

pelled to produce more compact arrangements of their internal bonds so that their interaction with neighboring units are repulsive only at shorter distances. A variable value of  $\sigma/b$  in our simulations, however, would distort the simplicity of the model, and, though it would improve the final results, it would probably not yield any further relevant information.

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## Monte Carlo Calculations for Linear and Star Polymers with Intramolecular Interactions. 2. Nonpreaveraged Study of Hydrodynamic Properties at the $\Theta$ State

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**ABSTRACT:** The hydrodynamic properties of linear and star polymers represented by a model with a Gaussian distribution of distances between neighboring elements and a Lennard-Jones potential to account for long-range interactions have been calculated by means of a Monte Carlo method based on the assumption of instantaneously rigid conformations and, therefore, free of preaveraging approximations. The results have been obtained for the value of the reduced temperature, which is shown in a preceding work to reproduce the unperturbed state of linear chains. Extrapolations to the long-chain limit give values of the hydrodynamic parameters  $P$ ,  $\Phi$ , and  $\beta$  that for linear chains are close to those obtained by similar calculations performed without the intramolecular potential. The results for stars at the same temperature are in fair agreement with experimental data of high molecular weight chains in  $\Theta$  conditions, which could not be reproduced with less detailed theoretical treatments.

## Introduction

The theoretical study of hydrodynamic properties of flexible chains in solution has generally made use of simple models in which intramolecular interactions are ignored or treated in a parametric way. Only very recently, several analytical<sup>1,2</sup> and simulation<sup>2,3</sup> treatments have considered a pairwise intramolecular potential, though these works are restricted to the study of translational properties calculated according to the Kirkwood approximation for the translational friction coefficient

$$f_t = \xi(N+1)^2 \left[ \sum_{i=1}^{N+1} \sum_{j=1}^{N+1} \langle H_{ij} \rangle \right]^{-1} \quad (1)$$

where  $N+1$  is the number of hydrodynamic units of a chain and the terms  $H_{ij}$  depend on intramolecular distances  $R_{ij}$  according to

$$H_{ij} = (\pi/3)^{1/3} b h^* R_{ij}^{-1} \quad \text{for } i \neq j$$

$$H_{ij} = 1 \quad \text{for } i = j \quad (2)$$

( $b$  is the mean statistical length between neighboring units and  $h^*$  is a hydrodynamic parameter, proportional to  $\xi$ ,

the translational friction coefficient of the units,

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

related also with the solvent viscosity  $\eta_0$ ). In eq 1  $\langle \rangle$  means conformational average. These studies analyzed the value of  $R_h$ , the hydrodynamic radius for long chains.  $R_h$  is defined as

$$R_h = f_t / 6\pi\eta_0 \quad (4)$$

It should be pointed out, however, that the Kirkwood approximation does not seem to be sufficiently accurate in most cases, leading to values of  $f_t$  significantly different from those obtained experimentally for long flexible chains<sup>4</sup> or calculated in a nonpreaveraged way for certain types of rigid structures.<sup>5</sup>

When applied to linear Gaussian chains, the Kirkwood formula also gives results that differ significantly from those calculated by a Monte Carlo average over supposedly rigid conformations, treated individually and avoiding the orientational preaverage<sup>6-8</sup> method proposed recently by Zimm.<sup>6</sup> Though possible coupling of hydrodynamic in-

teractions and chain dynamics may pose some doubts about the formal correctness of such Monte Carlo averages,<sup>9,10</sup> these calculations have been able to give the best theoretical predictions of hydrodynamic properties (translation and viscosity) for both linear<sup>6,7</sup> and branched<sup>8</sup> Gaussian chains. Moreover the Zimm algorithm has been shown to give bounds for the real values,<sup>9,10</sup> the results differing from these values by an amount that has not been clearly determined at present and is probably dependent on the polymer chemical structure.

Another approximate alternative to the Monte Carlo calculations is constituted by the use of formulas obtained through a correct preaveraged treatment of the hydrodynamic interactions.<sup>11</sup> In the case of the translational friction coefficient the corresponding formula is

$$f_t = \xi \sum_{i=1}^{N+1} \sum_{j=1}^{N+1} ((\mathbf{H})^{-1})_{ij} \quad (5)$$

and it gives noticeably different results with respect to the Kirkwood approximation when applied to certain types of branched structures,<sup>12</sup> though in linear chains differences are reduced to a marginal 2%.

