Kirkwood–Riseman Calculations for Hydrodynamic Properties of Flexible Branched Polymers

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ABSTRACT: Numerical results for hydrodynamic properties of uniform flexible branched polymers (trifunctional comblike polymers and star polymers of different functionalities) have been calculated by means of the Kirkwood–Riseman theory. The properties have been expressed in terms of the coefficients g, h, and g', which correspond to the ratios of the mean radius of gyration, the translational diffusion coefficient, and the intrinsic viscosity of branched chains to those of linear chains with the same molecular weight. Two standard treatments of the hydrodynamic interactions have been used, leading to significantly different results. The numerical values obtained with the most rigorous treatment clarify the ranges of validity of the approximate relations between the ratios suggested by Zimm and Kilb, Stockmayer and Fixman, and Kurata and Fukatsu. The qualitative behavior of experimental data is, in general, reproduced. Moreover, theoretical and experimental values of h are in close agreement for several types of stars.

Introduction

The hydrodynamic properties of linear flexible polymers have been extensively studied from both the theoretical and experimental points of view.[1] These studies have made it possible to relate experimental data with microscopic characteristics through simple limit expressions. Thus, for high molecular weights, the translational friction coefficient, f, is obtained as

$$f = K_f \eta_0 \langle S^2 \rangle^{1/2} \tag{1}$$

where K_f is a numerical constant, η_0 is the solvent viscosity, and $\langle S^2 \rangle$ is the mean quadratic radius of gyration of the chain. For the intrinsic viscosity, $[\eta]$, Flory's relation is applicable

$$[\eta] = \Phi' \frac{\langle S^2 \rangle^{3/2}}{M} \tag{2}$$

(Φ' is also a constant and M is the polymer molecular weight).

However, the effect of branching on these properties has been described mainly on a qualitative basis.[2] Thus, the intrinsic viscosity of branched chains has been investigated through adequate hydrodynamic treatments only in a few particular cases.[3–5] In one of the most detailed studies performed so far, Zimm and Kilb[3] generalized the Rouse–Zimm theory for linear flexible molecules in their unperturbed state to two different types of star molecules. They analyzed the numerical results for the parameter γ, defined by

$$g' = [\eta]_b / [\eta]_l = g^\gamma \tag{3}$$

where the subscripts b and l refer to a branched chain and a linear chain, both with the same molecular weight, and g corresponds to the ratio of the respective radii of gyration

$$g = \langle S^2 \rangle_b / \langle S^2 \rangle_l \tag{4}$$

For both types of star chains, Zimm and Kilb obtained $\gamma \simeq 0.5$. On the basis of this coincidence they proposed that eq 3 with $\gamma = 0.5$ might hold for all kinds of branched molecules. This result is, however, in conflict with simpler arguments. Thus, if one considers a chain with a very long backbone and many much shorter branches (for instance, a uniform comblike polymer with many branching units) so that its cross section is very small compared to the backbone's contour length, the chain's hydrodynamic behavior must be defined by the backbone. Then eq 2 can be applied and, in consequence, the value $\gamma = {}^3/_2$ is predicted.

Experimental data[2,6–9] obtained for different flexible branched chains yield a broad distribution of values of γ within the interval $0.5 \leq \gamma \leq 1.5$. In fact, the experimental variation of γ should be strongly dependent on the topology of the chain; i.e., it should be related to the degree and type of branching. Nevertheless, this dependence is not fully understood, in part due to the lack of a rigorous theoretical analysis.

Other approximate relations between different ratios have been proposed. Stockmayer and Fixman[10] suggested

$$g' = h^3 \tag{5}$$

where h is the ratio of friction coefficients

$$h = f_b / f_l \tag{6}$$

which can be simply obtained by applying the approximate Kirkwood formula to the calculation of f_b and f_l. Some experimental data[11] show, however, certain deviation from the theoretical values of h obtained this way. We should also consider the inequality predicted by Kurata and Fukatsu[12]

$$1 \leq h/g^{1/2} \leq 1.39 \tag{7}$$

The aim of this work is to obtain numerical results for the hydrodynamic properties of detailed theoretical models corresponding to different types of branched chains in their unperturbed state. These results can be useful to clarify the role of the chain topological form or, at least, to establish the ranges of validity for the different approximate theoretical relations, eq 3, 5, and 7. We study the influence on the results of the total number of hydrodynamic units, N (proportional to the number of real repeating units), for star polymers of different functionalities (denoted by the value of the variable F). Also, we study comblike polymers with $F = 3$ and with different values of m (number of branching points along the backbone). In both cases we consider a uniform distribution of units among the p subchains ($p = F$ for stars and $p = 2m + 1$ for our trifunctional comblike structures).

Our calculations are based on the general Kirkwood–Riseman theory, which accounts for hydrodynamic interactions between units.[1] In this theory, the form of the general expressions for the hydrodynamic properties is not affected by the type of connectivity between units. This constitutes an important practical advantage with respect to the Rouse–Zimm theory as extended by Zimm and Kilb, which includes calculations through the coordinate matrix **A**, built in a different way for every type of branching.

0024-9297/83/2216-1701$01.50/0

In the preaveraged version used here, the Kirkwood–Riseman theory introduces correlations between units by means of mean geometrical magnitudes. As in the Rouse–Zimm theory, our hydrodynamical units embody many real chemical groups so that, due to the chain's flexibility, a Gaussian distribution of distances between neighboring theoretical units can be properly assumed. Such a distribution allows us to obtain easily the required conformational averages.

