Hydrodynamic Properties of Flexible Branched Chains. Monte Carlo Nonpreaveraged Calculations for Stars and Preaveraged Results for Combs

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ABSTRACT: The hydrodynamic properties of long flexible branched polymers have been calculated by means of the Kirkwood–Riseman theory. A Monte Carlo procedure that avoids the Oseen tensor preaveraging has been used for uniform stars, and the results have been satisfactorily compared with the experimental data reported by Roovers et al. Also, preaveraged results have been obtained for randomly distributed combs through a method based on Monte Carlo generation of structures. Finally, we have obtained preaveraged values for uniformly branched combs with short and long side chains in order to study the influence of the fraction of backbone on the results.

Introduction

The hydrodynamic properties of flexible branched chains are not fully understood because of the difficulties inherent to their theoretical treatment. In a recent work,¹ we have tackled a systematic study of these properties for Gaussian uniform trifunctional comblike polymers and star chains with different functionalities. This study was performed by means of the preaveraged Oseen tensor version of the Kirkwood–Riseman theory.² The results were given in terms of the usual ratios of the properties of branched polymers, denoted by subscript b, to those of linear polymers with the same molecular weight, denoted by subscript l

\[ h = (f_b)/f_l \]  
\[ g' = [\eta]_b/[\eta]_l \]

where \( f \) is the translational friction coefficient and \([\eta]\) is the intrinsic viscosity.

The values obtained for combs cannot be directly compared with experimental data due to the lack of a wide range of well-characterized uniform comblike samples. However, Roovers et al.³–⁵ have developed adequate procedures for the synthesis of several uniform star polymers of different functionalities and have obtained experimental results from these samples. The comparison of the data obtained by these authors in 9 solvents with our theoretical values extrapolated to an infinite number of theoretical units (i.e., to high molecular weight) is reasonably fair for translational properties of stars with low functionalities, but disagreement is always found in the viscosity results. Some of the discrepancies can be attributed to the fact that this type of polymer does not follow Gaussian distributions of intramolecular distances in the 9 state, as recent experimental⁶ and Monte Carlo⁷ results have pointed out. We think that this effect may be corrected in part by choosing adequate parameters to describe the properties so that the expansion effects are minimized. We will show in the next section that this type of description gives satisfactory results for translational properties, but important deviations are still observed for viscosity. These differences can be mainly attributed to the theoretical hydrodynamic treatment. We believe that the main source of error in the treatment corresponds to the preaveraging of the Oseen tensor since this is the least rigorous approximation contained in the theory.⁸ In fact, our previous studies on rigid structures⁹ show that this approximation gives poor results for viscosity in the case of compact structures and, consequently, we think that the preaveraged theoretical results are not accurate for stars with high functionality, or number of arms, for which, on the other hand, we find the largest discrepancies with respect to the experimental data.

In the present work we try to overcome this difficulty by obtaining nonpreaveraged theoretical results for uniform star polymers. With this aim, we have employed a numerical method inspired in the Monte Carlo calculations performed by Zimm² for linear chains which consists of generating Monte Carlo samples of Gaussianly distributed conformations, taken as instantaneously rigid chains, calculating the hydrodynamic properties of each one of these chains by means of the Kirkwood–Riseman theory applied in a rigorous version and, finally, averaging the results over the conformational samples. The properties of the rigid chains are evaluated through the expressions derived by García de la Torre and Bloomfield,¹⁰ which were also used in a similar scheme that we have previously applied to the study of linear freely jointed, freely rotating, and real polymethylene chains.¹⁰