In this work we have evaluated the hydrodynamic properties of flexible linear and starlike polymers both modeled as statistical beads joined by bonds of Gaussianly distributed lengths. A Lennard-Jones (LJ) potential has been incorporated into the model to take into account intramolecular interactions between nonneighboring beads. The rationale of this model was described in a preceding paper,<sup>13</sup> where it was applied to the calculation of the mean quadratic radius of gyration,  $\langle S^2 \rangle$ . For the present study we add the assumption that each bead can be considered as a spherical friction unit, represented by the coefficient  $\xi$ . Our calculations have been performed through the Zimm method of Monte Carlo sampling which, according to the facts explained above, we believe is free from the most distorting theoretical approximations contained in the theories leading to direct double-sum formulas, such as the Kirkwood equation, or even in the correct preaveraged treatments. Due to the computational difficulties of the calculations (which will be detailed in the next section) we have been restricted to the study of a single choice of LJ parameters. We have set  $\sigma/b = 0.8$ , as in the realistic computation of dimensions performed earlier.<sup>13</sup> As for the energetic parameter, we have taken  $\epsilon/k_B T = 0.3$ , which was found to yield a linear dependence of  $\langle S^2 \rangle$  on  $N$  for linear chains, i.e., corresponds to the representation of experimental  $\Theta$  conditions for these chains. The same temperature and solvent conditions also hold for the  $\Theta$  point of long star polymers, as consistently revealed by experimental data (a detailed discussion on this matter is included in ref 13). We are currently undertaking a study of the variation of hydrodynamic properties with temperature (or solvent nature) for the present model.

Our aim here has been to investigate the following points:

(a) We investigated the numerical results for the parameters  $P$  and  $\Phi$ . These parameters are defined from the translational friction coefficient and the intrinsic viscosity,  $[\eta]$ , as

$$P = f_t / 6^{1/2} \eta_0 \langle S^2 \rangle^{1/2} \quad (6)$$

$$\Phi = [\eta] M / 6^{3/2} \langle S^2 \rangle^{3/2} \quad (7)$$

where  $M$  is the molecular weight of the chain, proportional to  $N + 1$ . The values obtained through the Zimm method for simple linear Gaussian chains,<sup>6-8</sup> i.e., without intramolecular potential, are in good agreement with the best experimental estimations of these parameters at  $\Theta$  con-

ditions.<sup>4,14</sup> Now, we try to confirm this agreement with a more realistic description of chains, represented by the incorporation of the LJ potential. The ratio

$$\rho = \langle S^2 \rangle^{1/2} / R_h = 6^{1/2} \pi / P \quad (8)$$

is also obtained. The experimental data for linear polymers at the  $\Theta$  temperature have not been adequately reproduced by previous theoretical<sup>1,2</sup> or simulation<sup>2,3</sup> procedures, based on the Kirkwood formula, probably due to the lack of accuracy of these hydrodynamic treatments, though, of course, the results obtained for  $P$  for Gaussian chains with the Zimm method<sup>6-8</sup> are able to describe these data. From  $P$  and  $\Phi$  we also calculate the Flory-Scherraga-Mandelkern parameter

$$\beta = (M[\eta]/100)^{1/3} \eta_0 / f_t = (\Phi/100)^{1/3} / P \quad (9)$$

also evaluated by Zimm for linear Gaussian chains.<sup>6</sup>

(b) We also investigated the ratios  $h$  and  $g'$  for star polymers with different values of  $F$ , the functionality or number of arms. These ratios are defined as

$$h = (f_t)_b / (f_t)_l \quad (10)$$

$$g' = [\eta]_b / [\eta]_l \quad (11)$$

where subscripts  $b$  and  $l$  denote a branched chain and a linear chain with the same molecular weight. Previous calculations based on the correct preaveraged formulas<sup>12</sup> for  $f_t$  and  $[\eta]$  and compared with experimental data<sup>15-19</sup> at  $\Theta$  conditions yielded reasonably good results for  $h$  (especially for low values of  $F$ ), while the experimental values of  $g'$  were poorly described. Monte Carlo calculations of the Zimm type performed for Gaussian chains<sup>8</sup> gave results in relatively better agreement with the data. This agreement is considerably enhanced if the comparison is not performed directly on  $h$  and  $g'$  but in terms of ratios of the respective parameters  $P$  and  $\Phi$  so that the effect of expansion of stars at  $\Theta$  conditions with respect to the dimensions of equivalent Gaussian star chains is minimized. This expansion is found both experimentally<sup>17</sup> and in simulation calculations<sup>13,20</sup> and should be in part responsible for the poor performance of the direct ratios  $h$  and  $g'$  obtained for models without intramolecular interactions. Since our model has incorporated a long-range potential, which is shown to mimic the expansion,<sup>13</sup> it can be supposed to reproduce more accurately the data for these ratios.