Theoretical Methods

The translational friction coefficient of a polymer in dilute solution can be obtained from the expression[13,14]

$$f = \xi \sum_{i=1}^{N} \sum_{j=1}^{N} (\mathbf{H}^{-1})_{ij} \tag{8}$$

where ξ is the friction coefficient of each one of the units (all them assumed identical) and $\mathbf{H}$ is the hydrodynamic interaction matrix, whose elements are[1]

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

$$H_{ij} = (\xi/6\pi\eta_0)\langle r_{ij}^{-1}\rangle \qquad \text{for } i \neq j \tag{9}$$

($\langle r_{ij}^{-1}\rangle$ is the mean reciprocal distance between units i and j).

Equation 8 is obtained from the Kirkwood–Riseman theory by taking a previous rotational and conformational average on the hydrodynamic interaction tensor, or the Oseen tensor. Another useful, though also approximate, expression for f is the well-known Kirkwood equation

$$f = N^2\xi[\sum_{i=1}^{N} \sum_{j=1}^{N} H_{ij}]^{-1} \tag{10}$$

Theoretical values provided by eq 8 and 10 have been compared with values obtained through more rigorous expressions for rigid molecules[15] or with Monte Carlo averages of conformations of flexible chains[14,16,17] (taken as instantaneously rigid). From these comparisons, it is concluded that eq 8 is, in general, more accurate than eq 10, though, sometimes, both lead to similar errors. It should be noted that eq 10 is very practical for obtaining numerical results or yielding analytical formulas, since it does not require the inversion of matrix $\mathbf{H}$.

The preaveraged version of the Kirkwood–Riseman theory gives the following expression for the intrinsic viscosity:[14,18]

$$[\eta] = (N_A\xi/6M\eta_0) \sum_{i=1}^{N} \sum_{j=1}^{N} (\mathbf{H}^{-1})_{ij}\langle \mathbf{R}_i \cdot \mathbf{R}_j\rangle \tag{11}$$

where N_A is the Avogadro number and $\langle \mathbf{R}_i \cdot \mathbf{R}_j\rangle$ represents the correlation between position vectors $\mathbf{R}_i$ and $\mathbf{R}_j$ referred to some viscosity center,[15,16] which is substituted here by the center of masses of the chain as a reasonable simplification. Then, $\langle \mathbf{R}_i \cdot \mathbf{R}_j\rangle$ can be written in terms of mean quadratic distances between units, $\langle r_{kl}^2\rangle$, according to the relations[1]

$$\langle \mathbf{R}_i \cdot \mathbf{R}_j\rangle = \tfrac{1}{2}[\langle R_i^2\rangle + \langle R_j^2\rangle - \langle r_{ij}^2\rangle] \tag{12}$$

$$\langle R_i^2\rangle = N^{-1} \sum_{k=1}^{N} \langle r_{ik}^2\rangle - \langle S^2\rangle \tag{13}$$

and

$$\langle S^2\rangle = N^{-2} \sum_{k>}^{N} \sum_{l=1}^{N} \langle r_{kl}^2\rangle \tag{14}$$

Tsuda derived some years ago[19-21] two approximate, though nonpreaveraged, formulas for $[\eta]$ that do not require the inversion of $\mathbf{H}$. The formulas have, however, complicated forms. Taking an orientational and conformational previous average on the Oseen tensor in the derivation of Tsuda's simplest formula, eq 21 of ref 20, leads to the very convenient result[22,23]

$$[\eta] = \frac{N_A\xi}{6M\eta_0}[\sum_{i=1}^{N} \langle R_i^2\rangle]^2[\sum_{i=1}^{N} \sum_{j=1}^{N} H_{ij}\langle \mathbf{R}_i \cdot \mathbf{R}_j\rangle]^{-1} \tag{15}$$

Since, in our model, all distances between units follow a Gaussian distribution, their mean quadratic averages are evaluated from

$$\langle r_{ij}^2\rangle = \nu_{ij}b^2 \tag{16}$$

where ν_{ij} is the number of ideal segments connecting units i and j. This number is $\nu_{ij} = |i - j|$ for a linear chain and can be easily obtained in the case of branched polymers through a convenient enumeration of the units.

On the other hand, the mean reciprocal distances are calculated from

$$\langle r_{ij}^{-1}\rangle = (6/\pi)^{1/2}\langle r_{ij}^2\rangle^{-1/2} \tag{17}$$

an expression valid for a Gaussian distribution of distances.

The parameters ξ, η_0, and b in eq 8–11, 15, and 16 can be grouped into a single parameter h^*

$$h^* = \xi/(12\pi^3)^{1/2}\eta_0 b \tag{18}$$

We set the value $h^* = 0.25$, which is significant in the Rouse–Zimm theory since it permits us to simplify Zimm's integrodifferential equation to its nondraining version for chains of arbitrary length.[4] Moreover, this value is very close to the value of ξ calculated for random coil units ($h^* = 0.265$[14]). In any case, it should be remarked that small differences in the choice of h^* lead to significantly different results for the hydrodynamic properties only in the case of very short chains, since the numerical values of the properties do not depend on h^* in the limit $h^*N^{1/2} \gg 1$.

