or oligomers of poly(dimethylsiloxane) (PDMS) can only
properties of relatively short-chain molecules like n-alkanes
peak begin to emphasize toward reptation. However, we
have not been able to reach definitively an asymptotic
region where the scaling relation \( D_c \sim M^2 \) can be tested
properly. Similarly, the bimodal behavior in \( G(\Gamma) \) suggests
that \( \Gamma \) values are susceptible to the instrumental
bandwidth limitation. If the two modes are very far apart,
we may be able to examine the dynamic behavior of each
mode individually. With neglect of the high-frequency
peak, distortion of \( \Gamma \) of the slow peak could become ap-
preciable as the characteristic frequencies of the two modes
become closer. Finally, polydispersity must necessarily
play a very important role in broadening the overlap
concentrations of the polymer matrix. Our dynamic
measurements of PS semidilute solutions showed that
single-exponential decay in \( g^{(1)}(K_r) \) at \( KL < 1 \) for the
cooperative diffusion coefficient could not be achieved until
\( C_{PS} > C_{PS}^* \). Thus, experimentally it is quite difficult
to reach the asymptotic behavior often associated with
polymer melts.

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Hydrodynamic Properties of Short Poly(dimethylsiloxane) Chains.
Numerical Results and Comparison with Experimental Data

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ABSTRACT: Numerical results for the friction coefficient and the viscosity of short poly(dimethylsiloxane)
molecules in solution have been obtained by using preaveraged or approximate formulas and also employing
a simulation method that avoids preaveraging. The latter method together with the choice of chain-
length-dependent radii for the frictional units yields results in excellent agreement with experimental data
for translation. The comparison between our results and experimental data is only fair in the case of viscosity
maybe because of the introduction of an approximate procedure to eliminate solvent effects. As a difference
with respect to our previous study of less flexible n-alkanes, our numerical values corresponding to chains
with the highest number of repeating units for which the calculations are flexible are already very close to
the long-chain limits. Therefore, our work covers the range of molecular weights going from the oligomeric
to the polymeric (Gaussian) behavior.

Introduction
The theoretical interpretation of the hydrodynamic properties of relatively short-chain molecules like n-alkanes
or oligomers of poly(dimethylsiloxane) (PDMS) can only
be performed through the use of realistic molecular models.
These models should take into account the varying
permeability to the solvent flow of chains with a different
number of frictional units. An appropriate procedure
consists in adopting the rotational isometric state (RIS) model to assign the position of the units, employing the Kirkwood–Riseman (KR) theory for the description of hydrodynamic interactions between units. One can perform accurate calculations for the hydrodynamic properties of rigid arrangements of units by means of an elaborate version of the KR theory. However, the properties of flexible chains require a conformational average in terms of perturbed distribution functions for the position vectors. Since these functions are very difficult to obtain or handle, the standard KR treatment for linear chains uses a preaveraged version of the hydrodynamic interaction tensor. The accuracy of this approximation is still a matter of research.

In the recent past, Zimm has introduced an alternative way to avoid the preaverage approximation. The Zimm model is based in obtaining the properties as averages over the results calculated for Monte Carlo samples of instantaneously rigid conformations. Though possible coupling of the chain flexibility with its hydrodynamic interactions may contribute to the real values of the properties (in fact, the rigid body approximation is shown to give upper or lower bounds to these values), the application of the Zimm model to linear and star chains yields results in significantly better agreement with the experimental data than that found with previous theoretical estimates from the preaveraged procedure.

Theoretical calculations for the hydrodynamic properties of RIS model of short polyethylene chains, obtained from approximate double-sum formulas, and nonpreaveraged, versions of the KR theory have been previously reported, and subsequent comparisons of the results with the experimental data have been performed in some cases. From these results, it seems apparent that it is possible to give a fair description of the properties of oligomers, though some difficulties remain. Thus, it is specially interesting to remark that the convenience of using a chain-length-dependent friction radius of the units has been pointed out in some of these works as the best way to find good agreement between theoretical and experimental values of the properties. Also, it is shown that a direct comparison of both sets of values is not possible in the case of the viscosity since specific corrections are needed to account for the noncontinuous nature of the solvent (whose molecular size is comparable to that of the friction units or the chain molecule).

The theoretical study of the hydrodynamic properties of short PDMS chains has been so far extended only to the calculation of the friction coefficient by means of the approximate double-sum formula also using a RIS model to evaluate relative distances between units. The comparison with experimental data is reasonably good, though some discrepancies are found in the region of very short chains that can be attributed to the approximations inherent to the hydrodynamic treatment. On the other hand, we have recently obtained averages and distribution functions for the end-to-end vector of these chain molecules. Consequently, we complete in this work the conformational study of short PDMS chains by evaluating both the translational friction and the viscosity through the use of different theoretical approaches (double-sum formulas and the preaveraged and nonpreaveraged versions of the KR theory). We include an analysis of the accuracy of these methods with respect to their performance in comparison with experimental data and a discussion on the differences and similarities with respect to the values that we have previously obtained for polymethylene chains. Specifically, their respective approaches to the Gaussian limit are studied in terms of several different molecular parameters.