As discussed in the preceding work,<sup>13</sup> the present model can allow us to study chains with a limited number of theoretical units. Though, in fact, each one of these units represents a Gaussian subchain, finite-size effects can be detected and, in some cases, they may distort the comparison of our results with data corresponding to real flexible chains. We have found in ref 13 that our simulations are able to reproduce the dependence of the dimensions on the molecular weight in the good solvent region (temperature above unperturbed conditions) and can also yield reasonably good estimations of the experimental data for  $g = \langle S^2 \rangle_b / \langle S^2 \rangle_l$  corresponding to the high molecular weight polymers. The variation of the dimensions with temperature obtained in our simulations is, however, greatly conditioned by model effect, biasing its utility in describing the dependence observed in real chains.

Therefore, an analysis of the ability of the model to reproduce the different experimental magnitudes related with hydrodynamic properties of real long chains should be performed not only in terms of the direct comparison between the experimental data and the high molecular weight limit extrapolations of theoretical values but also

by discussing the accuracy of such extrapolations. In fact, Fixman and Mansfield<sup>2</sup> have recently suggested that the corrections to the leading term for  $f_t$  are of the order of  $\ln N/N^{1/2}$  for models with attractive and repulsive interactions, while Guttman et al.<sup>3</sup> predict corrections of the order of  $N^{-1/2}$  for models without long-range interactions. These corrections imply a slow convergence to the limit. However, there is the possibility of studying magnitudes with a weak  $N$  dependence for which the accuracy of extrapolations is sufficiently good. Moreover, it should be considered that the nonpreaveraged calculation of the hydrodynamic properties is severely limited by the number of friction centers (see the next section) so that the study of samples of significantly longer chains cannot be currently afforded. Then, the present study serves, at least, to interpret the behavior of flexible chains with a moderate molecular weight and to see the differences between the results obtained with the present model and the preaveraged and nonpreaveraged calculations performed previously on Gaussian chains with a similar number of units. It will be shown in our analysis of results that they can be extrapolated to represent real long polymers in the case of certain magnitudes as the ratios  $h$  and  $g'$ .

### Numerical Methods

The description of the model and most aspects of the Monte Carlo sampling technique were given in the preceding paper.<sup>13</sup> Here we comment on some details concerning the calculation of the hydrodynamic properties and the modifications required in the sampling procedure in order to accomplish the evaluation of conformational averages of such properties.

**Hydrodynamic Calculations for a Rigid Conformation.** As explained in the Introduction, the Zimm method is based on performing hydrodynamic calculations for conformations that are assumed to be instantaneously rigid. For these calculations on rigid structures, we use a version of the Kirkwood-Riseman theory that makes use of the nonpreaveraged Oseen tensor for hydrodynamic interactions between chain elements. Then, the interaction equations are solved numerically by means of a computational algorithm summarized in a previous paper,<sup>21</sup> in which some additional details of the formalism can also be found.

The calculations consider a hydrodynamic size of the beads, associated with the friction coefficient  $\xi$  according to the Stokes law. Since the model used in this work contains beads representing subchains, we have introduced their size through the parameter  $h^*$  defined in eq 3 and set  $h^* = 0.25$ . This value is very near to the theoretical result for a Gaussian coil<sup>6</sup> and was used in our previous simulations for chains without intramolecular potential.<sup>8,12</sup> In previous work<sup>7,21</sup> the hydrodynamic size was represented by  $\sigma$ , but here  $\sigma$  denotes the LJ diameter.

**Monte Carlo Averages of Hydrodynamic Properties.** As in the preceding work<sup>13</sup> we use a Monte Carlo method based in stochastic processes controlled by the Metropolis criterion. Since we are considering the LJ parameters corresponding to  $\Theta$  conditions, we use process as described there. Thus, a bond vector is changed by step, implying that we should also change the position of the bond to which this vector applies and the positions of successive beads up to the end of the star arm (or to an end of the linear chain).

Since solving the interaction equations for each conformation is numerically equivalent to inverting a  $3N \times 3N$  matrix,<sup>21</sup> it can be roughly assumed to take a computational time proportional to  $N^3$ . Then, this time is verified to be for the interesting values of  $N$  much higher than that

required to generate a conformation and evaluate its intramolecular interaction energy (double sum proportional to  $N^2$ , according to eq 4 of ref 13). Consequently, the evaluation of hydrodynamic properties for all the generated chains in a set of conformations (set that we will call sample) is out of our computational capability. Then, we have used most conformations only to drive the stochastic process and have evaluated the hydrodynamic properties of a fraction (about 10%) of the total number of conformations in the sample. These selected conformations have been picked up in a random way. We have verified the validity of this procedure by evaluating  $\langle S^2 \rangle$  for the same samples averaged over the selected conformations and also over the whole sample. (According to eq 5 of ref 13, this evaluation corresponds also to a double sum whose computational time is proportional to  $N^2$  so that the latter type of averages can be more easily accomplished). Differences between averages obtained through both procedures are found to be always well within the statistical range of uncertainty involved in the computations, the statistical deviations of both types of results being similar.

