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

Juan J. Freire,* Rosa Prats, and Jesús Pla

Departamento de Quimica Fisica, Facultad de Ciencias Quimicas, Universidad Complutense, Madrid-3, Spain

José Garcia de la Torre

Departamento de Quimica Fisica, Facultad de Ciencias, Universidad de Murcia, Murcia, Spain. *Received November 2, 1983*

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

$$h = (f_t)_b/(f_t)_l \quad (1)$$

$$g' = [\eta]_b/[\eta]_l \quad (2)$$

where f_t 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 Θ 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 Θ state, as recent experimental[5] and Monte Carlo[6] 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.[2] In fact, our previous studies on rigid structures[7] 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 Zimm[8] 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 Garcia de la Torre and Bloomfield,[9] 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 chains[1] 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 backgone 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

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Table I
Experimental[3-5] and Previously Obtained[1] Theoretical Results for Long Uniform Star Polymers of Different Functionalities[a]

	F		
	6	12	18
g_{theor}	0.45	0.24	0.16
g_{exptl}	0.46	0.28	0.23
h_K	0.80	0.63	0.53
h_p	0.86	0.73	0.65
h_{exptl}	0.89	0.81	0.76
g'_T	0.72	0.54	0.45
g'_p	0.69	0.51	0.42
g'_{exptl}	0.63	0.41	0.35
$g^{1/2}_{exptl}$	0.68	0.53	0.48
h^3_{exptl}	0.70	0.53	0.44

[a] The theoretical hydrodynamic ratios are denoted as explained in text.

found in their properties with respect to those obtained for uniform chains, evaluated in all cases with the same preaveraged hydrodynamic treatment, together with the conclusions reached from the more rigorous study for uniform stars, may be helpful for a better general understanding of the experimental data of branched structures.

Nonpreaveraged Treatment for Stars

(a) Theoretical and Experimental Background. A summary of the previously reported theoretical results[1] for Gaussian stars in the limit of high molecular weight (infinite number of theoretical units, N) is shown in Table I, together with the experimental data for flexible star polymers obtained by Roovers et al.[3-5] in Θ solvents. Some of the data have been reported very recently[5] so that they could not be compared with our theoretical values in our previous work.[1] Three different values of the functionality, F, are included: $F = 6$, 12, and 18. The results affected by subscript p were obtained from theoretical expressions derived from the preaveraged version of the Kirkwood–Riseman theory. That is, for the translational friction coefficient we used

$$f_t = (12\pi^3)^{1/2}\eta_0 bh^* \sum_{i=1}^{N}\sum_{j=1}^{N}(\mathbf{H}^{-1})_{ij} \tag{3}$$

and for the intrinsic viscosity

$$[\eta] = (\pi^3/3)^{1/2}N_A bh^* \sum_{i=1}^{N}\sum_{j=1}^{N}(\mathbf{H}^{-1})_{ij}\langle \mathbf{R}_i\cdot\mathbf{R}_j\rangle \tag{4}$$

where N_A is the Avogadro number, η_0 is the solvent viscosity, b is the statistical distance between neighboring units (η_0 and b do not intervene in the calculation of ratios g' and h), h^* is a hydrodynamic parameter set to be $h^* = 0.25$,[1] $\mathbf{R}_k$ represents the vector position of unit k referred to a frame centered at the center of masses of the chain (which coincides with the viscosity center when the preaveraging approximation is performed[7]), and $\mathbf{H}$ is the the hydrodynamic matrix, defined as

$$H_{ij} = 1 \qquad \text{for } i = j$$

$$H_{ij} = (\pi/3)^{1/2}bh^*\langle r_{ij}^{-1}\rangle \qquad \text{for } i \neq j \tag{5}$$

where $\langle r_{ij}^{-1}\rangle$ is the mean reciprocal distance between units i and j. The conformational geometric averages involved in the formulas are obtained from the mean quadratic distances $\langle r_{ij}^2\rangle$, which are easily evaluated for any Gaussian branched structure (see ref 1 for more details).