**Theory and Methods**

Most of our calculations have been guided by the molecular model adopted in the previous work on short PDMS chains performed by Edwards et al. Thus, the equilibrium description of coordinates within a chain has been established according to the RIS model. We have adopted the RIS molecular parameters (bond lengths, bond angles, and rotational states) proposed by Flory and Chang. Some results have been obtained with a slightly different model in which excluded volume is introduced by means of a hard-sphere potential between units separated by more than four bonds along the chain backbone. As in the work by Edwards et al., we have considered the segments as friction units, centered in the silicon atoms. This procedure is convenient from the computational point of view, and moreover, we have verified that it gives considerably more adequate results than considering the groups as independent units with a mean frictional radius. On the other hand, the introduction of two different radii for these two groups would complicate the comparison with the experimental data, since we treat the frictional radii as fitting parameters.

**Hydrodynamic Properties.** The practical calculation of hydrodynamic properties has been performed in terms of the dimensionless coefficients

\[ f^* = f / 6 \pi \eta b \]

(1)

for translation, where \( f \) is the translational friction coefficient of the chain, \( \eta \) is the solvent viscosity, and \( b \) is the length of the Si–O bond (1.64 Å). If the small coupling with internal motions is neglected, this friction coefficient can be directly related to several experimental properties at dilute solution, e.g., the translational diffusion or the sedimentation coefficients. (In this work we include comparisons with bibliographic experimental data of the translational diffusion coefficient.) For viscosity we use

\[ [\eta]^* = [\eta] M / N A \]

(2)

where \([\eta]\) is the intrinsic viscosity of the chain, \( M \) is the molecular weight, and \( N A \) is Avogadro’s number.

We have used the following hydrodynamic treatments, all of them describing the hydrodynamic interaction between units.

**(a) Double-Sum Formulas.** They are based on approximate solutions for the KR equations including hydrodynamic interactions. For the translational friction coefficient, we employ the well-know Kirkwood formula

\[ f^* = (\sigma / b) N^2 \left[ \sum_{i=1}^{N} \sum_{j=1}^{N} H_{ij} \right]^{-1} \]

(3)

where \( N \) is the total number of friction units (in this case \( N = (N_b / 2) + 1 \), \( N_b \) being the total number of Si–O bonds along the chain), \( \sigma \) is their hydrodynamic radius, and

\[ H_{ii} = 1 \quad \text{for} \quad i = j \]

\[ H_{ij} = (\sigma / b) (R_{ij}^{-1}) \quad \text{for} \quad i \neq j \]

(4)

\(<R_{ij}^{-1}>\) being the mean reciprocal distance between the elements \( i \) and \( j \), expressed in dimensionless units relative to \( b \). (We will employ the same relative length units for all the different distances or vectors related to the position of groups or units within the chains.)

For viscosity we use the simplified Tsuda formula

\[ [\eta]^* = [\eta] M / N A \]

(2)
\[ \eta^* = \frac{(\sigma/b)\left(\sum_{i=1}^{N} (R_i^2)^{-1}\right) \left(\sum_{i=1}^{N} \sum_{j=1}^{N} H_{ij} (R_i R_j)\right)^{-1}}{} \] 

where \( R_i \) represents the position vector of unit \( i \) referred to the center of masses of the chain.

(b) Preaveraged Formulas. They are derived by correctly solving the KR equations corresponding to a conformational and orientational preaverage of the hydrodynamic interaction. For \( f^* \) we use the Horta and Fixman formula:

\[ f^* = \frac{(\sigma/b)\sum_{i=1}^{N} (H^{-1})_{ij}}{} \]

while for viscosity we employ the formula first derived by Gottlieb and Svetlov:

\[ \eta^* = \frac{(\sigma/b)\pi \sum_{i=1}^{N} (H^{-1})_{ij} (R_i R_j)}{} \]

Equations 5 and 7 include the factorization:

\[ \langle R_{i,j}^{-1} (R_i R_j) \rangle = \langle R_{i,j}^{-1} \rangle \langle R_i R_j \rangle \]

as an additional approximation.