Even when extended over the selected conformations, averages of hydrodynamic properties require high computational times. It should be noted, however, that the number of generated conformations in the stochastic process needed to obtain these averages is smaller than that needed to evaluate  $\langle S^2 \rangle$ , since the latter property presents generally broader distributions.<sup>21</sup> Thus, we have been able to obtain sufficiently accurate averages over stochastic processes involving 750–4000 conformations, i.e., evaluating the hydrodynamic properties of about 75–400 instantaneously rigid chains, with  $N = 18$ –54, employing a reasonable amount of time in a VAX-750 computer.

As in the calculations for  $\langle S^2 \rangle$ , we disregard the conformations generated at the initial steps of the processes in order to allow the system to relax to its equilibrium distribution. Of course, the hydrodynamic properties are not calculated in this initial part of the process. As established also in the calculations for  $\langle S^2 \rangle$ , the first conformation of each process is checked and accepted only if its energy is not high so that relaxation can be achieved in a fast way.

Stochastic processes or samples are defined by a seed number which initiated the sequence of pseudorandom numbers determining the bead positions. As in ref 13 we use eight different samples and obtain final values for the hydrodynamic properties by treating the averages corresponding to these samples as independent data. Then their arithmetic means and standard root mean square deviations are calculated. The number of samples has been duplicated for linear chains whose properties exhibit broader distributions.

### Numerical Results and Discussion

We express the numerical results of our simulation procedure in terms of the following dimensionless hydrodynamic coefficients:

$$f_t^* = f_t / 6\pi\eta_0 b \quad (12)$$

$$[\eta]^* = [\eta]M / N_A b^3 \quad (13)$$

Table I contains the mean values and standard deviations obtained for these coefficients for chains of different lengths, i.e., different values of  $N$  and different numbers of arms,  $F$  ( $F = 2$  for linear chains). The root mean square deviations associated with most results are very satisfactory. It should be remarked that, though we only evaluate the hydrodynamic properties of a small number of chains in each sample, the number of different conformations involved in each stochastic process is about 10 times higher

**Table I**  
**Monte Carlo Results for Hydrodynamic Properties of**  
**Linear and Different Types of Star Chains with**  
**Intramolecular LJ Potential**

<i>F</i>	<i>N</i>	$f_t^*$	$[\eta]^*$	<i>h</i>	<i>g'</i>
2	19	1.367 ± 0.005	35.4 ± 0.4		
2	25	1.599 ± 0.008	55 ± 1		
2	37	2.00 ± 0.01	108 ± 3		
2	49	2.36 ± 0.04	181 ± 12		
2	55	2.53 ± 0.03	216 ± 8		
6	19	1.27 ± 0.01	23.0 ± 0.3	0.93 ± 0.01	0.65 ± 0.02
6	37	1.82 ± 0.01	68 ± 2	0.91 ± 0.01	0.63 ± 0.04
6	49	2.13 ± 0.02	107 ± 4	0.90 ± 0.03	0.59 ± 0.07
12	25	1.35 ± 0.01	25.9 ± 0.4	0.84 ± 0.01	0.47 ± 0.02
12	37	1.68 ± 0.01	50.0 ± 0.8	0.84 ± 0.01	0.46 ± 0.02
12	49	1.93 ± 0.01	73 ± 2	0.82 ± 0.02	0.40 ± 0.04
18	19	1.186 ± 0.003	17.0 ± 0.2	0.87 ± 0.01	0.48 ± 0.02
18	37	1.59 ± 0.01	41 ± 1	0.80 ± 0.01	0.38 ± 0.02
18	55	1.96 ± 0.02	76 ± 3	0.77 ± 0.02	0.35 ± 0.04

(vide supra) and, moreover, each conformation differs from the preceding one in the positions of all beads placed along a part of an arm (process as described in ref 13), so that a step is equivalent to several steps of a process in which only a position is changed. This stochastic procedure, together with a distribution of the hydrodynamic properties associated with the different conformations that is considerably narrower than that associated with the geometrical properties (as shown explicitly for the freely rotating model<sup>21</sup>), explains the small statistical deviations of our simulation results. In fact, the possibility of obtaining sufficiently good estimations of averages by calculating the hydrodynamic properties of a very restricted number of conformations has been the basis of previous works on Gaussian chains performed by Zimm and ourselves.<sup>6-8,21</sup>