Other theoretical results were obtained by means of simpler though less rigorous expressions that do not require the inversion of matrix $\mathbf{H}$. We call these expressions double-sum formulas. Thus, for translational properties the well-known Kirkwood formula was employed:

$$f_t = (12\pi^3)^{1/2}\eta_0 bh^* N^2[\sum_{i=1}^{N}\sum_{j=1}^{N}H_{ij}]^{-1} \tag{6}$$

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[11,12]

$$[\eta] = (\pi^3/3)^{1/2}N_A bh^* M^{-1}[\sum_{i=1}^{N}\langle R_i^2\rangle]^2[\sum_{i=1}^{N}\sum_{j=1}^{N}H_{ij}\langle \mathbf{R}_i\cdot\mathbf{R}_j\rangle]^{-1} \tag{7}$$

the results being denoted by subscript T.

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

$$g = \langle S^2\rangle_b/\langle S^2\rangle_l \tag{8}$$

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

$$\langle S^2\rangle = N^{-2}\sum_{i}^{N}\sum_{j}^{N}\langle r_{ij}^2\rangle \tag{9}$$

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_p and h_K. In particular, the value of h_p 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_K are always lower than those of h_p (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'_p and g'_T 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

$$P = f_t/6^{1/2}\eta_0\langle S^2\rangle^{1/2} \tag{10}$$

for friction, and

$$\phi = [\eta]M/6^{3/2}\langle S^2\rangle^{3/2} \tag{11}$$

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

$$r_P = P_b/P_l = h/g^{1/2} \tag{12}$$

and

$$r_\phi = \phi_b/\phi_l = g'/g^{3/2} \tag{13}$$

these ratios cannot be affected much by a uniform ex-

Table II
Theoretical and Experimental Values of the Ratios r_P and r_ϕ for Long Uniform Stars[a]

	F			
	6	12	18	rigid sphere[b]
$(r_P)_K$	1.19	1.29	1.32	
$(r_P)_p$	1.29	1.50	1.62	
$(r_P)_{exptl}$	1.31	1.54	1.59	
$(r_P)_{MC}$	1.28 ± 0.01	1.53 ± 0.02	1.65 ± 0.02	1.62 ± 0.03
$(r_\phi)_T$	2.42	4.68	7.04	
$(r_\phi)_p$	2.33	4.45	6.58	
$(r_\phi)_{exptl}$	2.02	2.77	3.17	
$(r_\phi)_{MC}$	1.92 ± 0.07	3.2 ± 0.3	3.7 ± 0.5	3.66 ± 0.06
$(r_\phi)_{ind}$	2.11	3.31	4.29	
g^{-1}_{theor}	2.22	4.17	6.25	

[a] See text for notation. [b] From the theoretical values of the properties combined with the Monte Carlo nonpreaveraged values for long linear chains.

Table III
Indirect Estimates and Preaveraged Values of g', together with Monte Carlo Nonpreaveraged Values of g', h^r, and h, for Long Uniform Stars

	F		
	6	12	18
$g^{1/2}_{theor}$	0.67	0.49	0.40
g'_p	0.69	0.51	0.42
h_p^3	0.64	0.39	0.27
g'_{MC}	0.58 ± 0.02	0.38 ± 0.03	0.24 ± 0.03
h^r_{MC}	0.67 ± 0.04	0.47 ± 0.03	0.28 ± 0.01
h_{MC}	0.86 ± 0.01	0.75 ± 0.01	0.66 ± 0.01

pansion of the polymer. In Table II we see that the ratios $(r_P)_p$ calculated from eq 1, 3, 8,9, and 12 are in good agreement with the ratios obtained from experimental results. Notwithstanding, the values of $(r_\phi)_p$ obtained from eq 2, 4, 8, 9, and 13 are much higher than the experimental ones. Therefore, it seems apparent that for this type of polymer the translational properties are adequately described with the preaveraged Kirkwood–Riseman theory (in other words, theoretical deviations may fall within the range of experimental error), but the same type of treatment does not yield reasonably good results for viscosity.