(c) Nonpreaveraged Calculations. We have obtained also nonpreaveraged results through the Zimm method described in the Introduction. Thus, we generate samples of conformations whose properties are evaluated by adopting the rigid-body approximation and obtain final averages over these samples. As in the Monte Carlo simulations employed to calculate geometrical averages that will be described later, we assign the sequence of rotational angles that defines a conformation in the RIS model according to conditional probabilities. These probabilities are calculated from statistical weights associated with first-order and second-order interaction energies between groups that (together with the rest of the molecular parameters for unperturbed PDMS chains) have been taken from Flory and Chang. Excluded volume is introduced in some instances. References 27 and 28 contain further details on these Monte Carlo procedures.

The hydrodynamic properties of the rigid conformations are obtained by means of a theoretical approach that avoids the orientational preaverage of hydrodynamic interaction. These interactions are described by an extended version of the Oseen tensor. Translational–rotational coupling is also considered, and the viscosity center for position vectors is now rigorously defined. Details on the computational algorithm used to solve the interaction equations can be found in previous work. It should be remarked for further discussion that the results are dependent on the choice of the radius for the frictional units, as in the double-sum and preaveraged treatments.

We have made use of four different samples of conformations in each case. Every one of these samples is generated from a different value of the seed number that initiates the sequence of choices in the simulation process. The mean values of properties corresponding to each sample are treated as independent data, and therefore, we obtain the uncertainties associated with the final results from the statistical study of these sets of data. The number of conformations generated per sample is 500 for \( N_b < 50 \) and 300 for \( N_b = 50 \) (the longest chain included in these simulations). Though these numbers are not very high, the uncertainties in the final results are small since the conformational distribution of the hydrodynamic properties is considerably narrower than in the case of end-to-end distances or dimensions.

Geometrical Averages. It can be observed that the double-sum and preaveraged formulas are obtained in terms of averaged distances between pairs of units, since we need to know the different values of \( \langle R_{i,j}^{-1} \rangle \) in eq 4 and also the averages \( \langle R_i R_j \rangle \) in eq 5 and 7 that can be evaluated as:

\[ \langle R_i R_j \rangle = \frac{1}{N_b} \sum_{k=1}^{N_b} (\langle R_{i,k} \rangle^2 + \langle R_{j,k} \rangle^2) - \langle R_{i,j} \rangle^2 - \langle S^2 \rangle \]

where \( \langle S^2 \rangle \) is the mean radius of gyration of the chain that can also be expressed in terms of the averages \( \langle R_{i,j} \rangle \)

\[ \langle S^2 \rangle = N_b^2 \sum_{i=1}^{N} \sum_{j=1}^{N} \langle R_{i,j} \rangle^2 \]

The averaged distances between friction units \( i \) and \( j \) have been estimated as the mean end-to-end distances corresponding to chains joining both units. Thus, if these units are separated by \( N_b \) bonds, we take

\[ \langle R_{i,j} \rangle \approx \langle R^2 \rangle_{N_b} \]

\( (N_b = 2|i-j|) \). The mean quadratic end-to-end distances have been previously obtained in our study of the distribution function of PDMS chains. We have verified that for \( N_b = 6, 8, 36, \) and 60, the approximation represented by eq 11 is good since chains with different lengths yield very similar averages \( \langle R_{i,j} \rangle \) for every given value of \( |i-j| \) and these results are always very close to the corresponding result for \( \langle R^2 \rangle_{N_b} \) previously calculated. (The results for \( \langle R_{i,j} \rangle \) were obtained by building chains with the desired number of bonds but ignoring the length contributions of the bonds preceding unit \( i \) or following unit \( j \) in the iterative equations that determine the end-to-end distance. This type of exact calculation for the end-to-end distance using iterative equations has been described in ref 20.)

The reciprocal averages \( \langle R^{-1} \rangle_{N_b} \) (which do not admit an exact iterative treatment) have been obtained by a complete enumeration of conformations in the cases for which \( N_b \leq 10 \). (These exact simulations have been performed according to previously reported methods.) We have also calculated the values for these quantities corresponding to \( N_b = 10, 20, \ldots, 90, 100 \) from our numerical results for the end-to-end distribution function, \( F(R) \). Thus, the desired averages are calculated as

\[ \langle R^{-1} \rangle_{N_b} = 4\pi \int_{0}^{\infty} R F(R) dR \]

by using a Newton–Cotes method of numerical integration. The values of \( \langle R^{-1} \rangle_{N_b} \) not directly obtained by simulation or calculated from eq 12 have been evaluated from numerical interpolation of the quantity

\[ C_R(N_b) = \langle R^{-1} \rangle_{N_b} / \langle R^2 \rangle_{N_b}^{1/2} \]

represented in Figure 1. It can be observed that \( C_R \) tends to its Gaussian limit for long chains, \( C_R = (6/\pi)^{1/2} \), faster than in the case of \( n \)-alkanes, indicating higher flexibility for the PDMS chains. Our highest value corresponding to \( N_b = 100 \) is about 3% below this limit. From the values of \( C_R \) interpolated from Figure 1 and the values of \( \langle R^2 \rangle_{N_b} \) (that we know in all the cases from our exact iterative calculations), we obtained the different reciprocal averages involved in the evaluation of the hydrodynamic properties.