The results for  $f_t^*$  and  $[\eta]^*$  contained in Table I, together with the results for  $\langle S^2 \rangle$  in unit lengths referred to *b* contained in Table II of ref 13 for the set of parameters here considered, allow us to obtain numerical values of the parameters *P* and  $\Phi$  through eq 6, 7, 13, and 14. These values and those calculated for Gaussian chains with the Zimm method<sup>8</sup> are shown in Table II, where we include our estimates for the long-chain limit, obtained by extrapolation in a linear regression analysis of *P* and  $\Phi$  vs.  $N^{-1/2}$ , which takes into account numerical uncertainties.<sup>22</sup>

In a similar way, we have obtained the corresponding values for  $\rho$  and  $\beta$ , using the values of *P* and  $\Phi$  and eq 8 and 9. These results are also in Table II, with the corresponding extrapolations for long chains. In some cases (marked in Table II) the statistical correlation of a linear dependence is low so that we have decided to express the extrapolated values of the parameters as simple arithmetic means (with their root mean square deviations) over all the samples considered for the different values of *N*. In fact, a look at Table II reveals that some of our extrapolated values of the parameters *P*,  $\Phi$ , and  $\rho$  (especially in the case of star chains) can only be taken as indicative, since the variation of these parameters with varying *N* is still remarkable for the relatively short chains studied here. (The finite-size effects described in the Introduction are in these cases clearly manifested.) With this objection in mind, we will subsequently discuss the main conclusions that can be sketched from our results for the different parameters.

**Linear Chains.** The values of *P* and  $\Phi$  for long linear chains obtained with intramolecular potential are in good agreement with the experimental estimations<sup>4,14</sup> *P* = 5.7–6.0,  $\Phi$  =  $2.5 \times 10^{23}$ , though the former are slightly smaller. Something similar can be said with respect to their comparison with the results obtained with the Zimm method for Gaussian chains.<sup>6-8</sup> The fact of a significant variation of *P* and  $\Phi$  with *N*, which is not found in Gaussian chains, may serve as an explanation (together with experimental details) of the dispersion of the bibliographic data for these parameters.<sup>4,14</sup> At any rate, it seems that the introduction of intramolecular interactions confirms the previously established estimations for these useful hydrodynamic quantities.

The present calculations and those performed for Gaussian chains with the Zimm method provide also good estimations for the limit value for  $\rho$ , which agrees closely with the experimental result<sup>4</sup>  $\rho$  = 1.28. However, the Kirkwood approximation for a Gaussian chain leads to  $\rho$  = 1.50. We can attribute this difference and the smaller, though also significant, differences obtained in previous studies<sup>1-3</sup> on more realistic chain models to the lack of accuracy of the Kirkwood formula. Since the result for a Gaussian chain obtained with the correct preaveraged treatment, eq 5, differs only by a 2% of that calculated