It can be noted that the type of connectivity between the chain's units is introduced through eq 16. Then, the numerical results for the properties ($\langle S^2\rangle$, f, or $[\eta]$) are easily obtained once the distribution of units between the different subchains is completed. Obviously, this distribution is very simple in the case of uniform chains studied in this work. Analytical formulas for g and h obtained with eq 14 and the Kirkwood approximation, eq 10, respectively, were obtained some time ago by Kurata and Fukatsu[1,12] for polymers of high molecular weights with uniform (as well as random) distributions. Nevertheless, analytical expressions are not available for the ratio h calculated through the more rigorous eq 8 (i.e., through $\mathbf{H}^{-1}$). The calculations for g' should be also performed numerically, though, of course, estimates of this ratio can be achieved with eq 3 or 5, assuming that those relations are sufficiently accurate.

Numerical Results

Equations 3, 4, 6, and 8–18 allow us to obtain numerical results for the ratios g, h (h_p will denote the ratios obtained with friction coefficients calculated from eq 8 and h_K those obtained with values of f from eq 10), g' (g'_p will represent the ratios corresponding to intrinsic viscosities evaluated from eq 11 and g'_T those calculated with eq 15) and the exponent γ (γ_p will be the exponents obtained from g'_p and γ_T those evaluated from g'_T). The ratios, and consequently the exponents, are independent of the proportionality constant relating M to N and, therefore, only the latter variable needs to be considered. We have obtained results with values of N up to $N = 100$ for stars and $N = 150$ for combs for the magnitudes whose calculation includes the evaluation of $\mathbf{H}^{-1}$. For the rest of magnitudes the range

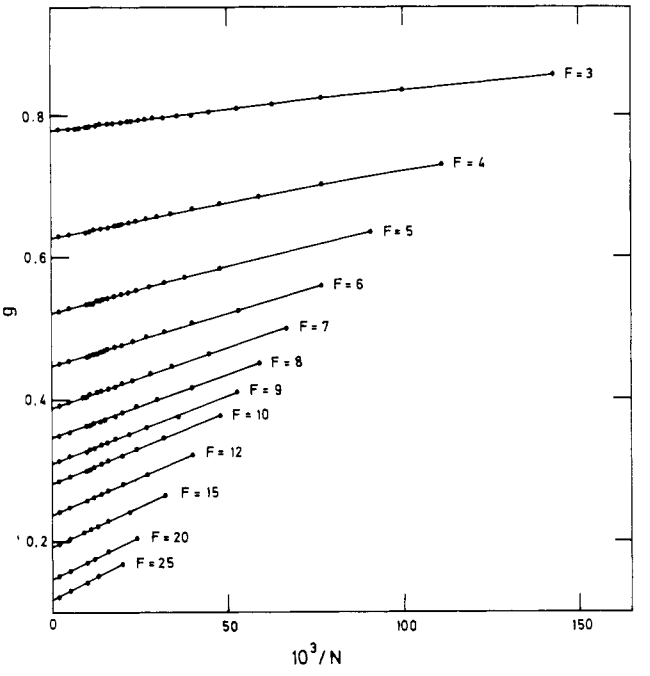

Figure 1. g vs. N^{-1} for stars of different functionalities.

of results extends up to $N = 500$.

Since our main aim is to study the influence of the branching characteristics on the properties of long chains, it is desirable to eliminate the dependence of N on the results, once the branching variables m and F have been set, by considering chains with a high value of the variable n_m, the number of units per subchain. This can be done by extrapolation to $N^{-1} \rightarrow 0$ of the results associated with every type of branching. It should be remarked that in the case of uniform combs the extrapolated values are still N dependent, since the number of branching points is related to the total number of units. For stars, notwithstanding, the extrapolated ratios are totally independent of the molecular weight. This scheme is in qualitative agreement with some experimental results. Thus, the experimental logarithmic plots of hydrodynamic properties vs. molecular weight for star molecules of different functionalities in the same solvent conditions are almost linear, all exhibiting identical slopes also coincident with those of the corresponding linear chains.[8,11] Similar representations show, however, a completely different behavior in the case of randomly branched polymers[6,7,11] (they are not linear and, in the case of intrinsic viscosity representations, the variation with M is significantly less pronounced).

In order to perform the extrapolations we have plotted the results vs. N^{-1} for many different choices of m and F within the ranges $m = 2$–50 for trifunctional combs and $F = 3$–25 for stars. We will comment here on the most significant features of these representations. (The whole set of extrapolation curves and numerical values is available upon request.) In Figure 1 we show some of the plots corresponding to the ratio g for stars. For combs, the plots present a more noticeable curvature, though extrapolations are also easily achieved. It should be noted that g increases with increasing values of N^{-1} for both comb and star chains. The opposite behavior is, however, found in conformational calculations of short stars based on the realistic isomeric state model.[24] Nevertheless, as expected, the latter results and ours become practically coincident in the limit of long chains, in which we are mainly interested. Figure 2 presents results of h_p vs. N^{-1} for combs (the equivalent curves for stars are practically linear). The corresponding results for h_K in the case of stars are contained in Figure 3 (moderate curvatures are also observed for combs). Figure 4 includes values of g'_p yielded by