Analysis of Results

(a) Choice of Radius for the Frictional Units. The radius of the frictional units, \( \sigma \), is directly involved in the calculation of hydrodynamic properties. This radius can be directly chosen as a fitting parameter, assuming that
it does not depend on the chain length. Another possibility
is to use as the adjustable parameter the quantity \( h^* \) (in
our previous notation\(^{10,16} \)) or \((c\_b)\) (employed in the
previous work on PDMS chains by Edwards et al.\(^{19}\))

\[
\begin{align*}
  h^* &= (3/\pi)^{1/2} (c\_b) = (3/\pi)^{1/2}(\sigma/b)(\langle N_b \rangle/\langle R^2 \rangle)^{1/2} \\
  \end{align*}
\]

(14)

Then, eq 14 means that \( \sigma \) is varying with the charac-
teristic ratio of the chain \((R^2)/\langle N_b \rangle/\langle N_p \rangle\), reaching an asym-
ptotic limit for long polymers. This type of variation of \( \sigma \)
has been proposed previously\(^{10,11,15} \) for the study of \( n \)-al-
kanes in different solvents. This way the frictional radius of
a unit corresponds to the size of a segment in a freely
jointed chain with the same \((R^2)\) of the actual molecule.
The connectivity between units in the freely jointed model
seems to be more consistent with the chain flexibility and
with the use of the Ossen tensor that assumes disconnected
units.\(^{11} \) The adequacy of this approximation may be better
for chains of high flexibility (as the PDMS) which are more
accurately represented by ideal models. However, the
relative positions between units that characterize the
diffusive motion of the chain should be still calculated
according to more realistic descriptions of the molecule
(in our case the RIS model). Such a mixed description gives
a better description of the experimental data through some
of the numerical treatments previously investigated,
though in our previous analysis of results obtained through
the Zimm method\(^{16} \) we could not reach a definitive con-
clusion on the advantages of choosing either a fixed or
variable value of \( \sigma \).

In this work we have adopted alternatively \( \sigma \) and \( h^* \) (or
\((c\_b)\)) as the fitting parameter, in order to establish which
procedure gives a better description of the data of PDMS
chains.

(b) Solvent Corrections. In our previous work for \( n \)-alkanes,\(^{10,16} \) we discussed the difficulties of comparing
experimental data for viscosity with the conformational
intrinsic viscosity, obtained through the numerical methods
described above. In fact, the data include contributions
from important solvent effects and solvent–polymer in-
teractions since the chain and solvent molecules are of
similar sizes. In a first approximation, we can assume that
these effects are additive, as it is indicated in the \( n \)-alkane
case by the shifts in the experimental curves of intrinsic
viscosity vs. number of friction units produced by the
change of solvent.\(^{10} \) Then, the conformational intrinsic
viscosity can be obtained from the experimental value,
\([\eta]_{\text{exp}}\) as

\[
[\eta]_{\text{exp}} = [\eta]_{\text{exp}} = [\eta]_{\text{isol}} \tag{15}
\]

where \([\eta]_{\text{isol}}\) takes care of all the solvent effects.

As in our most recent treatment for \( n \)-alkanes,\(^{16} \) we estimate \([\eta]_{\text{isol}}\) following the method of Bloomfield and

co-workers\(^{15,17} \) based on thermodynamic arguments. Ac-

According to this treatment and our analysis of data of several
different mixtures of solvents,\(^{16} \) \([\eta]_{\text{isol}}\) is decomposed as

\[
[\eta]_{\text{isol}} = [\eta]_s + a[\eta]_G + b[\eta]_V \tag{16}
\]

where \([\eta]_s\) is the contribution due to the differences of
viscosity between solute and solvent (ideal intrinsic vis-
cosity), \([\eta]_G\) is that corresponding to the activation free
energy per mole of solution, according to the absolute rate
theory of liquids, and \([\eta]_V\) is the value given by the alter-
native formulation in terms of free volume. Our analysis of
results for different mixtures allowed us to propose equal
weights for the latter two contributions,\(^{16} \) i.e., \( a = b = 1/2 \).
(Other combinations have been tried with less satisfactory
performances.)