In the case of comblike polymers we cannot afford a general study based on conformational Monte Carlo calculations because of the high diversity of interesting structures and the huge number of hydrodynamic units involved in some of them. Nevertheless, the structural models considered in our previous work on flexible branched chains¹ admit simple but significant modifications. Here, we investigate several types of nonuniform trifunctional combs through the Kirkwood–Riseman theory in its preaveraged version, i.e., with the same type of hydrodynamic treatment used in ref 1 for uniform chains. Thus, we obtain results for randomly distributed combs as averages over samples of Monte Carlo generated structures. Also, we investigate nonuniform structures composed of uniform side chains and uniform subchains along the backbone but with a number of units (or polymeric mass) in the branches independent of that in the backbone subchains so that the mass fraction in the backbone is not directly determined by the number of branching units. We will call these nonuniform structures uniformly branched combs. Though these structural models for combs do not describe properly most real samples, we hope that the similarities and differences
We call these expressions double-sum formulas. Thus, for translational properties the well-known Kirkwood formula was employed:

\[ f_t = (12\pi^3)^{1/2}r_0h* N^2 \sum_{i=1}^{N} \sum_{j=1}^{N} H_{ij}^{-1} \]  

(6)

The results obtained this way are denoted here with subscript K. For viscosity we applied the double-sum formula provided by the preaveraged version of the treatment proposed by Tsuda \(^1,12\)

\[ [\eta] = (\pi^3/3)^{1/2}N_h h* M^{-1} \sum_{i=1}^{N} \sum_{j=1}^{N} H_{ij}(R_i-R_j)^{-1} \]

(7)

the results being denoted by subscript T.

We also include in Table I values of the ratio between mean radii of gyration, \(g\)

\[ g = \langle S^2 \rangle_b / \langle S^2 \rangle_t \]

(8)

where the values of \(\langle S^2 \rangle\) are simply obtained from

\[ \langle S^2 \rangle = N^2 \sum_{i=1}^{N} \sum_{j=1}^{N} (r_{ij})^2 \]

(9)

The results contained in Table I allow us to sketch some conclusions. First, the experimental data for \(g\) are always greater than the theoretical values, the differences increasing for higher functionalities. Though some degree of rigidity may be present, \(^13\) the main cause of this effect can be attributed to the chain expansion, which is also manifested in Monte Carlo calculations for lattice models. \(^6\)

The expansion should influence the hydrodynamic properties and, consequently, the experimental data for \(h\) and \(g\) should be greater than the theoretical results in the absence of other effects. This prediction holds for the ratios \(h_6\) and \(h_{12}\). In particular, the value of \(h_6\) for \(F = 6\) is very close to the experimental result while for \(F = 12\) and \(18\) the theory gives values significantly lower than the experimental data. The values of \(h_{12}\) are always lower than those of \(h_6\) (differences between the results obtained from eq 3 and 6 are remarkable for these structures in comparison with the 2\% difference found for linear chains \(^1\)). Nevertheless, the values of \(g_6^{F=6}\) and \(g_6^{F=12}\) are considerably higher than the experimental results. Thus, some major problem should remain in the approximate theoretical calculations. The observed fact that such a problem is especially important for viscosity agrees with our previous knowledge that this property is greatly influenced by the hydrodynamic approximations. \(^7\) In order to show explicitly the deficiencies due to the hydrodynamic treatment we try to minimize the expansion effect by performing comparisons in terms of the Flory parameters. For long chains, we have

\[ P = f_t / 6^{1/2}r_0\langle S^2 \rangle_1^{1/2} \]

(10)

for friction, and

\[ \phi = [\eta]M / 6^{3/2}\langle S^2 \rangle_1^{3/2} \]

(11)

for viscosity. These parameters are not sensitive to molecular dimensions, depending mainly on the hydrodynamic shape of the chain. Defining the corresponding ratios

\[ r_p = P_b / P_t = h / g^{1/2} \]

(12)

and

\[ r_o = \phi_b / \phi_t = g^{3/2} / g^{3/2} \]

(13)

these ratios cannot be affected much by a uniform ex-
Hydrodynamic Calculations for Branched Chains