From a practical point of view, it is convenient to know whether the ratios associated with the viscosity can be calculated from other properties through approximate expressions. Thus, the exponent γ defined as

$$g' = g^\gamma \tag{14}$$

with the value $\gamma \simeq 0.5$ proposed by Zimm and Kilb[14] may allow us to estimate g' from the results for g. However, Table I shows the experimental disagreement between g' and $g^{1/2}$. On the other hand, we have considered the Stockmayer–Fixman relation[15]

$$g' \simeq h^3 \tag{15}$$

but, as also can be observed in Table I, this is not in good accordance with the experimental values of h^3 and g'. Moreover, eq 15 is not consistent with the preaveraged theoretical results, while these results seem to support the validity of eq 14 with $\gamma = 0.5$, as the different theoretical values denoted by subscript p in Table III point out. All these contradictory conclusions reinforce the need for performing nonpreaveraged calculations with a more refined version of the Kirkwood–Riseman theory in order to obtain more correct theoretical results. This is done in this work by means of a Monte Carlo sampling procedure.

(b) Monte Carlo Calculations of Conformational Properties. We have generated different statistical samples of conformations for each type of Gaussian uniform star polymer, defined according to its functionality. Each sample is characterized by a specific seed number that initiates the generation of a sequence of Gaussianly distributed numbers whose mean value and squared deviation are equal to 0 and $^1/_3$, respectively. The sequence is obtained from samples of pseudorandom numbers yielded by a standard Fortran subroutine. The Gaussian values are then assigned to describe the coordinates x_i,y_i,z_i of the different bond vectors constituting the conformations included in the sample. Therefore, these conformations are composed of randomly oriented bond vectors with Gaussianly distributed lengths so that the statistical bond length is $b = 1$ in arbitrary units. If the center of coordinates is placed at the central unit of the star, N, the coordinates of the other theoretical elements are given by

$$X_i = x_i; \qquad Y_i = y_i; \qquad Z_i = z_i \tag{16a}$$

when unit i is one of the F first neighbors of unit N, and

$$X_i = X_{i-1} + x_i; \qquad Y_i = Y_{i-1} + y_i; \qquad Z_i = Z_{i-1} + z_i \tag{16b}$$

otherwise.

Once all the coordinates have been computed for a given conformation in a sample, this conformation is treated as a rigid chain composed of N friction units, each with a friction coefficient ξ

$$\xi = (12\pi^3)^{1/2}\eta_0 b h^* \tag{17}$$

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[9] and summarized in a previous paper.[10] 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_r, and the intrinsic viscosity can be expressed in the following dimensionless forms:

$$f_t^* = f_t/6\pi\eta_0 b \tag{18}$$

$$f_r^* = f_r/6\pi\eta_0 b^3 \tag{19}$$

and

$$[\eta]^* = [\eta]M/N_A b^3 \tag{20}$$

The nonpreaveraged values of these properties will be hereafter indicated as $(f_t^*)_{np}$, $(f_r^*)_{np}$, and $[\eta]_{np}^*$. The computed algorithm used to obtain the nonpreaveraged values also yielded the double-sum results for translation $(f_t^*)_K$ (eq 6) and $[\eta]_T^*$ (eq 7) for the viscosity of individual chains.

In Monte Carlo simulation of chains without excluded volume, chain conformations showing an appreciable overlap between chain elements are sometimes generated.

Table IV
Monte Carlo Results for Different Types of Gaussian Chains[a]