**Table II**  
**Values of Hydrodynamic Parameters Obtained with Different Theoretical Treatments<sup>a</sup>**

<i>F</i>	<i>N</i>	<i>P</i>		$10^{-23}\Phi$		$\rho$		$10^{-6}\beta$	
		G	LJ	G	LJ	G	LJ	G	LJ
2	19	5.95 ± 0.04	5.16 ± 0.03	2.46 ± 0.06	1.71 ± 0.03	1.29 ± 0.01	1.49 ± 0.01	2.37 ± 0.06	2.31 ± 0.03
2	25	6.04 ± 0.08	5.20 ± 0.07	2.56 ± 0.10	1.70 ± 0.08	1.27 ± 0.02	1.49 ± 0.03	2.26 ± 0.06	2.30 ± 0.07
2	37	6.00 ± 0.12	5.29 ± 0.09	2.42 ± 0.19	1.81 ± 0.08	1.28 ± 0.03	1.45 ± 0.01	2.24 ± 0.10	2.30 ± 0.07
2	49	6.07 ± 0.13	5.49 ± 0.14	2.59 ± 0.22	2.04 ± 0.19	1.27 ± 0.03	1.39 ± 0.05	2.26 ± 0.11	2.31 ± 0.13
2	55	6.08 ± 0.18	5.55 ± 0.09	2.68 ± 0.27	2.05 ± 0.10	1.26 ± 0.04	1.35 ± 0.02	2.28 ± 0.14	2.29 ± 0.07
2	∞	6.2 ± 0.2	5.9 ± 0.2	2.54 ± 0.08*	2.3 ± 0.02	1.27 ± 0.02*	1.27 ± 0.03	2.28 ± 0.05*	2.27 ± 0.13
6	19	8.13 ± 0.07	6.47 ± 0.06	5.38 ± 0.03	2.73 ± 0.05	0.95 ± 0.01	1.19 ± 0.01	2.15 ± 0.02	2.16 ± 0.03
6	37	7.97 ± 0.14	6.68 ± 0.06	5.1 ± 0.5	3.03 ± 0.12	0.96 ± 0.02	1.15 ± 0.01	2.16 ± 0.11	2.17 ± 0.05
6	49	8.00 ± 0.04	6.9 ± 0.1	5.20 ± 0.06	3.27 ± 0.16	0.96 ± 0.01	1.11 ± 0.02	2.16 ± 0.02	2.15 ± 0.03
6	∞	7.8 ± 0.2	7.4 ± 0.2	4.9 ± 0.2	3.9 ± 0.3	0.98 ± 0.03	1.03 ± 0.04	2.18 ± 0.06	2.16 ± 0.02*
12	25	9.82 ± 0.02	7.20 ± 0.07	8.84 ± 0.04	3.54 ± 0.06	0.784 ± 0.001	1.07 ± 0.01	2.10 ± 0.01	2.03 ± 0.03
12	37	9.70 ± 0.06	7.52 ± 0.07	8.6 ± 0.2	4.04 ± 0.10	0.793 ± 0.005	1.02 ± 0.01	2.11 ± 0.03	2.12 ± 0.04
12	49	9.63 ± 0.11	7.58 ± 0.07	8.5 ± 0.3	3.97 ± 0.15	0.80 ± 0.01	1.01 ± 0.01	2.12 ± 0.05	2.09 ± 0.05
12	∞	9.2 ± 0.3	8.6 ± 0.3	7.6 ± 0.8	5.5 ± 0.4	0.83 ± 0.02	0.86 ± 0.04	2.16 ± 0.02	2.08 ± 0.02*
18	19	11.5 ± 0.06	7.30 ± 0.03	13.7 ± 0.3	3.57 ± 0.06	0.671 ± 0.003	1.054 ± 0.004	2.08 ± 0.12	2.09 ± 0.02
18	37	10.8 ± 0.08	7.80 ± 0.06	11.8 ± 0.3	4.35 ± 0.13	0.710 ± 0.005	0.99 ± 0.01	2.11 ± 0.17	2.09 ± 0.04
18	55	10.6 ± 0.6	8.08 ± 0.12	11.1 ± 0.4	4.80 ± 0.25	0.727 ± 0.004	0.95 ± 0.01	2.10 ± 0.14	2.09 ± 0.07
18	∞	9.3 ± 0.2	9.1 ± 0.2	7.4 ± 0.9	6.3 ± 0.4	0.80 ± 0.01	0.82 ± 0.02	2.10 ± 0.08*	2.09 ± 0.1
rigid sphere		9.93		9.23		0.774		2.12	

<sup>a</sup> G and LJ denote the results obtained for the Gaussian chain<sup>8</sup> and with a LJ intramolecular potential. \* Estimation of the extrapolated value as an arithmetic mean (see text).

from the Kirkwood formula, it seems that the most important contribution to the discrepancies can be charged to preaveraging. In this respect, it should be also mentioned that Guttman et al.<sup>3</sup> have recently obtained values through the Kirkwood formula, concluding that the results obtained with an attractive and repulsive potential at the  $\Theta$  point are somewhat smaller than those calculated for a Gaussian chain. In our simulation, we have also computed values of  $f_t^*$  with the Kirkwood formula as we did previously for Gaussian chains.<sup>8</sup> As in the case of the nonpreaveraged values, the LJ results for  $\rho$  present a marked decrease with increasing  $N$ , while the Gaussian values remain practically constant. Our extrapolations of the Kirkwood values yield the results  $\rho = 1.42 \pm 0.03$  for the LJ model and  $\rho = 1.45 \pm 0.02$  for the Gaussian chains, which, even considering the difficulties inherent to our extrapolations (they cannot exactly reproduce the Gaussian limit given above), seem to confirm the Guttman et al. findings. Though the differences may be somewhat blurred by statistical uncertainties, the extrapolated results for  $\rho$  of the LJ and the Gaussian models obtained in this work with the nonpreaveraged method are practically identical.

Our simulations with the LJ potential yield a limit value for the parameter  $\beta$  very close to that calculated with the Zimm method for a Gaussian chain, though considerably smaller than the unrealistic value predicted by the preaveraged theory,<sup>11</sup>  $\beta = 2.72 \times 10^6$ . Therefore,  $\beta$  is shown to be closer to the rigid-sphere result.

Then, the most important conclusion that can be stated from our study of linear chains is that the intramolecular potential gives results in unperturbed conditions very close to those predicted by the simpler Gaussian chains, though slight differences are noticed in some properties.