<table>
<thead>
<tr>
<th>Table II</th>
<th>Theoretical and Experimental Values of the Ratios ( r_p ) and ( r_s ) for Long Uniform Stars*</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F )</td>
<td>( 6 )</td>
</tr>
<tr>
<td>( (r_p)_K )</td>
<td>1.19</td>
</tr>
<tr>
<td>( (r_p)_F )</td>
<td>1.29</td>
</tr>
<tr>
<td>( (r_p)_{MC} )</td>
<td>1.34</td>
</tr>
<tr>
<td>( (r_p)_{MC} )</td>
<td>1.28 ± 0.01</td>
</tr>
<tr>
<td>( (r_p)_F )</td>
<td>2.42</td>
</tr>
<tr>
<td>( (r_p)_{MC} )</td>
<td>2.33</td>
</tr>
<tr>
<td>( (r_s)_{MC} )</td>
<td>2.02 ± 0.07</td>
</tr>
<tr>
<td>( (r_s)_{MC} )</td>
<td>2.11</td>
</tr>
<tr>
<td>( \sigma^2 )</td>
<td>2.22</td>
</tr>
</tbody>
</table>

*See text for notation. From the theoretical values of the properties combined with the Monte Carlo nonpreaveraged values for long linear chains.

<table>
<thead>
<tr>
<th>Table III</th>
<th>Indirect Estimates and Preaveraged Values of ( g' ), together with Monte Carlo Nonpreaveraged Values of ( g' ), ( h^2 ), and ( h ), for Long Uniform Stars</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F )</td>
<td>( 6 )</td>
</tr>
<tr>
<td>( g'_{\text{ther}} )</td>
<td>0.67</td>
</tr>
<tr>
<td>( g' )</td>
<td>0.69</td>
</tr>
<tr>
<td>( h^2 )</td>
<td>0.64</td>
</tr>
<tr>
<td>( h^2_{MC} )</td>
<td>0.58 ± 0.02</td>
</tr>
<tr>
<td>( h^2_{MC} )</td>
<td>0.67 ± 0.04</td>
</tr>
<tr>
<td>( h^2_{MC} )</td>
<td>0.86 ± 0.01</td>
</tr>
</tbody>
</table>

The properties for this chain are calculated in a rigorous way. Then we perform averages of the properties over the values obtained for all the different conformations in each sample. The final results are given as the statistical means and deviations evaluated from the averages corresponding to the different samples. These averages are treated, consequently, as if they were independent measurements of an experimental magnitude.

(c) Hydrodynamic Properties of Rigid Structures.

In the hydrodynamic calculations we have used a rigorous version of the Kirkwood–Riseman theory that includes numerical solution of the interaction equations and employs the nonpreaveraged tensor for hydrodynamic interaction between chain elements of finite size. The translational properties are referred to the center of diffusion and \( [\eta] \) is calculated at the correct viscosity center. The formalism and computational algorithms have been reviewed and summarized in a previous paper.

The calculation of properties for each chain in the samples avoids therefore both orientational and conformational preaveraging.

The translational friction coefficient, rotational friction coefficient, \( f \), and the intrinsic viscosity can be expressed in the following dimensionless forms:

\[
f^* = f_i / 6\pi\eta_0 b^3
\]

and

\[
[\eta]^* = [\eta] M / N_\lambda b^3
\]
Monte Carlo Results for Different Types of Gaussian Chains