The calculation of the different contributions to eq 16
for mixtures of PDMS in toluene at 25 °C that we report
here are guided by the expression given in ref 17. The
values for the parameters and properties of solvent, solute,
and mixtures involved in these expressions have been
taken from bibliographic data. Thus, we have used values
of the molar volume and characteristic temperature, vol-
ume, and pressure of toluene reported by Heintz et al.\(^{29} \)
while its viscosity is taken from ref 30. The viscosity of
PDMS has been interpolated from results corresponding
to polymers with different weight-average molecular
weights, \( M_w \), reported by Dodgson et al.\(^{31} \) Also, we use
interpolations from data of characteristic temperatures,
pressures, and volumes of PDMS with different values of
\( M_w \) as described in ref 29 to perform the calculations.
Similar interpolations from values contained in ref 29 are
employed to estimate the parameters \( S_2/S_1 \) (for infinite
dilution) and \( \chi_{12} \), the latter being practically constant for
\( M > 1.000 \). These parameters also intervene in the cal-
culation of the different contributions to \([\eta]_{\text{isol}}\).

Finally, the molar volumes of PDMS chains at 25 °C
have been interpolated from the data reported by Sutton
and Mark\(^{28} \) for pure oligomers at 20 and 30 °C. The value
applying to a chain of 300 repeating units obtained by
Baker et al.\(^{34} \) serves to complete the range for the inter-
polation of results for different chain lengths. Though
the interpolation procedures do not guarantee an extremely
precise estimation of the magnitudes (especially in the
latter case of molar volumes), the accuracy is in all cases
higher than that required to obtain \([\eta]_{\text{isol}}\), since the cal-
culations are based in approximate theoretical assumptions
that cannot yield exact results. At any rate, the uncer-
tainties in the interpolated results are always smaller than
0.01 %.

The different contributions that we have obtained for
\([\eta]_{\text{isol}}\) are given in Table I, together with interpolations for
convenient values of the number of theoretical units ob-
tained from direct experimental data of intrinsic viscos-
ities for different molecular weights measured by Dodgson
and Semlyen\(^{40} \) for the PDMS + toluene system at 25 °C. We
only cover the low molecular weight region of these data,
since excluded volume effects are important in this system
for high molecular weights, and the numerical calculations
of these effects through a detailed description of chains
with a high number of friction units is not feasible.

It can be observed in Table I that the solvent corrections
are small compared to the absolute values of the experi-
mental data. In fact, they are only considered less impor-
tant than those found for \( n \)-alkane chains. These small
contributions can be also predicted from the similarities
shown by the data of intrinsic viscosities of short PDMS
chains in different solvents contained in ref 35. (Since for
these short chains excluded volume effects depending on
the solvent quality are not important, the discrepancies

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between values corresponding to the same chain in different solvents would be directly attributed to the finite size solvent effects. According to the calculations, the main reason for such small corrections in the present case is the low value of the ratio \( \eta_1/M_w \) (\( \eta_1 \) is the solvent molar volume) due to the presence of massive \((Si-O)\_n\) groups in the polymer. All the different corrections are proportional to this ratio, and therefore, the contributions are smaller than in the lighter n-alkane chains of similar lengths. (This mass effect is especially remarkable for the contribution \( [\eta]_L \).

(c) Theoretical Results. A selection of our results for \( f^* \) can be found in Table II. We include the results corresponding to the choices of \( \sigma \) and \( \langle c_0 \rangle \) that best fit the experimental data, taken from the complete set of numerical results obtained with the different choices of \( \sigma \) and \( h^* \) used in our calculations. We show results obtained with the Kirkwood and preaveraged approximations and Monte Carlo means, together with their statistical errors, obtained through the nonpreaveraging Zimm method. Some values have been calculated taking into account the excluded volume effects by means of a hard-sphere intramolecular potential of diameter \( d = 2 \) (in Si-O bond length units) for long-range interactions, between units separated by more than four real bonds along the chain. It can be observed that excluded volume is not an important effect in the considered region of low molecular weights in which the simulation methods are applicable (differences never exceed 4% with respect to the equivalent chain without long-range interactions). We also include in Table II Monte Carlo results, with their statistical errors, obtained by direct application of the Kirkwood formula to each conformation. Compared with the values obtained with the same formula through the use of geometrical averages, they serve as an indication about the validity of our numerical procedures to obtain these averages. Differences between both sets of results are always below 2%.

Quantitative differences between the results obtained with the different methods or approximations are not very high, though they tend to increase with increasing molecular weights (the differences in the Gaussian limit are more relevant as reported previously\(^{35,7}\)). Since the Zimm method cannot be extended to very long chains, the approximate formulas could be useful in these cases by taking into account the systematic differences found for the values obtained with different methods.\(^{7}\) However, we have not carried out an extensive investigation of the high molecular weight region because the PDMS chains are flexible enough to reproduce the Gaussian behavior just above the studied range of molecular weights, as both translational properties\(^{36}\) and viscosity\(^{36}\) of unperturbed chains clearly show. On the other hand, the study of the properties of long chains with excluded volume interactions may reproduce the behavior in good solvents. However, this study is numerically difficult, even when the simplest formulas are employed because it requires the calculation of geometrical averages through simulation methods and, therefore, it would be more adequate for an independent investigation.