**Star Chains.** The values of  $P$ ,  $\Phi$ ,  $\rho$ , and  $\beta$  for star chains of different functionalities are shown in Table II. Differences between the present results and those obtained for Gaussian chains<sup>8</sup> are more remarkable than in the case of linear polymers. Thus,  $P$  and  $\Phi$  are considerably lower for the model with intramolecular interactions than for a Gaussian chain of the same type and number of elements, though discrepancies are consistently and considerably smaller between the values extrapolated to the long-chain limit for a given type of star due to the significant and opposite variation with  $N$  exhibited by the results obtained with both models. It should be pointed out that we have also observed model-dependent variations of the parameters  $P$  and  $\Phi$  with  $N$  in the case of linear chains without intramolecular interactions. For instance,  $P$  has been found to increase with increasing  $N$  for linear Gaussian chains, though it decreases with increasing  $N$  in the case of linear freely jointed chains.<sup>7</sup>

The experimental data of  $P$  and  $\Phi$  reported in ref 17 are close to the limit values of the Gaussian chains, while the data given in ref 18 (only for translation) are in good agreement with the model investigated in this work. (See Table III for comparison.) Nonetheless, it should be pointed out that the parameters are very sensitive to small changes in the values of one of the properties involved so that they are greatly affected by experimental or computational details. The tentative character of our extrapolated values should be again stressed. In consequence, we believe that the ratios of the values of the same property for different types of chains (such as  $h$  and  $g'$ ) should give us a clearer idea about the performance of these models (vide infra).

It can be observed that the parameters tend to their rigid-sphere limits as  $F$  increases. The small change in  $\beta$

Table III  
Theoretical and Experimental Magnitudes Related with  
Hydrodynamic Properties<sup>a</sup>

parameter	$F$		
	6	12	18
$P_{\text{exptl}}$	8.3 <sup>b</sup>	9.5, <sup>b</sup> 8.6 <sup>c</sup>	9.8, <sup>b</sup> 9.0 <sup>c</sup>
$\Phi_{\text{exptl}}$	5.2	7.1	8.2
$h_{\text{DS}}$	0.798	0.626	0.529
$h_{\text{P}}$	0.860	0.727	0.647
$h_{\text{G}}$	$0.86 \pm 0.01$	$0.75 \pm 0.01$	$0.66 \pm 0.01$
$h_{\text{LJ}}$	$0.89 \pm 0.02$	$0.82 \pm 0.03$	$0.73 \pm 0.02$
$h_{\text{exptl}}$	0.89 <sup>d</sup>	0.81, <sup>b</sup> 0.75 <sup>c</sup>	0.76, <sup>b</sup> 0.71 <sup>c</sup>
$g'_{\text{DS}}$	0.722	0.537	0.447
$g'_{\text{P}}$	0.694	0.510	0.421
$g'_{\text{G}}$	$0.58 \pm 0.02$	$0.38 \pm 0.03$	$0.24 \pm 0.03$
$g'_{\text{LJ}}$	$0.59 \pm 0.03$	$0.39 \pm 0.06$	$0.28 \pm 0.04$
$g'_{\text{exptl}}$	0.63 <sup>e</sup>	0.41 <sup>b</sup>	0.35, <sup>b</sup> 0.31 <sup>f</sup>

<sup>a</sup> DS and P denote results obtained from the preaveraged and the double-sum formulas<sup>12</sup> and G and LJ denote Monte Carlo results for Gaussian chains<sup>8</sup> and for the present model with an intramolecular potential at the unperturbed state. <sup>b</sup> Reference 17. <sup>c</sup> Reference 18 (for  $F = 12$  the data correspond to the highest molecular weight).  $P$  is obtained from  $\rho$ ; see our eq 8. <sup>d</sup> Reference 16. <sup>e</sup> Reference 15. <sup>f</sup> Reference 19.

with varying  $F$  reveals that this parameter is almost insensitive to the global shape and to the density of segments in the chain. This variation is considerably slower than that predicted by the preaveraged treatment and, together with the still lower variation with  $N$ , points out the usefulness of  $\beta$  in estimations of molecular weights from combined viscosity and translational data for linear or branched polymers.