<table>
<thead>
<tr>
<th>F</th>
<th>N</th>
<th>(\langle f^*\rangle_K)</th>
<th>(\langle f^*\rangle_{np})</th>
<th>(\langle f^*\rangle_{K})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>19</td>
<td>1.22 + 0.01</td>
<td>1.34 + 0.01</td>
<td>4.22 + 0.01</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>1.41 - 0.02</td>
<td>1.57 - 0.02</td>
<td>6.9 - 0.3</td>
</tr>
<tr>
<td>2</td>
<td>37</td>
<td>1.70 + 0.05</td>
<td>1.91 + 0.04</td>
<td>11.9 + 0.6</td>
</tr>
<tr>
<td>2</td>
<td>49</td>
<td>1.98 + 0.05</td>
<td>2.23 + 0.05</td>
<td>19 + 1</td>
</tr>
<tr>
<td>2</td>
<td>55</td>
<td>2.09 + 0.06</td>
<td>2.37 + 0.07</td>
<td>23 + 2</td>
</tr>
<tr>
<td>6</td>
<td>19</td>
<td>1.04 + 0.01</td>
<td>1.22 + 0.01</td>
<td>3.19 + 0.04</td>
</tr>
<tr>
<td>6</td>
<td>25</td>
<td>1.19 + 0.01</td>
<td>1.40 + 0.01</td>
<td>4.92 + 0.03</td>
</tr>
<tr>
<td>6</td>
<td>37</td>
<td>1.41 + 0.03</td>
<td>1.69 + 0.03</td>
<td>8.6 + 0.5</td>
</tr>
<tr>
<td>6</td>
<td>49</td>
<td>1.61 + 0.01</td>
<td>1.96 + 0.01</td>
<td>13.3 + 0.3</td>
</tr>
<tr>
<td>12</td>
<td>25</td>
<td>1.014 + 0.005</td>
<td>1.240 + 0.002</td>
<td>3.14 + 0.03</td>
</tr>
<tr>
<td>12</td>
<td>37</td>
<td>1.19 + 0.01</td>
<td>1.50 + 0.01</td>
<td>5.60 + 0.14</td>
</tr>
<tr>
<td>12</td>
<td>49</td>
<td>1.35 + 0.02</td>
<td>1.72 + 0.02</td>
<td>8.5 + 0.3</td>
</tr>
<tr>
<td>18</td>
<td>19</td>
<td>0.86 + 0.01</td>
<td>1.032 + 0.005</td>
<td>1.72 + 0.03</td>
</tr>
<tr>
<td>18</td>
<td>37</td>
<td>1.07 + 0.01</td>
<td>1.38 + 0.01</td>
<td>4.2 + 0.1</td>
</tr>
<tr>
<td>18</td>
<td>55</td>
<td>1.25 + 0.02</td>
<td>1.65 + 0.01</td>
<td>7.3 + 0.3</td>
</tr>
</tbody>
</table>

See text for notation.

Such conformations can pose some problems in the subsequent hydrodynamic calculations that can be avoided in the case of the nonpreaveraged values. Thus, we have used the Rotne–Prager interaction tensor for overlapping elements, while Zimm8 employed an ad hoc expression based on the friction coefficient of two interpenetrating Gaussian segments. The two procedures are expected to yield nearly identical results, as concluded in our earlier study.10 In the case of calculations with preaveraging, we have found that for translation our results for individual overlapping conformations may deviate more than usual from the nonpreaveraged values but they are still reasonable. However, we often get clearly erratic, unphysical results for viscosity. Therefore \(\eta_P\) may not be significant and it has been left out of the analysis of results that we present next.

(d) Numerical Treatment of the Final Results. We have obtained results for uniform stars with functionalities 

\(F = 2, 6, 12, \text{ and } 18 \) (\(F = 2\) corresponds to a linear chain whose properties are employed in the evaluation of the ratio) with a total number of units \(N = 19, 25, 37, 49, \text{ and } 55\). Four different samples have been built in all cases. (Sometimes the last sample could not be completed due to computational time limitations but the weighted contribution of its generated conformations was considered together with the results associated with the first three samples.) The number of conformations contained in each sample, \(n\), has been chosen according to the value of \(N\) as follows: \(N = 19, n = 50; N = 25, n = 40; N = 37, n = 25; N = 49, n = 15; N = 55, n = 12\). The arithmetic means and statistical deviations for the reduced properties are given in Table IV.

