^2(f)\rangle/m^{1.2}$ and $\langle R_m{}^2(f)\rangle/m^{1.2}$ for $n = 50$ and $f = 3$ on the simple cubic lattice. The expansion of the interior is quite obvious, though it is accentuated by this way of presenting the data. In fact, the maximum fractional increase is roughly 11%, and this occurs at about $m = 17$. For comparison, the corresponding maximum fractional increase for $f = 5$ is about 15% and occurs about halfway along the branch. The greater expansion for $f = 5$ presumably reflects the greater number of monomers contributing to the expansion.

4. Discussion

Simulation studies form a valuable bridge between experiments and theory. By creating an idealized model system, in this case a dilute solution of regular star-branched polymers, it is often possible to test the mathematical approximations inherent in a theoretical treatment. Of the two approaches currently in the literature, the renormalization group work of Miyake and Freed[5] is the easier to connect with, as it makes definite predictions about the numerical values of $g(f)$ and $B(f)/B(1)$. The scaling treatment[4] is harder to test, since it only predicts the functional form of $g(f)$. In both descriptions, however, packing considerations are believed to be important near the core for large f, and, in the long-chain limit, the exponent $\nu(f)$ characterizing the N dependence of the dimensional properties is thought to be independent of f and is identified with ν, the exponent associated with a self-avoiding walk. Our results support both of these points.

In section 2, we calculated the ratio $g(f)$, defined by 1.1, for various lattices with $f \leq 6$ in both two and three dimensions and compared our results with other available estimates for uniform stars. The experimental data in Table II include measurements on polymer systems in both good and Θ solvents. In fact, it is not clear what experimental criterion is suitable for the definition of Θ conditions for these systems. In some experimental work,[1] it is assumed that the appropriate solvent-plus-temperature condition for the branched polymer is the same as that yielding a vanishing second virial coefficient for the linear chain of the same material. It has been suggested[2,11] that $g(f)$ is insensitive enough to solvent effects so as to show no difference, within experimental error, in changing from good to (presumably) Θ conditions. The Miyake and Freed description seems to agree with this view, at least for small f: a plot of $g(f)$ against their excluded-volume parameter (ζ)[28] shows, for various values of f, a slightly positive slope near $\zeta = 0$ (the Gaussian limit of no excluded volume), which increases in magnitude with f. However, in all cases the lines soon approach zero slope, certainly well before $\zeta = \infty$ (the self-avoiding walk limit of complete excluded volume). In addition, notice that the Zimm and Stockmayer values, which were derived under the condition of no interference between branches, are well within the range of experimental and simulation results for all values of f. Therefore, adopting this view that $g(f)$ is relatively insensitive to excluded-volume effects has allowed us to make comparisons with a wider selection of literature estimates. As the data in Table II indicate, for $f = 3$, 4, and 6, our values are in excellent agreement with published work. The comparison with Miyake and Freed's prediction is closest for small f, the differences growing with increased number of branches. These authors themselves expect that their estimates will be poorer for $f \gtrsim 6$, and it is interesting to note from Table II that for smaller f all values are similar, while for $f = 6$ the renormalization group result is significantly larger than the others. A larger value for $g(f)$ implies a larger value for $\langle S_N{}^2(f)\rangle$; i.e., the importance of interactions between branches in swelling the star is being overestimated. The results of Mazur and McCrackin[9] are not represented in Table II because it is not easy to extract the relevant "raw" data from their paper. In that Monte Carlo treatment the authors weight the configurations by a Boltzmann factor which depends on the energetic interactions between nearest nonbonded segments. Unfortunately, the data that are most suitable for comparison with our own, a plot of $g(f)$ vs. $1/N$ for the case of complete excluded volume, show rather variable behavior at large N, and the authors themselves decline to extrapolate to infinite N. Finally for these results, it is worth emphasizing that given the functional form assumed in eq 1.3—this choice having been supported by detailed numerical analysis—the results for $g(f)$ are insensitive to a small change in the exponent ν.

Section 3 focused on the end-to-end length of a single branch. Here it is not possible to make comparisons with real systems. However, in three dimensions the Monte Carlo results and the predictions of Miyake and Freed are in agreement for small f, with the differences becoming more marked as f increases. The discrepancies in two dimensions are much more severe, as might be expected from an $\mathcal{O}(\epsilon)$ treatment. In this section we also investigated the internal dimensions of a branch, examining the expansion of the interior section along the branch due to the outer section of the chain, and found this effect to be small.

The results of this work, along with those of other Monte Carlo studies, show that simulation techniques provide an accessible, realistic approach in describing the dimensional properties of uniform star-branched polymers. In this paper, we have compared our results in three dimensions both with experimental measurements on real systems and with the predictions of the detailed theoretical description developed by Miyake and Freed. With respect to the latter, we find that, typically, our estimates (of a quantity such as $g(f)$) match theirs quite closely for stars having a small number of branches, the differences increasing with f. This indicates that a more extensive theoretical treatment is indeed necessary for systems having a large ($f \geq 6$) number of branches. In two dimensions, the discrepancies are more severe.