In Table III we present the results obtained for \( [\eta]^* \) using two different choices for \( \langle c_0 \rangle \), which implies a chain-length-dependent friction radius, \( \langle c_0 \rangle = 0.2 \) and 0.3. Again, these results have been calculated with the double-sum and preaveraged formulas and with the Zimm method. Some results obtained for excluded volume chains (\( d = 2 \)) are also shown. The differences between values obtained with different methods are small, though slightly higher than those found for \( f^* \).

### Table I

<table>
<thead>
<tr>
<th>( M_w )</th>
<th>( N )</th>
<th>( [\eta]_L )</th>
<th>( [\eta]_G )</th>
<th>( [\eta]_v )</th>
<th>( [\eta]_L )</th>
<th>( [\eta]_{Lep} )</th>
<th>( [\eta]_{Lorr} )</th>
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<td>1198</td>
<td>16</td>
<td>0.235</td>
<td>-0.326</td>
<td>-0.040</td>
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<td>0.026</td>
<td>0.067</td>
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<td>1.854</td>
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<td>0.082</td>
<td>2.101</td>
<td>2.003</td>
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<tr>
<td>1938</td>
<td>26</td>
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<td>-0.258</td>
<td>0.094</td>
<td>0.088</td>
<td>2.261</td>
<td>2.156</td>
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</table>

*Intrinsic viscosities in cm³/g.

### Table II

<table>
<thead>
<tr>
<th>( \sigma )</th>
<th>( N )</th>
<th>( \langle c_0 \rangle )</th>
<th>( \langle c_0 \rangle = 0.4 )</th>
<th>Experimental Data</th>
</tr>
</thead>
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<td>1.9976 ± 0.0003</td>
<td>1.9441</td>
<td>1.9566 ± 0.0004</td>
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<td>8</td>
<td>2.9209</td>
<td>2.9222 ± 0.0006</td>
<td>2.9880</td>
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<td>3.8377 ± 0.003</td>
<td>3.9805</td>
<td>4.0102 ± 0.0004</td>
</tr>
<tr>
<td>16</td>
<td>4.1600</td>
<td>4.1500 ± 0.005</td>
<td>4.2372</td>
<td>4.2742 ± 0.0005</td>
</tr>
<tr>
<td>19</td>
<td>4.6418</td>
<td>4.6256 ± 0.008</td>
<td>4.5851</td>
<td>4.6013 ± 0.0005</td>
</tr>
<tr>
<td>21</td>
<td>4.9928</td>
<td>4.7455 ± 0.035</td>
<td>4.8144</td>
<td>4.8144 ± 0.0005</td>
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<tr>
<td>26</td>
<td>5.1989</td>
<td>5.2757 ± 0.01</td>
<td>5.3241</td>
<td>5.3747 ± 0.0005</td>
</tr>
</tbody>
</table>

*Obtained directly or from Monte Carlo, MC, simulations. *Friction unit radii are indicated by \( \sigma \) or \( \langle c_0 \rangle \).
Numerical Results for $[\eta]^*$ from the Double-Sum (DS) and Preaveraged (PR) Formulas and from the Zimm Method without and with Excluded Volume (EV) Compared with Corrected and Interpolated Values from the Experimental Data for $[\eta]$ Reported in Reference 25a

<table>
<thead>
<tr>
<th>$N$</th>
<th>DS</th>
<th>PR</th>
<th>Zimm</th>
<th>Zimm (EV)</th>
<th>exptl</th>
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<tr>
<td>4</td>
<td>40.96</td>
<td>42.11</td>
<td>43.83 ± 0.03</td>
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<tr>
<td>5</td>
<td>69.86</td>
<td>73.08</td>
<td>76.05 ± 0.04</td>
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<tr>
<td>8</td>
<td>188.8</td>
<td>202.9</td>
<td>209.23 ± 0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>557.5</td>
<td>601.8</td>
<td>598.2 ± 0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>714.8</td>
<td>770.8</td>
<td>759 ± 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>978.5</td>
<td>1063.8</td>
<td>1032 ± 3</td>
<td></td>
<td></td>
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<tr>
<td>21</td>
<td>1171</td>
<td>1260.7</td>
<td>1218 ± 3</td>
<td>1078</td>
<td></td>
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<tr>
<td>26</td>
<td>1706</td>
<td>1837</td>
<td>1756 ± 6</td>
<td>1567</td>
<td></td>
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</tbody>
</table>

$[\eta]^*$ = 0.3

Friction unit radii are indicated by $(c_b)$.