The results for the linear chains can be compared with the values previously obtained by Zimm8 with the same molecular model and using a similar numerical method, with the above-mentioned slight theoretical differences in the description of the hydrodynamic interaction between units. Following the treatment of results performed by Zimm, we obtain the parameter \(P\) from the values of \(f^*\) as

\[
P = 6\pi \langle f^* \rangle / (N - 1)^{1/2}
\]

and we have plotted \(P_{np} - P_K\) (i.e., the difference between the Monte Carlo results obtained for \(f^*_K\) and \(f^*_{np}\)) vs. \(N^{1/2}\). The intercept yielded by this plot (i.e., the difference between the nonpreaveraged and the Kirkwood formula values extrapolated to an infinite number of units) together with the limit \(P_K = 5.11\) for a long flexible linear chain2 serves as an estimate of \(P_{np}\) in the same limit. We have obtained \(P = 6.08\), in good accordance with Zimm’s result \(P = 5.99\) and with recent experimental estimates for \(P\) ranging between the values \(P_{exp} = 5.7 - 6.0.18\).

The parameter \(\phi\) related to viscosity is calculated for linear chains of arbitrary length from

\[
\phi = N_\kappa \langle \eta_P \rangle / (N - 1)^{3/2}
\]

In this case, however, we cannot apply a similar treatment using a long-chain reference value corresponding to the double-sum formula since, as previously explained, we have not computed the values of \(\langle \eta_P \rangle\) for individual conformations and therefore, we ignore the differences between the nonpreaveraged and the double-sum results \(\phi_{np} - \phi_P\) for different values of \(N\). Nevertheless, if guided by Zimm’s conclusions one admits that the nonpreaveraged values of \(\phi\) should be almost independent of \(N\); an estimation of the limit result for \(\phi_{np}\) corresponds to the simple arithmetic mean of the results obtained with all the different values of \(N\) used for the linear chains in this work. In this way we have obtained \(\phi_{np} = 2.54 \times 10^2\), also in excellent accordance with Zimm’s \(\phi_\kappa = 2.51 \times 10^2\) and with the experimental estimation \(\phi_{exp} = 2.5 \times 10^2\).

(Similar results for \(P\) and \(\phi\) have been also recently obtained by Oono and Kohimoto, who applied a theoretical treatment based on the renormalization group theory.15) Thus our procedure is confirmed to be equivalent to the Zimm method from the practical point of view, both reproducing the experimental estimates for \(P\) and \(\phi\). Therefore, though some theoretical considerations lead to the conclusion that the Monte Carlo samplings over rigid conformations are only able to give an upper limit for the hydrodynamic properties,18,19 we think that the remaining differences are small and within the statistical or experimental error range for most significant cases.

From the results for the branched and linear chain with the same number of units, we have obtained the Monte Carlo nonpreaveraged values for \(h\) and \(g^*, h_{np}\) and \(g^*_{np}\), and the Monte Carlo values for \(h_K\). We also obtained in this way numerical nonpreaveraged results, \(h^*_{np}\) for the ratio of rotational friction coefficients

\[
h = \langle f^*_1 \rangle / \langle f^*_h \rangle
\]

We have estimated the high molecular weight values of the ratios as the intercepts of plots of these quantities vs. \(N^{-1}\), as we did in our previous work with the preaveraged results.1 However, since the Monte Carlo ratios present a certain statistical error and, moreover, we do not have results available for many values of \(N\), a numerical fitting method is now preferred to the graphic procedure previously used.1 Thus our results have been fitted by a standard numerical routine, assuming a linear dependence on \(N^{-1}\). Regression has been carried out by using the maximum likelihood principle as described by Anderson et al.20 This method provides the fitting parameter values together with their estimated uncertainties.

The nonpreaveraged extrapolated Monte Carlo ratios obtained as the intercepts with this procedure are denoted by subscript MC and are shown in Table III. The ratios \(r_p\) and \(r_g^*\) calculated from \(h_{np}, g^*_{np}\) and \(g^*_{np}\) through eq 12 and 13 are shown in Table II and are also denoted by subscript MC. The extrapolated Monte Carlo values for \(h_K\) are not shown explicitly in the tables as they coincide with the results obtained from eq 6, within the statistical error range, in all cases.

(e) Discussion. From the results shown in Tables II and III we have established some conclusions. With respect to the ratio \(h^*\), it should be considered that the
the accuracy of the indirect theoretical method described above is comparable to that of empirical estimates of \( g' \) as \( h_{\exp}^1 \) or \( g_{\exp}^{1/2} \).