F	N	$(f_t^*)_K$	$(f_t^*)_{np}$	(f_r^*)	$[\eta]_{np}^*$
2	19	1.22 ± 0.01	1.34 ± 0.01	4.22 ± 0.01	31.3 ± 0.8
2	25	1.41 ± 0.02	1.57 ± 0.02	6.9 ± 0.3	50 ± 2
2	37	1.70 ± 0.05	1.91 ± 0.04	11.9 ± 0.6	87 ± 7
2	49	1.98 ± 0.05	2.23 ± 0.05	19 ± 1	143 ± 12
2	55	2.09 ± 0.06	2.37 ± 0.07	23 ± 2	177 ± 18
6	19	1.04 ± 0.01	1.22 ± 0.01	3.19 ± 0.04	20.2 ± 0.3
6	25	1.19 ± 0.01	1.40 ± 0.01	4.92 ± 0.03	30.8 ± 0.2
6	37	1.41 ± 0.03	1.69 ± 0.03	8.6 ± 0.5	54 ± 5
6	49	1.61 ± 0.01	1.96 ± 0.01	13.5 ± 0.3	85 ± 1
12	25	1.014 ± 0.005	1.240 ± 0.002	3.14 ± 0.03	19.8 ± 0.1
12	37	1.19 ± 0.01	1.50 ± 0.01	5.60 ± 0.14	35.2 ± 0.8
12	49	1.35 ± 0.02	1.72 ± 0.02	8.5 ± 0.3	54 ± 2
18	19	0.86 ± 0.01	1.032 ± 0.005	1.72 ± 0.03	11.1 ± 0.2
18	37	1.07 ± 0.01	1.38 ± 0.01	4.2 ± 0.1	27.0 ± 0.6
18	55	1.25 ± 0.02	1.65 ± 0.01	7.3 ± 0.3	46.7 ± 1.5

[a] 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 Zimm[8] 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 $[\eta]_T^*$ 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, and 18 (F = 2 corresponds to a linear chain whose properties are employed in the evaluation of the ratios) with a total number of units N = 19, 25, 37, 49, 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 Zimm[8] 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_t^* as

$$P = 6\pi f_t^*/(N-1)^{1/2} \tag{21}$$

and we have plotted $P_{np} - P_K$ (i.e., the difference between the Monte Carlo results obtained for $(f_t^*)_{np}$ and $(f_t^*)_K$) 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 chain[2] serve as an estimation of P_{np} in the same limit. We have obtained P = 6.08, in good accordance with Zimm's result P_Z = 5.99 and with recent experimental estimates for P ranging between the values P_{exp} = 5.7–6.0.[16]

The parameter ϕ related to viscosity is calculated for linear chains of arbitrary length from

$$\phi = N_A[\eta]^*/(N-1)^{3/2} \tag{22}$$

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 $[\eta]_T^*$ for individual conformations and therefore, we ignore the differences between the nonpreaveraged and the double-sum results $\phi_{np} - \phi_T$ for different values of N. Nevertheless, if guided by Zimm's conclusions one admits that the nonpreaveraged values of ϕ should be almost independent of N; an estimation of the limit result for ϕ_{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 $\phi_{np} = 2.54 \times 10^{23}$, also in excellent accordance with Zimm's $\phi_Z = 2.51 \times 10^{23}$ and with the experimental estimation[16] $\phi_{exp} \simeq 2.5 \times 10^{23}$. (Similar results for P and ϕ have been also recently obtained by Oono and Kohmoto, who applied a theoretical treatment based on the renormalization group theory.[17]) 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 ϕ. 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^r_{np} for the ratio of rotational friction coefficients

$$h = (f_r)_b/(f_r)_l \tag{23}$$

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_ϕ calculated from h_{MC}, g'_{MC}, and g 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^r, it should be considered that the

preaveraged Kirkwood–Riseman theory leads to the relation[2]

$$f_r = 4N_A^{-1}\eta_0 M[\eta] \tag{24}$$

and, therefore, h^r and g' become identical. However, our Monte Carlo nonpreaveraged results reveal remarkable differences between their respective values, h^r 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_{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_ϕ, associated with viscosity, are similar to the experimental estimates. It should be remarked that both r_P and, especially, r_ϕ 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_ϕ 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 Θ 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_ϕ, 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^3 would constitute an adequate estimation for g'. Table III shows that the values g'_{MC} and h_p^3 are in fact in good agreement, especially for high functionalities. A subsequent evaluation of r_ϕ from h_p^3 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 $(r_\phi)_{ind}$ 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, $(r_\phi)_p$.

We can see in Table III that the values of g'_{MC} differ drastically from the Zimm and Kilb estimation, $g' = g^{1/2}$. Combining this expression with eq 13, we get $r_\phi = g^{-1}$, 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 above is comparable to that of empirical estimates of g' as h_{exp}^3 or $g_{exp}^{1/2}$.