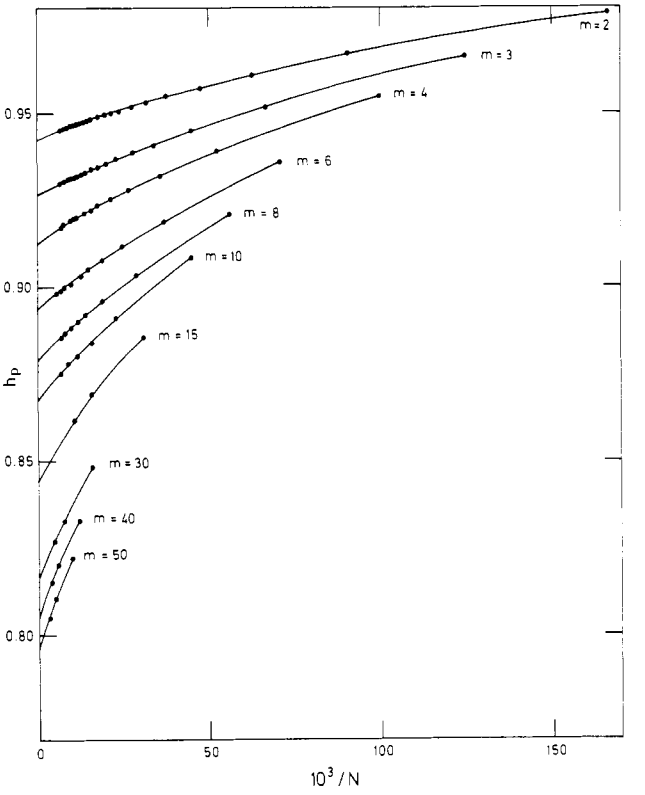

Figure 2. h_p vs. N^{-1} for combs with different values of m.

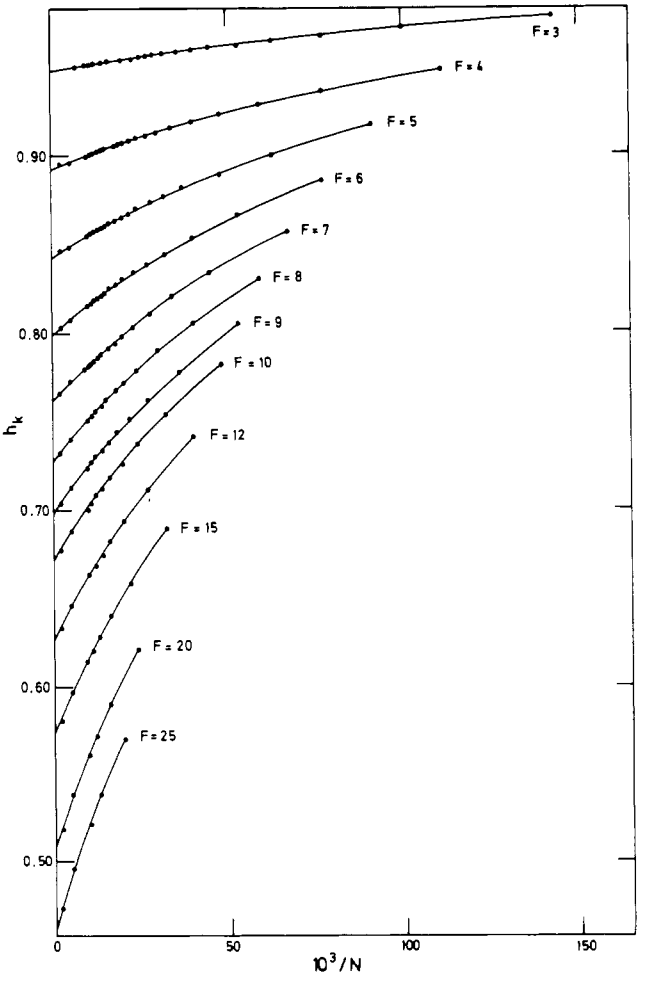

Figure 3. h_K vs. N^{-1} for stars of different functionalities.

Table I
Results for Stars Extrapolated to $n_m^{-1} = 0$ or Calculated from Limiting Formulas[a]

F	g	g_{KF}	h_K	h_{KF}	h_p	$h_p/g^{1/2}$	h_p^3	g_p'	g_T'
3	0.780	0.778	0.948	0.947	0.962	1.09	0.890	0.900	0.918
4	0.628	0.625	0.892	0.892	0.920	1.17	0.794	0.814	0.836
5	0.522	0.520	0.842	0.842	0.891	1.23	0.707	0.747	0.773
6	0.446	0.444	0.798	0.798	0.860	1.29	0.636	0.694	0.722
7	0.388	0.388	0.760	0.759	0.832	1.34	0.576	0.650	0.678
8	0.345	0.344	0.726	0.725	0.806	1.37	0.524	0.613	0.640
9	0.309	0.309	0.698	0.696	0.783	1.41	0.480	0.582	0.609
10	0.281	0.280	0.670	0.669	0.763	1.44	0.444	0.555	0.583
12	0.236	0.236	0.626	0.623	0.727	1.50	0.384	0.510	0.537
13	0.218	0.219	0.598	0.600	0.711	1.52	0.358	0.491	0.520
15	0.190	0.191	0.574	0.570	0.683	1.57	0.319	0.459	0.484
18	0.160	0.160	0.529	0.528	0.647	1.62	0.271	0.421	0.447
20	0.146	0.145	0.508	0.504	0.627	1.64	0.246	0.401	0.424
25	0.118	0.117	0.460	0.457	0.586	1.71	0.201	0.360	0.382

[a] See text for details.