The Monte Carlo values of \( r_2 \) and \( r_3 \) for \( F = 18 \) are practically coincident with the ratios of the hydrodynamic parameters of a hard sphere to the Monte Carlo nonpreaveraged parameters of a long linear chain, also included in Table II. Thus, the hard-sphere hydrodynamic behavior must hold for higher functionalities, and, consequently, further numerical simulations for these chains would be irrelevant. These calculations would be, on the other hand, difficult to accomplish, due to the high number of chain units that would be involved in the theoretical models.

**Preaveraged Results for Nonuniform Combs**

(a) Random Combs. We have performed calculations with the preaveraged formulas for nonuniform trifunctional comb-like polymers with a random distribution of units among the different subunits. The results have been obtained as averages over Monte Carlo samples of structures. For each structure we have evaluated the hydrodynamic properties according to eq 3 and 4, following the numerical procedures and graphical extrapolations to high molecular weight (or to \( N^{-1} = 0 \)) detailed in our previous work for uniform chains.1 Our aim has been to study the influence of random distribution with respect to the uniform structural model, while maintaining the other factors constant, including the hydrodynamic treatment.

The definition of structures in the random samples has been made by taking into account the conditional probabilities associated with the number of units associated in each subchain. As we build chains with \( N \) units and \( p \) subchains (for our trifunctional combs \( p = 2m + 1, m \) being the number of branching points), the number of units in subchain \( i \), \( n_i \), must be between the limits

\[
1 \leq n_i \leq N - 1 - p + i - \sum_{j=1}^{i-1} n_j = N_m, \quad 1 \leq i \leq p - 1
\]  

if one has previously assigned the number of units for subchains 1 to \( i - 1 \). For the last subchain, \( p \), the number of units is determined as

\[
n_p = N - 1 - \sum_{j=1}^{p-1} n_j
\]

Smaller values of \( n_i \) should have higher conditional probabilities since they allow us to perform more different arrangements of units among the subsequent subchains. We have verified that the conditional probability for one of the \( N_m \) possible values of \( n_i, m_i \), is given by

\[
p(m_i) = p'(n_i) / \sum_{n_i=1}^{N_m} p'(n_i)
\]

where the different nonnormalized conditional probabilities \( p'(n_i) \) are evaluated as

\[
p'(n_i) = \frac{\left( N - 2 - \sum_{j=1}^{i-1} n_j \right)}{p - i - 1}
\]

for each of the subunits 1 to \( i - 1 \). Our Monte Carlo procedure consists of dividing the range of real numbers between 0 and 1 into \( N_m \) intervals with lengths given by the probabilities corresponding to the different values of \( n_i \). Then we use a pseudorandomly chosen number within this range to define \( n_i \), according to the interval to which this selected number belongs. This process applies for every one of the subunits.

We can see in Table III that the values of \( g'_{\text{MC}} \) differ drastically from the Zimm and Kilb estimation, \( g' = g^{1/2} \). Combining this expression with eq 13, we get \( n_o = g' \), whose performance is revealed to be very poor in Table II. Therefore, our Monte Carlo nonpreaveraged calculations reverse the preliminary conclusions about the indirect estimates of \( g' \) obtained with the preaveraged values. That is, the Zimm and Kilb approximation should be disregarded for this type of polymer while the Stockmayer and Fixman expression may be tentatively accepted. In fact, the accuracy of the indirect theoretical method described

\[
N_{\text{MC}} = \left( \frac{15}{100} \right)^{1/2}
\]

and, therefore, \( h' \) and \( g' \) become identical. However, our Monte Carlo nonpreaveraged results reveal remarkable differences between their respective values, \( h' \) being always higher than \( g' \). Unfortunately, there is not any experimental technique that is currently able to give reliable data for \( f_r \) in order to test these theoretical results.