The Monte Carlo values of r_p and r_ϕ 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 comblike 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

$$1 \leq n_i \leq N - 1 - p + i - \sum_{j=1}^{i-1} n_j = N_m, \qquad 1 \leq i \leq p - 1 \tag{25}$$

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

$$n_p = N - 1 - \sum_{j=1}^{p-1} n_j \tag{26}$$

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

$$p(m_i) = p'(m_i) / \sum_{n_i=1}^{N_m} p'(n_i) \tag{27}$$

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

$$p'(n_i) = \binom{N - 2 - n_i - \sum_{j=1}^{i-1} n_j}{p - i - 1} \tag{28}$$

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.

Table V
Results for Long Randomly Distributed Combs[a]

m	g	h_K	h_p	g'_p
2	0.829	0.948	0.960	0.906
3	0.771	0.931	0.947	0.871
4	0.732	0.916	0.936	0.846
5	0.701	0.903	0.926	0.818
6	0.676	0.893	0.916	0.798
7	0.654	0.884	0.909	0.781

[a] See text for notation.

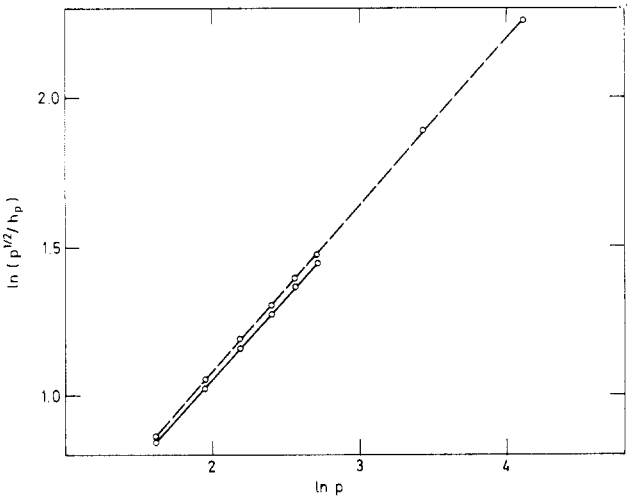

Figure 1. $p^{1/2}h_p^{-1}$ vs. p for long uniform (broken line) and randomly distributed (solid line) comblike polymers.

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'_p 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;[2] this confirms the validity of our numerical methods. In Figures 1 and 2, $p^{1/2}/h_p$ (proportional to the sedimentation coefficient s and inversely proportional to f_t) and $p^{1/2}g'_p$ (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'_p vs. m^{-1} for both distributions. It can be observed that a single value of g'_p 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.[1]

(b) Uniformly Branched Combs with Short or Long Side Chains. We have also obtained numerical results

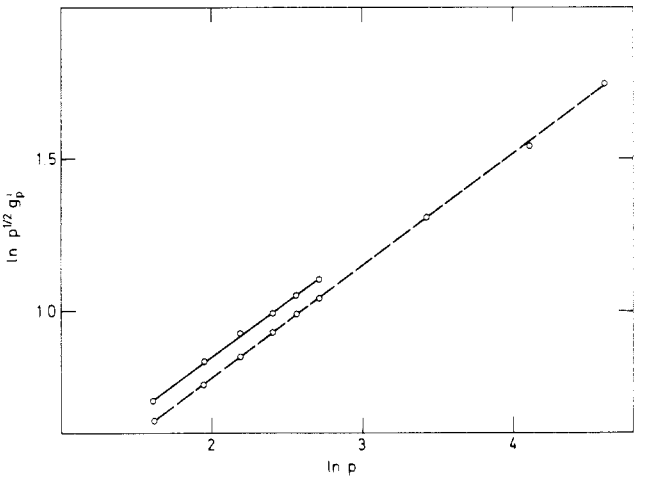

Figure 2. $p^{1/2}g'_p$ vs. p for long uniform (broken line) and random (solid line) combs.