Table II
Results for Combs Extrapolated to $n_m^{-1} = 0$ or Calculated from Limiting Formulas[a]

m	g	g_{KF}	h_K	h_{KF}	h_p	$h_p/g^{1/2}$	h_p^3	g_p'	g_T'
2	0.710	0.712	0.921	0.922	0.943	1.12	0.839	0.848	0.826
3	0.665	0.668	0.902	0.903	0.926	1.14	0.794	0.811	0.770
4	0.635	0.638	0.888	0.888	0.913	1.15	0.761	0.786	0.730
5	0.615	0.617	0.875	0.876	0.903	1.15	0.736	0.764	0.696
6	0.600	0.601	0.867	0.866	0.894	1.15	0.715	0.746	0.672
7	0.588	0.589	0.859	0.858	0.885	1.15	0.693	0.732	0.654
8	0.579	0.580	0.852	0.851	0.878	1.15	0.677	0.720	0.634
9	0.572	0.572	0.846	0.845	0.871	1.15	0.661	0.708	0.614
10	0.563	0.566	0.839	0.840	0.867	1.16	0.652	0.698	0.604
15	0.543	0.546	0.821	0.820	0.843	1.14	0.599	0.664	0.560
30	0.523	0.524	0.791	0.791	0.813	1.12	0.537	0.598	0.506
40	0.515	0.518	0.779	0.781	0.803	1.12	0.518	0.584	0.482
50	0.511	0.515	0.775	0.773	0.794	1.11	0.501	0.571	0.469

[a] See text for details.

combs (the plots for stars are linear). Similar representations have also been plotted for g'_T. In the case of combs, these plots show a strong curvature for low values of N^{-1} that, nevertheless, does not significantly affect the accuracy of the extrapolated results. The plots of γ vs. N^{-1} also exhibit some curvature. Moreover, the curves of γ_p vs. N^{-1} for combs with low values of m present some irregularities, though extrapolated values can be adequately estimated even in these cases. In fact, all the extrapolated values of γ are sensibly identical (within a 1% error range) with those obtained from application of eq 3 to the corresponding extrapolated values of g and g'.

Table I summarizes the results obtained for the different extrapolated ratios in the case of stars with different functionalities, and Table II presents equivalent results for trifunctional combs with different numbers of branch points. In these tables we have also listed values of h_p^3 and $h_p/g^{1/2}$ obtained from the extrapolated results of h_p and g contained in the tables. These values allow us to investigate the validity of eq 5 and 7. Moreover, we present values of g_{KF} and h_{KF}, the numerical results obtained for g and h from the analytical formulas derived by Kurata and Fukatsu.[1,12] The close agreement between these results and our extrapolated values of g and h_K should be noticed; this confirms the accuracy of our numerical and graphical procedures. Table III shows the good agreement between our extrapolated results for g'_p and theoretical values of g' calculated through the Zimm and Kilb theory for stars with long branches in the nondraining limit[3] or by setting $h^* = 0.25$.[4]

The extrapolated values of γ_p and γ_T are represented in Figures 5 and 6 vs. F^{-1} for stars and vs. m^{-1} for trifunctional combs, respectively. The limiting value for stars of many branching should[25] be $\gamma = {}^1/_2$, while for combs

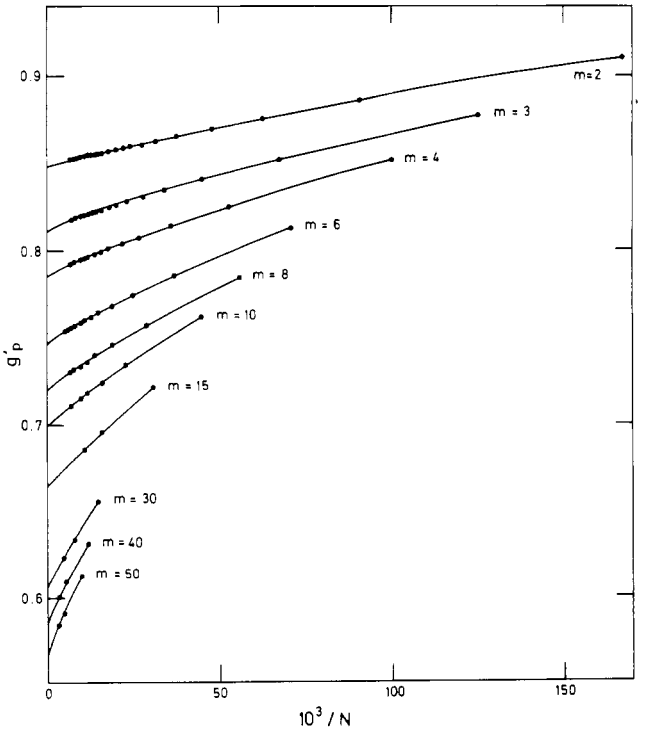

Figure 4. g'_p vs. N^{-1} for combs with different values of m.

with many branch points the value $\gamma = {}^3/_2$ should be reached. In the latter case, a graphical estimation of γ for high values of m by a further extrapolation in the region close to $m^{-1} = 0$ seems to be very difficult. Thus, we consider it useful to give in Figure 7 graphical representations of g'_p vs. m^{-1} for combs with either $n_m = 1$ or with

Table III
Comparison between Our Numerical Results for Stars (Extrapolated to $n_m^{-1} = 0$), Estimates of g' as $g^{1/2}$, Results from the Zimm and Kilb Theory, and Experimental Data in Θ Solvents

	this work				Zimm and Kilb	experimental	
F	h_K	h_p	g_p'	$g' = g^{1/2}$	g'	h	g'
4	0.892	0.920	0.814	0.792	0.814[a]	0.94[c]	0.76[d]
6	0.798	0.860	0.694	0.668		0.89[c]	0.62[d]
8	0.726	0.806	0.613	0.587	0.625[a]		
13	0.598	0.711	0.491	0.467	0.494[b]		

[a] Reference 3. [b] Reference 4. [c] Reference 11. [d] Reference 8.