The values of \( h_p \) presented in Table I and those of \( h_{\text{MC}} \) shown in Table III are very similar. Nevertheless, the Monte Carlo results for \( g' \) differ substantially from the preaveraged ones. Moreover, the comparison with experimental data in Table II shows that the preaveraged and Monte Carlo values are in good agreement with the data for the ratio \( r_p \), related to the translational properties, but only the Monte Carlo results for \( r_o \), associated with viscosity, are similar to the experimental estimates.

It should be remarked that both \( r_p \) and, especially, \( r_o \) are very sensitive to statistical or experimental errors in the properties so that the 20% difference between the Monte Carlo and experimental values of \( r_o \) found for the star chain with \( F = 18 \) can be considered fairly small, though indicative of remaining deficiencies in the theoretical model. Perhaps a more realistic description of the chain in its \( \Theta \) state could yield more accurate theoretical values for the hydrodynamic properties.

In any case, it seems clear that the preaveraged treatment is adequate for the ratio \( r_p \) but is not reliable enough to predict \( r_o \), for which a direct evaluation should be done through Monte Carlo sampling combined with calculations avoiding preaveraging. The good performance of the preaveraged formulas for \( r_p \) is due to a quantitatively similar effect of the preaveraging approximation on the linear and star chain since, as we have described above, there is a 15% difference between the preaveraged and the Monte Carlo nonpreaveraged values of \( P \) for long linear chains. Thus, it is apparent that we should expect a similar difference for any star chain of high molecular weight.

If one accepts the values of \( (r_p)_p \) as correct and ignores the expansion effects, the preaveraged values \( h_p \) can be also accepted. Then according to the Stockmayer–Fixman relation, eq 15, the quantity \( h_p^2 \) would constitute an adequate estimation for \( g' \). Table III shows that the values \( g'_{\text{MC}} \) and \( h_p^2 \) are in fact in good agreement, especially for high functionalities. A subsequent evaluation of \( r_o \) from \( h_p^2 \) would eliminate most expansion effects and give us a theoretical quantity obtained from the preaveraged expressions for translational properties that can be compared with experimental viscosity data. In Table II we include the values \( (r_o)_{\text{ind}} \) obtained in this indirect way. It can be observed that these values, though not in complete agreement with those obtained directly with the Monte Carlo method or with the experimental results, can be considered at least as rough estimations, as they are significantly better than the results calculated from the preaveraged viscosity formula, \( (r_o)_p \).

We can see in Table III that the values of \( g'_{\text{MC}} \) differ drastically from the Zimm and Kilb estimation, \( g' = g^{1/2} \). Combining this expression with eq 13, we get \( n_o = g' \), whose performance is revealed to be very poor in Table II. Therefore, our Monte Carlo nonpreaveraged calculations reverse the preliminary conclusions about the indirect estimates of \( g' \) obtained with the preaveraged values. That is, the Zimm and Kilb approximation should be disregarded for this type of polymer while the Stockmayer and Fixman expression may be tentatively accepted. In fact, the accuracy of the indirect theoretical method described

\[
N_{\text{MC}} = \left( \frac{15}{100} \right)^{1/2}
\]
The final results are obtained as arithmetic means of the hydrodynamic properties over all the generated structures. We have used for every type of chain several statistical samples, each composed of 30 structures. Table V contains the extrapolated values for \( h_p \) and \( g'_b \), calculated in this way, together with the extrapolated Monte Carlo results for \( g \) and \( h_K \), obtained from application of eq 8 and 6, respectively, for each structure. The values of \( g \) and \( h_K \) in Table V are in good agreement with the results obtained for these ratios from the analytical formulas derived by Kurata and Fukatsu; this confirms the validity of our numerical methods. In Figures 1 and 2, \( p^{1/2}h_p^{-1} \) (proportional to the sedimentation coefficient \( s \) and inversely proportional to \( f_b \) and \( p^{1/2}g'_b \) (proportional to \( [\eta] \)) are plotted vs. \( p \) (proportional to the molecular weight) and compared to equivalent results for uniform combs. It can be observed that the curves for uniform and random structures exhibit similar trends, differing only in the absolute values of the properties. Since the proportionality constant relating \( p \) to \( M \) is not usually known for experimental samples, it seems difficult to distinguish between both types of distributions from the molecular weight dependence of their hydrodynamic data.