$F_{\text{PDMS}}$ + TOLUENE, $T = 25^\circ$C

Figure 2. $N^{1/2}/f^*$ vs. $N_0$ from theoretical values of $f^*$ obtained from Monte Carlo simulation (MC), Zimm method, or the Kirkwood formula, with friction unit radii as indicated. Values from experimental data of translational diffusion coefficients are also included.

Discussion

(a) Comparison with Experimental Data. In Table II we include values of $f^*$ calculated from experimental data. In Table III we show results for $[\eta]^*$ calculated from eq 2, using the interpolated values of the experimental data reported in ref 26, corrected to substract the solvent effects and contained as $[\eta]^*$ in Table I. Graphic comparisons are, nevertheless, simpler and more appealing.

Figure 2, we have plotted different theoretical results for translation, obtained from the Kirkwood formula and the Zimm method, together with experimental data. All these results are presented in the form of $N^{1/2}/f^*$ vs. $N_0$ plots. This way the performance of the different methods is more clearly manifested. We can see that only the use of a chain-length-dependent radius for the frictional units reproduces the upturn of the curves observed for very low molecular weights. Moreover, the application of the Zimm method (free of preaveraging approximations) represents a substantial improvement in the description of the experimental data. In fact, the calculations through this method performed with $(c_b) = 0.4$ are able to give an excellent reproduction of the data for PDMS in toluene at 25 °C. Excluded volume results (not included in Figure 2) are very close to those from unperturbed chains so that this effect is not relevant in the agreement between experiments and theory within the considered range of molecular weights. The value $(c_b) = 0.4$, together with eq 14 and the limiting value of the characteristic ratio for very long chains, yields the asymptotic result $\sigma = 2.3$ Å for the friction radius of the units. This value compares well with molecular predictions. From Bondi’s tables of van der Waals volumes, the van der Waals radius of the $-(\text{SiMe}_20)_n$ units is found to be $r_w = 2.8$ Å. According to current theories of the Stokes-Einstein type, the friction radius should be $\sigma = \frac{1}{3}\frac{r_w}{h}$.

Figure 3. Numerical results for $[\eta]^*$ obtained by Monte Carlo simulation (MC) vs. $N_0$. Values from interpolated data of intrinsic viscosities, including corrections for solvent effects, are also presented.

According to eq 14, $(c_b) = 0.4$ is equivalent to $h^* = 0.41$. This value is about twice the result obtained for $n$-alkanes. The considerably higher size of the friction units used in this work compared to the $-(\text{CH}_2)_n$ groups accounts for this difference.

In Figure 3 we present some of the values for $[\eta]^*$ obtained from numerical calculations and from experimental data. (The theoretical results are represented by fitting curves, the representation also used for some of the theoretical values of translational properties in Figure 2.) It can be observed that the points obtained from the experimental data lie between the theoretical curve corresponding to $(c_b) = 0.2$ and 0.3. It should be remarked that, as for translational properties, the introduction of the excluded volume effect does not improve the performance of the theoretical results. The theoretical description of the experimental values is, however, poorer than in the case of translation, and the best choices for $(c_b)$ are significantly smaller for viscosity. Something similar, though with smaller differences between the theoretical description of both properties, was found in our study of $n$-alkanes, where, furthermore, we could not reach such a remarkable agreement between theory and experiments as the one found here for the translational friction coefficients. We believe that the problems inherent to the role of the solvent in the viscosity of oligomeric solutions and the deficiencies of an approximate treatment as that used in the present work to describe this role may be responsible for most of the differences found in the case of this property with respect to the comparison with experimental data. At any rate, the results for viscosity should be considered as fair, since we have been able to reproduce the main trends and order of magnitudes of the data. Finally we should remark that the RIS model used in this work to describe the PDMS chains is slightly more realistic than the one employed in our previous work for $n$-alkanes. There, second-order interactions between units separated by four bonds were suppressed and their effect grouped with the...
long-range interactions, avoiding this way the use of conditional probabilities in the generation of conformations.10,14 Though we think that the effect of this approximation on the final results must be small, it may have some influence on the slightly poorer description of the translational properties that we found for the latter molecules. In the study of Edwards et al. for n-alkanes,16 the rigorous RIS model is adopted, but unfortunately, the results are presented in a more indirect way that precludes an easy comparison with our values.