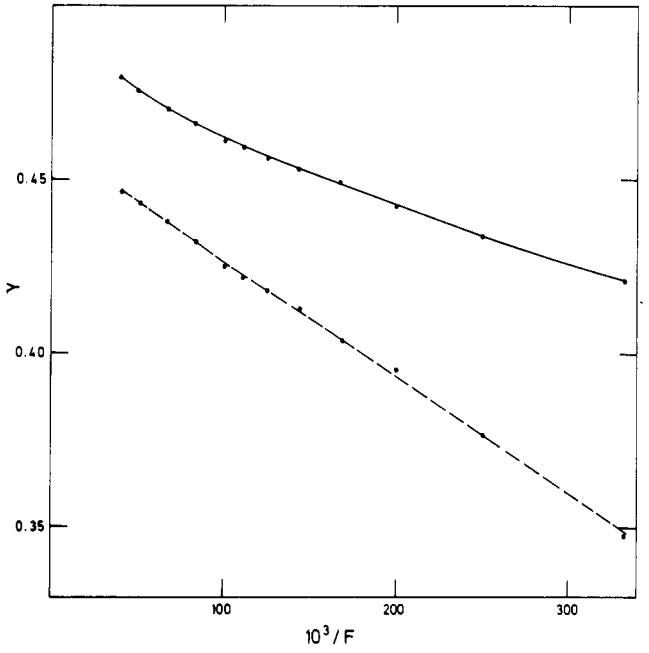

Figure 5. Extrapolated values of γ_p (solid line) and γ_T (broken line) vs. F^{-1} for stars.

$n_m^{-1} = 0$ (limit associated with the extrapolated results taken from Table II or Figure 4). The unfilled circle point at $m^{-1} = 0$ represents the theoretical value $g' = 2^{-3/2}$ obtained from eq 2 and 3 for a chain with $m^{-1} = 0$, i.e., a uniform comb with many branches whose hydrodynamic behavior should be equivalent to that of a linear chain with the same backbone length.

Discussion

From the results contained in Tables I and II and Figures 5 and 6 we can establish several interesting conclusions. First, the numerical values are very sensitive to the theoretical treatment. Thus, the values of h obtained through the approximate Kirkwood expression, eq 8, h_K or h_{KF}, differ from those obtained from the more rigorous eq 10, h_p. This effect is very significant in the case of stars of high functionalities, for which the difference between h_p and h_K is about 20%. It should be remarked that differences between diffusion coefficients obtained from eq 8 and 10 are only 1.7% for linear chains.[1] Moreover, eq 15 gives results noticeably different for the intrinsic viscosity from those obtained with the most rigorous eq 11 in the case of combs with many branch points, though both sets of results are in closer agreement for stars. On the basis of all these facts we believe that a further refinement of the hydrodynamic formalism which avoids the Oseen tensor preaveraging and considers translational–rotational coupling and a correct viscosity center could be able to yield somewhat more precise results. Second, our more rigorous numerical values show that eq 3 with $\gamma = 0.5$ constitutes an excellent approximation for stars with a few long branches. As expected, the approximation is considerably poorer for long uniform combs with many branch points. Third, eq 5 and 7 are reasonably correct for combs with low values of m and stars of low functionality but they are not adequate for longer combs and, especially, for stars with many branches (differences between h_p^3 and g'_p amount to 15% or more for $F > 8$, and $h_p/g^{1/2}$ exceeds the value 1.39 for high functionalities, though the less rigorous results for $h_K/g^{1/2}$ are always

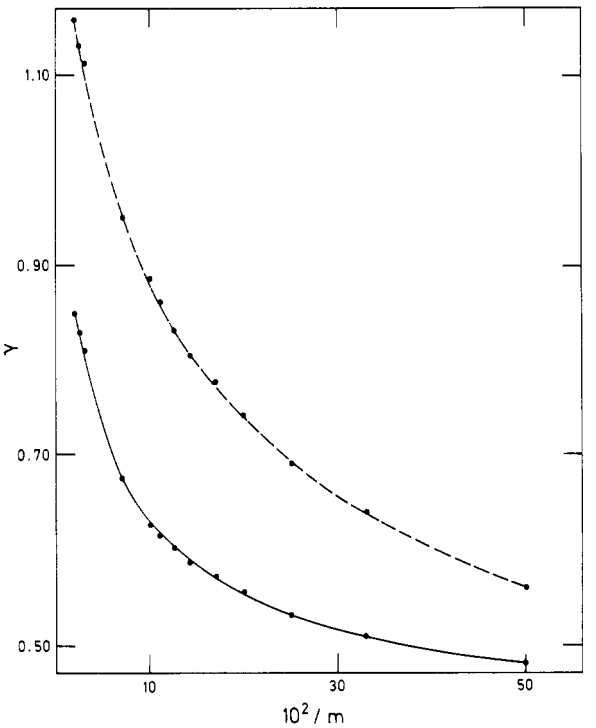

Figure 6. Extrapolated values of γ_p (solid line) and γ_T (broken line) vs. m^{-1} for combs.