On the other hand, we can notice that random chains yield higher values for both \( h \) and \( g' \) than uniform polymers. Thus, the type of distribution has a noticeable influence in the estimation of the number of branching units from experimental data of these ratios. As an illustration, in Figure 3 we show \( g'_b \) vs. \( m^{-1} \) for both distributions. It can be observed that a single value of \( g'_b \) corresponds to significantly different values of \( m \) for the two types of chains. Differences become smaller as \( m \) increases so that for \( m^{-1} = 0 \) we reach the common value \( g' = 2^{-3/2} \), since the polymer adopts the hydrodynamic shape of a linear chain.²

(b) Uniformly Branched Combs with Short or Long Side Chains. We have also obtained numerical results from the preaveraged formulas, eq 3 and 4, for chains with the same number of units in all the backbone subchains but with shorter or longer uniform subchains. The final values for the properties have been evaluated by graphical extrapolations to \( N^{-1} = 0 \), following the scheme used previously for completely uniform chains.

Defining \( n_b \) as the ratio of the number of units in the side chains to that of the backbone subchains, this variable is added to \( N \) and \( m \) in the description of the polymer structure. By introducing \( n_b \) as a variable, we try to account for the fact that, in many instances, synthetic procedures yield samples with nonrelated values of \( m \) and \( \lambda \), the fraction of polymer in the backbone

\[
\lambda = \frac{(m + 1)}{[n_b (F - 2) + m + 1]}
\]

Figures 4 and 5 contain the extrapolated values of \( h_p / g^{1/2} \) and \( \gamma_p \) (i.e., the exponent \( \gamma \) calculated from \( g'_b \)) vs. \( \lambda \) for different values of \( m \). It can be noticed that these quantities are in general dependent of both \( \lambda \) and \( m \). In fact, \( \gamma_p \) seems to depend strongly on \( m \), while \( h_p / g^{1/2} \) is almost independent of this variable for \( n_b < 1 \) (short side chains). Though there is some experimental basis²⁴ for performing universal representations of \( \gamma \), we have verified that, for the theoretical preaveraged values, these representations depend on \( m \) in a complicated way, resembling somewhat the plots shown in Figures 4 and 5.

We believe that the results summarized in Figures 4 and 5, though not totally conclusive, give some idea about how to extract information on the branching structure of this type of sample and, perhaps more significantly, point out

---

### Table V

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<th>( g )</th>
<th>( h_K )</th>
<th>( h_p )</th>
<th>( g'_b )</th>
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</table>

*See text for notation.*

---

Figure 1. \( p^{1/2}h_p^{-1} \) vs. \( p \) for long uniform (broken line) and randomly distributed (solid line) comb-like polymers.

Figure 2. \( p^{1/2}g'_b \) vs. \( p \) for long uniform (broken line) and random (solid line) combs.

Figure 3. \( g'_b \) vs. \( m^{-1} \) for long uniform (broken line) and random (solid line) combs. The point at \( m^{-1} = 0 \) corresponds to the theoretical limit value of \( g' \).
Hydrodynamic Calculations for Branched Chains

the difficulties inherent in the study of hydrodynamic properties of poorly characterized branched polymers. Of course, heterogeneous distribution of units, not introduced in these calculations, may have a quantitative influence on the final values, as we have shown above for \( n_b = 1 \), though we think that it should not change much the qualitative description of the properties. It is possible that more noticeable variations are found by introducing a more correct nonpreaveraged hydrodynamic treatment, such as the one used in this work to study uniform stars. However, an exhaustive rigorous investigation that considers all the variables describing this type of comb is beyond our current computing possibilities and, therefore, the present analysis of the separate influence of the different contributions seems to be the only feasible approach.

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References and Notes