(b) Chain Parameters. In order to perform a more complete study of the transition of molecular properties from the short chain to the Gaussian region in unperturbed conditions and also with the aim of clarifying the use of these properties to estimate molecular magnitudes, we have calculated the parameters

$$C_\text{S} = \langle R^2 \rangle / \langle S^2 \rangle$$

(17)

$$P = (f_b / b) / B^{1/2} \rho_0 \langle S^2 \rangle^{1/2}$$

(18)

$$\phi = (\langle \eta / \rho_0 \rangle M / \rho_0^{3/2} \langle S^2 \rangle^{3/2})$$

(19)

(we are expressing $R^2$ and $S^2$ in units relative to length $b$) and

$$\beta = (M \langle \eta \rangle / 100)^{1/3} \rho_0 f_b$$

(20)

From our results for $f^*$ and $[\eta]^*$ and the previously obtained values of $\langle R^2 \rangle$, if eq 1 and 2 are combined with eq 17–20 and $\langle S^2 \rangle$ is evaluated according to eq 10 in terms of the different averages $(R_i f_i^2)$, such calculations are feasible. ($\langle S^2 \rangle$ is an interesting property by itself since it can be experimentally estimated, e.g., from scattering data.)

The results for $C_\text{S}$ are shown graphically in Figure 4. It can be observed that the asymptotic value $C_\text{S} = 6$, corresponding to a Gaussian chain, is approached as $N$ increases, the differences with respect to this limit being small (less than 10%) for $N > 26$. This fact points out again the high flexibility of the PDMS oligomers. In Table IV, we present a selection of our numerical results for $\langle S^2 \rangle$, $P$, $\phi$, and $\beta$. The results for $P$ and $\phi$ have not been calculated for excluded volume model chains, because we would need greater samples than those used here to simulate $\langle S^2 \rangle$. (The distribution functions of hydrodynamic properties are considerably narrow in comparison with the distribution of dimensions.14) Then, only nonsimulation values corresponding to unperturbed chains are available. For $\beta$ (that combines $f$ and $[\eta]$), we present results for chains with and without excluded volume. We do not think that the computational effort to evaluate the geometrical averages needed to analyze the influence of excluded volume in the other parameters would be justified in the present case.

The main conclusion from the set of results corresponding to the molecular parameters of the different chains is (as it has been stated above for $C_\text{S}$) that the longest chains are already very close to the Gaussian behavior as the parameter values are close to their limits for long Gaussian chains. This approach to the long-chain limits is remarkably faster than in the case of n-alkanes.14 The choice or type of parameter used to describe the friction of the units produces differences in the values that are only marginal for these longer chains. We have tried extrapolations of the values of $P$ and $\phi$ obtained from the Zimm simulations for $(c_\phi) = 0.4$ to the long-chain limit. We use in these extrapolations the results corresponding to the three longest chains and perform linear regression analysis of the values vs. $(N - 1)^{-1/2}$ and $(N - 1)^{-1}$. (A linear dependence on $(N - 1)^{-1/2}$ can be expected according to the classical Kirkwood–Riseman theory,24 but the partial permeability of the chains may modify this correlation to the $(N - 1)^{-1}$ dependence of free-draining chains.) We obtain $P_\infty = 5.72$ and $\phi_\infty = 2.26 \times 10^{10}$ using the $(N - 1)^{-1/2}$ dependence and $P_\infty = 6.16$ and $\phi_\infty = 2.59 \times 10^{10}$ with the

### Table IV

<table>
<thead>
<tr>
<th>$N$</th>
<th>$(S^2)$</th>
<th>$P$</th>
<th>$\phi$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
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<td>4</td>
<td>3.53</td>
<td>8.59</td>
<td>9.03</td>
<td>9.31</td>
</tr>
<tr>
<td>5</td>
<td>5.12</td>
<td>7.67</td>
<td>8.42</td>
<td>8.58</td>
</tr>
<tr>
<td>8</td>
<td>10.45</td>
<td>6.36</td>
<td>7.29</td>
<td>7.56</td>
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<td>21.96</td>
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<td>73.49</td>
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<td>50</td>
<td>93.42</td>
<td>5.65</td>
<td>5.78</td>
<td>5.86</td>
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</table>

*Friction unit radii are indicated by $\sigma$ or $\langle c_\phi \rangle$. *Gaussian limit.*
with detailed models as the RIS chain are feasible. (See reached in the study of Gaussian chains.4** The values
To our knowledge, these extrapolations from the oligomeric
to the long-chain limit have not been performed for hy-
(1987). The same conclusions were
obtained for the PDMS chains by using the Zimm method
are about $\beta = 2.16 \times 10^2$ for the longest chains. This result
is slightly smaller than the long-chain Gaussian limit.4,9
Excluded volume is not important for these relatively short
chains, and then, as expected, it does not affect the value of $\beta$, a parameter that does not depend much on the form
or size of the molecules8 and, consequently, is also insen-
sible to the model details.

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Ministerio de Educació n y Ciencia (PFFI).

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