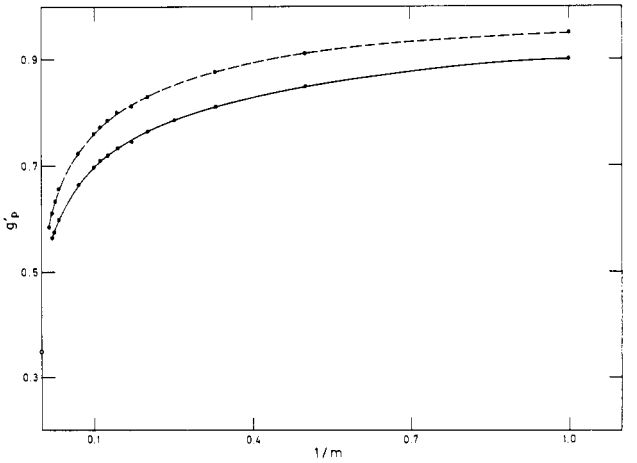

Figure 7. g'_p vs. m^{-1} for combs. Solid line, $n_m^{-1} = 0$ (extrapolated values); broken line, $n_m^{-1} = 1$. The unfilled circle represents the theoretical value of g'_p at $m^{-1} = 0$.

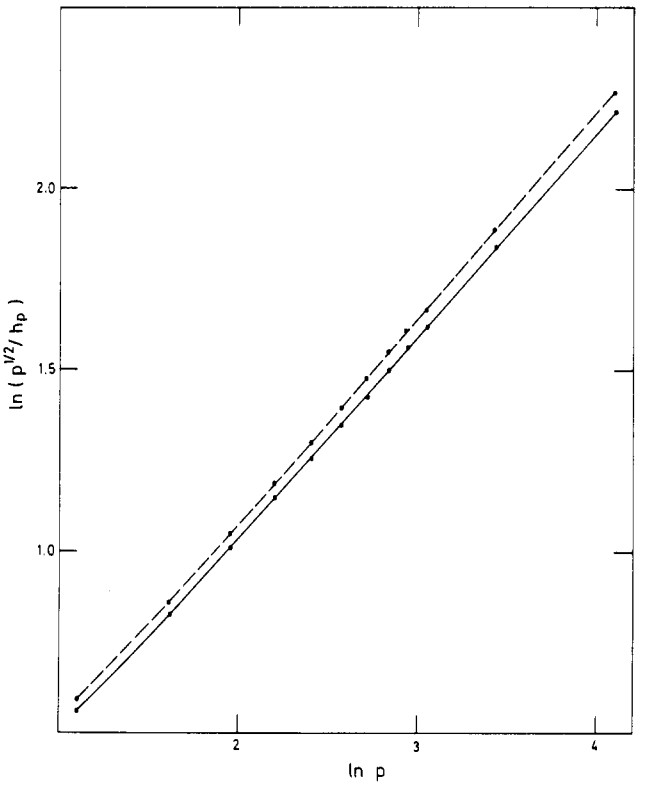

Figure 8. $p^{1/2}h_p^{-1}$ (proportional to s) vs. p (proportional to M) for combs. Solid line, $n_m^{-1} = 0$ (extrapolated values); broken line, $n_m^{-1} = 1$.

within the predicted limits).

Direct comparison of our results with experimental data is difficult since many experimental samples (especially those corresponding to comblike polymers) are not adequately described by the models and approximations used in this work. Nevertheless, it is satisfactory to point out that, as shown in Table III, our more rigorous values of h, h_p, are in good agreement with experimental data obtained with stars of four and six branches.[8,11] This constitutes a significant improvement with respect to the previous comparison of the same data with theoretical results obtained from the Kirkwood equation, h_K or h_{KF}.

Since our more rigorous values of g', g'_p, for stars with low F are very similar to estimates for g' based on eq 3 with $\gamma = 0.5$, both kinds of results show a similar performance with respect to experimental data[8] of these polymers, as can be observed in Table III.

Some experimental studies for randomly branched polymers[6,7] have yielded results that can be compared with our theoretical values for combs, at least on a qualitative basis, since in both types of chains the number of branching points depends directly on the molecular weight. In order to perform such comparisons we have plotted in Figures 8 and 9 logarithmic representations of $p^{1/2}h_p^{-1}$ and $p^{1/2}g'_p$ (magnitudes proportional to the sedimentation coefficient, s, and the intrinsic viscosity of high molecular weight chains, respectively) vs. p (proportional to M for monodisperse polymer fractions with a uniform distribution of branch points). As in the experimental curves,[6,7] we obtain upward and downward curvatures for s and $[\eta]$, respectively. However, the theoretical deviations, especially for high values of n_m, are less pronounced than those exhibited by the experimental data. In fact, the intrinsic viscosity curve for $n_m^{-1} = 0$ is practically linear within the whole range of p, showing a slope of ca. 0.36, greater than the local slopes of ca. 0.25 observed for the high molecular weight range in Figure 5 of ref 6 and Figure 2 of ref 7. Of

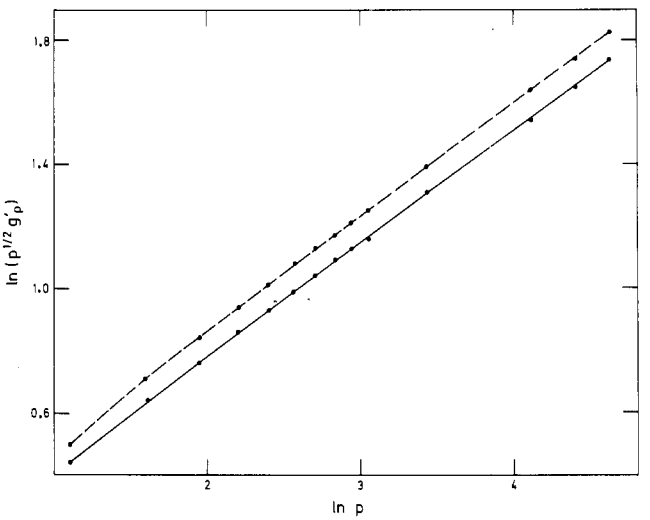

Figure 9. $p^{1/2}g'_p$ (proportional to $[\eta]$) vs. p for combs. Solid line, $n_m^{-1} = 0$ (extrapolated values); broken line, $n_m^{-1} = 1$.

course, a better agreement cannot be expected because the molecular topology of the experimental samples differs significantly from our uniform comblike theoretical chains.