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References and Notes

(1) Roovers, J. E.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1983**, *16*, 214.
(2) Huber, K.; Burchard, W.; Fetters, L. J. *Macromolecules* **1984**, *17*, 541.
(3) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.
(4) Daoud, M.; Cotton, J. P. *J. Phys.* **1982**, *43*, 531.
(5) Miyake, A.; Freed, K. F. *Macromolecules* **1983**, *16*, 1228.
(6) Birshtein, T. M.; Zhulina, E. B. *Polymer* **1984**, *25*, 1453.
(7) Vlahos, C. H.; Kosmas, M. K. *Polymer* **1984**, *25*, 1607.
(8) Bauer, B. J.; Hadjichristidis, N.; Fetters, L. J.; Roovers, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 2410.
(9) Mazur, J.; McCrackin, F. *Macromolecules* **1977**, *10*, 326.
(10) Kolinski, A.; Sikorski, A. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 3147.
(11) Zimm, B. H. *Macromolecules* **1984**, *17*, 2441.
(12) Lipson, J. E. G.; Whittington, S. G.; Wilkinson, M. K.; Martin, J. L.; Gaunt, D. S. *J. Phys. A: Math. Gen.* **1985**, *18*, L469.
(13) Wilkinson, M. K.; Gaunt, D. S.; Lipson, J. E. G.; Whittington, S. G. *J. Phys. A: Math. Gen.* **1986**, *19*, 789.
(14) Rosenbluth, A. W.; Rosenbluth, M. N. *J. Chem. Phys.* **1955**, *23*, 356.
(15) We have performed similar calculations in two dimensions for the square ($f \leq 4$) and triangular ($f \leq 6$) lattices.
(16) Provided that $\nu(f) = \nu(1)$ this definition is consistent with eq 1.1.
(17) Le Guillou, J. C.; Zinn-Justin, *J. Phys. Rev. B: Condens. Matter* **1980**, *21*, 3976.
(18) Roovers, J. E.; Bywater, S. *Macromolecules* **1972**, *5*, 385; **1974**, *7*, 443.
(19) Hadjichristidis, N.; Roovers, J. E. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 2521.
(20) In two dimensions, the analysis of exact enumeration data yields $g(3) = 0.68 \pm 0.01$, $g(4) = 0.51 \pm 0.01$, $g(5) \simeq 0.40$, and $g(6) \simeq 0.33$, whereas the $\mathcal{O}(\epsilon)$ calculations of Miyake and Freed give $g(3) = 0.819$, $g(4) = 0.709$, $g(5) = 0.640$, and $g(6) = 0.594$. It seems that in two dimensions, even more than in three, their treatment overestimates the interference between branches, although alternatively this may reflect the increasing importance of the ϵ^2 term in two dimensions.
(21) In two dimensions, the analogous scaling prediction[6] is $g(f) \sim f^{-1}$. We find that all our data ($f \leq 6$) are consistent with $fg(f) \simeq 2.03$, though the agreement is less good than in three dimensions.
(22) See, for instance: Whittington, S. G. *Adv. Chem. Phys.* **1982**, *51*, 1.
(23) Domb, C. *J. Chem. Phys.* **1963**, *38*, 2957.
(24) Derrida, B. *J. Phys. A: Math. Gen.* **1981**, *14*, L5.
(25) Nienhuis, B. *Phys. Rev. Lett.* **1982**, *49*, 1062.
(26) Djordjevic, Z. V.; Majid, I.; Stanley, H. E.; dos Santos *J. Phys. A: Math. Gen.* **1983**, *16*, L519.
(27) Rapaport, D. C. *J. Phys. A: Math. Gen.* **1985**, *18*, L39.
(28) See Figure 4 of ref 5.

Conjectures on the Transport of a Melt through a Gel

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ABSTRACT: Certain networks (with X monomers between branch points) may possibly be swollen by a melt of linear, chemically identical, chains (M monomers per chain). We discuss two basic transport properties of these systems: (1) permeability of the swollen gel with respect to the M chains; (2) diffusion of a labeled M chain. We find *six* different regimes for the permeability, depending on the values of X and M and the distance between entanglements (N_e) in the melt. In one of the six regimes, the permeability K is controlled by the friction of an M chain on surrounding M chains, which are themselves entangled with the network: K then becomes independent of the gel parameters (of X). For diffusion of a labeled M chain, we are led to distinguish only *three* different regimes: free draining, reptation, and "strangulation". In the first two regimes, the diffusion constant $D^*(M)$ is expected to be independent of X. In the strangulation regime, the chain reptates in a tube defined by the network.

I. Introduction

Can a network (X) be swollen by mobile chains (M) of the same chamical composition? Clearly, the invasion of X by M is at best very slow. But, more fundamentally, the final swelling equilibrium is controversial.[1,2] The existence, or absence, of swelling depends on certain weak terms in the free energy; an essential role may be played by the compatibility (or incompatibility) or the cross-linking units with the M chains.[2]

In the present text, we shall assume that the gel is indeed swollen by the M chains. Furthermore, we consider that the network has been synthesized under good solvent conditions so that there is no delicate distinction between chemical neighborhood and spatial neighborhood in the system of cross-links.[3] Finally the distribution of length of the network chains (of X) is assumed to be relatively narrow. Then we can think of the X chains as following a "c^* theorem":[4] each chain occupies a volume with linear dimension D, and each volume D^3 is occupied by one chain. The gel fraction is $\phi = Xa^3/D^3$ where a^3 is a monomer volume. We focus our attention on cases where $\phi \ll 1$, i.e., to gels that are strongly swollen (the M fraction $1 - \phi$ is then close to unity).

The equilibrium swelling laws (the formulas for $D(X,M)$) are then easily deduced from the behavior of a single X chain dissolved in a matrix of (chemically identical) M

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