From the results for  $f_t^*$  and  $[\eta]^*$  contained in Table I for different values of  $F$ , the ratios  $h$  and  $g'$  can be determined. As usual,<sup>8,12</sup> these ratios have been extrapolated to the long-chain limit by means of a linear regression analysis of their variation with  $N^{-1}$ . From the values of  $h$  and  $g'$  that we have included in Table I, it can be observed that the extrapolations can be performed with reasonably good accuracy (compared with the precision associated with the corresponding experimental data) since the ratios show a relatively weak dependence on  $N$ . Moreover, this dependence (a moderate decrease with increasing  $N$ ) is very similar to the one we have previously found in the case of Gaussian chains, so that it does not seem to be significantly conditioned by model effects, a difference with respect to the behavior of the parameters  $P$  and  $\Phi$ . (The  $N = 19$ ,  $F = 18$  case constitutes a singular one since it contains a bead per branch.) In the preceding work,<sup>13</sup> the ratio  $g$  could also be extrapolated to the high molecular weight limit with reasonable accuracy. The usefulness of the extrapolated values to reproduce the experimental data of  $g$  for real long polymers in their unperturbed state with repulsions between units close to the chain center was discussed there, and an identical discussion applies to ratios  $h$  and  $g'$ . For the sake of comparison, the extrapolated values of  $h$  and  $g'$  are contained in Table III, where values previously obtained with the Zimm method for Gaussian chains<sup>8</sup> and with the double-sum and correct preaveraged formulas<sup>12</sup> are included together with experimental data.<sup>15-19</sup> It can be observed that the present calculations with intramolecular potential are able to describe fairly the data. Indirect estimations of  $h$  and  $g'$  with less detailed treatments and models were discussed previously<sup>8</sup> and may exhibit a similar degree of accuracy in some cases. However, only models with intramolecular potentials and Monte Carlo averages over properties for conformations calculated in a nonpreaveraged way seem to be able to be in simulta-

neous agreement with experimental data of dimensions (see preceding paper<sup>13</sup>) and hydrodynamic properties, reproducing the respective ratios  $g$ ,  $h$ , and  $g'$ . The influence of intramolecular interactions is higher for the ratio  $g$ , since radii of gyration are more sensitive than hydrodynamic properties to the location of the inner segments of the chain, for which repulsive effect are important.

The remaining discrepancies with the data can be attributed to the model poor description of interactions in the very compact central part of the star chains, discussed previously,<sup>13</sup> and in the possible deficiencies still present in the treatment of hydrodynamic interactions represented by the Oseen tensor, neglecting the possible coupling between these interactions and flexibility,<sup>9,10</sup> finite-size effects not eliminated in the extrapolations to high  $N$ , etc. Nevertheless, the results here described allow us to think that the general assumptions implicit in this work are sufficient to give a first coherent simultaneous explanation of all these properties for both linear and star polymers at their unperturbed state. Further refinements may have to take in consideration the particular chemical structure of the chains.

Very recent work by Zimm<sup>23,24</sup> on wormlike star molecules is also based in his method of Monte Carlo simulation over rigid conformations and gives results in the flexible chain limit that are similar to those obtained by us for the Gaussian model.<sup>8</sup> However, Zimm's results are restricted to  $F \leq 6$ ; i.e., they correspond to stars in which discrepancies between the preaveraged theory and the data are not very remarkable. At any rate, these results show that only null or small stiffness in the arms can reproduce the experimental ratios. We believe that, in comparison with stiffness, the mutual repulsion of the chain elements close to the central part of the chain, described in our present model with intramolecular interactions, is a significantly more important effect. In fact, the Zimm calculations also take into account this effect in a first approximation by placing in a symmetric way the units surrounding the center of the chain.

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## Ring-Opening Polymerization of Deoxothiolphostones: Synthesis of Poly(phosphine sulfides)

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**ABSTRACT:** Ring-opening polymerization of new cyclic monomers of five- and six-membered deoxothiolphostones (**1a** and **1b**) is described. The polymerization of monomer **1a** is induced by a cationic initiator or thermally. Monomer **1b** is only polymerized with a cationic initiator. The polymerization of **1a** and **1b** produces poly(phosphine sulfides) **2a** and **2b**, respectively. The reaction mechanism of cationic as well as thermal polymerizations is discussed. These polymerizations involve a new mechanism of the C—S bond cleavage via an Arbuzov-type reaction to produce the P=S group. Poly(phosphine sulfide) **2a** is converted to polyphosphine **11** or to poly(phosphine oxide) **10** via a common phosphorane polymer, **9**. Chelating properties of poly(phosphine sulfide) are also examined.

## Introduction

Recently we have reported the cationic ring-opening polymerization of a five-membered deoxophostone (2-phenyl-1,2-oxaphospholane) to give a poly(phosphine oxide)<sup>1</sup> and the reduction of the polymer to a polyphosphine,<sup>2</sup>

(eq 1). A kinetic study on the polymerization of the deoxophostone<sup>3</sup> and the preparation of a chelating resin from the same monomer<sup>4</sup> have also been reported.

As an extension of these studies the present paper deals with ring-opening polymerization of five- and six-mem-