More satisfactory comparisons between calculations from the theory and experimental data may be possible by eliminating some defects in both the theoretical model and the synthetic schemes. The latter could be improved in order to obtain more monodisperse fractions with more precisely determined branching characteristics. The hydrodynamic calculations may incorporate local correlations. Thus, the deviations from Gaussian statistics of the relative positions between real hydrodynamic units close to the branching points could have some influence on the final results, as recent realistic geometrical calculations have pointed out.[26,27] Excluded volume effects may be significant in certain cases, but their effect on the expansion factors of branched chains is not fully understood.[28-30] In fact, the ratios h and g' seem to be almost independent of M for stars with few branches. Notwithstanding, experimental values of g for stars with higher functionalities indicate stronger intramolecular interactions.[31]

Finally, we remark that our topological models are not adequate for certain types of experimental fractions of branched chains. Uniform distributions of units are hard to achieve. Further, many synthetic branched polymers have a different number of repeating units in the branches and in the subchains along the backbone. This characteristic is often described by the variable λ, the fraction of material in the backbone. For uniform or randomly branched polymers, λ is directly determined by m. Nevertheless, λ is an independent variable in many experimental samples.[9] In fact, some theoretical relations between g, m, and λ have been proposed.[2,32] We believe that a systematic theoretical investigation on this point should determine the influence of the ratio of the molecular weight (or number of units) of the subchains along the backbone to that of the branches on the properties for previously fixed values of N and m.

Acknowledgment. We are grateful to Professor J. Garcia de la Torre of the Universidad de Murcia, Professor J. M. Barrales-Rienda of CSIC, and Professor A. Horta of UNED for helpful discussions.

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Dilute Solution Properties of Poly[*N*-(*n*-octadecyl)maleimide]. 4. Cloud Points, Θ Solvents, and Molecular Weight Dependence of Intrinsic Viscosity in *n*-Alkyl Alcohols as Θ Solvents

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ABSTRACT: Cloud point curves of poly[*N*-(*n*-octadecyl)maleimide] (PMI-18) in a homologous series of *n*-alkyl alcohols have been studied to determine Θ temperatures and thermodynamic interaction parameters. The solvents used are 1-butanol (Θ = 393.7 K), 1-hexanol (Θ = 352.1 K), 1-octanol (Θ = 326.8 K), and 1-decanol (Θ = 312.5 K). The intrinsic viscosity vs. molecular weight relationships in 1-hexanol, 1-octanol, and 1-decanol at their respective Θ temperatures have been determined (with 1-butanol, Θ is higher than the normal boiling point and $[\eta]_\Theta$ could not be determined). The $[\eta]$–M relationships present two regimes. In the region of oligomers, $[\eta]$ remains independent of molecular weight. In the high molecular weight region, the data follow a Mark–Houwink equation $[\eta] = K_\Theta M^{1/2}$, typical of unperturbed random coils. The characteristic ratio, C_∞, and the temperature coefficient of unperturbed dimensions, $d \ln \langle R^2 \rangle_0 / dT$, are obtained from K_Θ. The intrinsic viscosity is calculated theoretically by using a realistic hydrodynamic scheme previously developed for the comblike structure of PMI-18. Comparison between these theoretical $[\eta]$'s and experiment suggests that the conformation of the lateral *n*-octadecyl chains of PMI-18 is strongly solvent-temperature dependent. At the Θ temperatures of 1-decanol and 1-octanol the PMI-18 chains have a considerably lower hydrodynamic volume than at the Θ temperature of 1-hexanol.

Introduction

The preceding papers in this series deal with the fractionation[1] and the dilute solution properties[2] of poly[*N*-(*n*-octadecyl)maleimide] (subsequently referred to as PMI-18) in a number of thermodynamically good solvents, namely, benzene, tetrahydrofuran, toluene, *o*-dichlorobenzene, and 1-chloronaphthalene, all at 25 °C. The main purpose of the present paper is to determine Θ conditions for this polymer and to study its hydrodynamic behavior under such Θ conditions. Single-solvent media are chosen in the present study in order to obviate any effect arising from possible solvent–solvent interactions in ternary systems.

The theory of Shultz and Flory[3] allows for the determination of the Θ temperature, for a given polymer–solvent system, by studying the phase separation or the cloud point curve for several molecular weight fractions. The theory is known to describe adequately the behavior of flexible and moderately flexible linear polymers. It is of interest to test the same theory for branched structures such as our PMI-18, which is a comblike polymer, with a presumably semistiff backbone and flexible long *n*-alkyl side chains.

In fact, validity for comblike polymers has been tested by Chinai et al.[4–7] for poly(*n*-alkyl methacrylates) by studying Θ temperatures estimated from phase separation and second virial coefficients from osmotic measurements. Thus the values of the osmotic second virial coefficient for poly(*n*-octyl methacrylate)[4] in the ideal solvent 1-butanol (Θ = 16.8 °C determined from phase separation studies) were found to be zero or close to zero for all fractions,

0024-9297/83/2216-1707$01.50/0