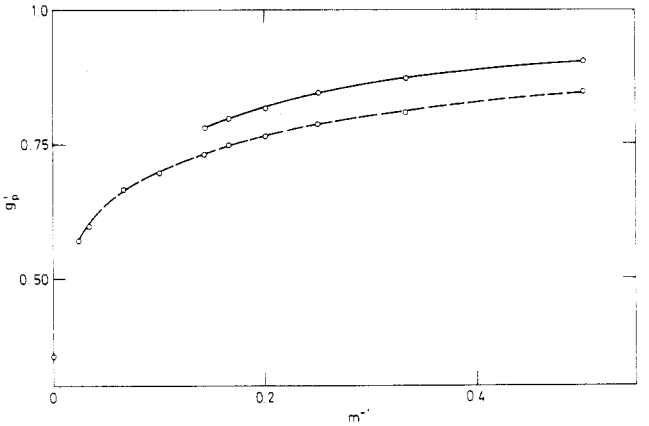

Figure 3. g'_p vs. m^{-1} for long uniform (broken line) and random (solid line) combs. The point at $m^{-1} = 0$ corresponds to the theoretical limit value[1] of g'.

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 een evaluated by graphical extrapolations to $N^{-1} = 0$, following the scheme used previously for completely uniform chains.[1]

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[21] with nonrelated values of m and λ, the fraction of polymer in the backbone

$$\lambda = (m + 1)/[n_b m(F - 2) + m + 1] \qquad (29)$$

Figures 4 and 5 contain the extrapolated values of $h_p/g^{1/2}$ and γ_p (i.e., the exponent γ calculated from g'_p) vs. λ for different values of m. It can be noticed that these quantities are in general dependent of both λ and m. In fact, γ_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 basis[21] for performing universal representations of γ vs. g, 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

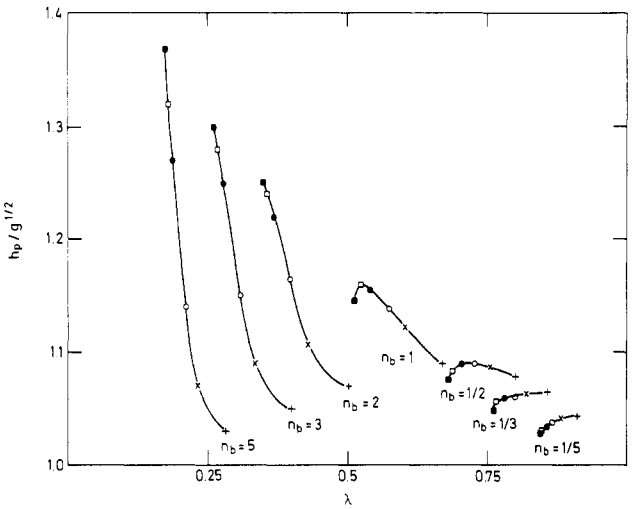

Figure 4. $h_p/g^{1/2}$ vs. λ for uniformly branched combs with different values of the ratio n_b: (+) $m = 1$; (×) $m = 2$; (○) $m = 3$; (●) $m = 6$; (□) $m = 10$; (■) $m = 15$.

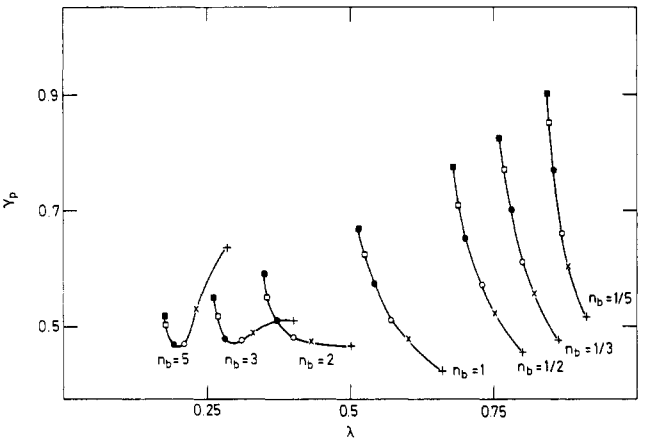

Figure 5. γ_p vs. λ for long uniformly branched combs with different values of n_b. Notation as in Figure 4.

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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