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**Registry No.** (DMAEMA)(MMA) (copolymer), 26222-42-4; silica, 7631-86-9.

# Monte Carlo Calculation of Hydrodynamic Properties of Cyclic Polymers in Ideal Solution

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ABSTRACT: Monte Carlo simulation and the rigid-body treatment have been used to calculate the radius of gyration, $\langle s^2\rangle$, friction coefficient, $f$, and intrinsic viscosity, $[\eta]$, of cyclic polymers at nearly ideal conditions. Three chain models, one with fixed bond lengths, another with Gaussian bonds, and another including balanced, attractive, and repulsive interactions, have been studied. They all yield the expected chain-length dependence of $\langle s^2\rangle$, $f$, and $[\eta]$ at ideal conditions. The results are finally expressed in terms of the Flory parameters $\Phi$ and $P$, combining $\langle s^2\rangle$ with, respectively, $[\eta]$ and $f$, and the ratios $q_s$, $q_f$, and $q_\eta$ of the properties of the cyclic polymer to those of the linear polymer of the same length. We have analyzed experimental data for polystyrene and poly(dimethylsiloxane). The conditions at which cyclic polymers behave ideally are different from those for linear polymer, and therefore the use of the $q$ ratios is somewhat ambiguous or even misleading. On the other hand, our simulation results indicate that the $q$'s may be model dependent. We thus conclude that the Flory parameters are more significant. Our results for $\Phi$ and $P$ of cyclic polymers are in much better agreement with the experimental ones than those calculated by Bloomfield and Zimm through a treatment in which hydrodynamic interaction was preaveraged. This conclusion complements a similar one obtained for linear polymer, stressing the need of a rigorous treatment of hydrodynamic interactions.

## Introduction

Kramers determined over 40 years ago that the ratio of the intrinsic viscosity of a cyclic or ring macromolecule,[1] $[\eta]_c$, to that of a linear macromolecule of the same molecular weight, $[\eta]_l$

$$q_\eta = [\eta]_c/[\eta]_l \qquad (1)$$

was $^1/_2$ in the absence of hydrodynamic interaction and excluded-volume effects. Zimm and Stockmayer[2] explained that this value was identical with that of the ratio of the mean-squared radii of gyration

$$q_s = \langle s^2\rangle_c/\langle s^2\rangle_l \qquad (2)$$

When these studies were published, ring polymers were mostly an academic curiosity, in contrast with the actual importance of this type of polymers, as summarized in a recent book.[3]

Interest on cyclic macromolecules rose suddenly in the 1960s after the discovery that DNA exists as large closed rings.[4-6] The applicability in molecular biology prompted theoretical studies of the conformation and hydrodynamics of cyclic polymers. A classical reference is the work of Bloomfield and Zimm,[7] who applied Zimm's bead-and-spring theory[8] to the calculation of $[\eta]$ and Kirkwood formula[9] for the translational friction coefficient, $f$, or the diffusion coefficient $D = kT/f$. Bloomfield and Zimm studied the influence of both hydrodynamic interaction and excluded volume on the $q_\eta$ ratio and on the ratio of friction coefficients

$$q_f = f_c/f_l \qquad (3)$$

In the absence of excluded-volume effects, when the intra-

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chain distances obey Gaussian statistics, these authors found $q_\eta = 0.66$ and $q_f = 0.85$.

Avoiding reference to polymers with other topology, two constants combining hydrodynamic properties and dimensions can be formulated for cyclic polymers as usually done for linear polymers. These are the parameters

$$\Phi = [\eta]M/6^{3/2}\langle s^2\rangle^{3/2} \tag{4}$$

and

$$P = f/6^{1/2}\eta_0\langle s^2\rangle^{1/2} \tag{5a}$$

Sometimes the parameter

$$\rho = R_G/R_H = 6^{1/2}\pi/P \tag{5b}$$

is used instead of $P$. In the preceding definitions, $M$ is the molecular weight of the polymer and $\eta_0$ is the viscosity of the solvent. $R_H$ and $R_G$ are, respectively, the hydrodynamic radius, $f/6\pi\eta_0$, and the radius of gyration, $\langle s^2\rangle^{1/2}$. Subscripts l or c will be attached to $\Phi$ and $P$ to denote linear and cyclic chains, respectively. Bloomfield and Zimm[7] obtained $\Phi_c = 5.23 \times 10^{23}$ and $P_c = 6.14$ for cyclic macromolecules using the above-mentioned hydrodynamic theories. These results (in the absence of excluded-volume effects) were independently reproduced by Fakatsu and Kurata.[10]

In the case of linear chains, these approximate theories[11] gave $\Phi_l = 2.8 \times 10^{23}$ and $P_l = 5.1$. However, as shown later on, accurate determinations of viscosity and diffusion made in recent years, for nearly monodisperse, high-$M$, linear polymers, have yielded results that deviated appreciably from these predictions. The discrepancy prompted Monte Carlo simulations with rigid-body hydrodynamics[12-14] and nonpreaveraged hydrodynamic interaction, which gave $\Phi_l = 2.5 \times 10^{-23}$ and $P_l = 6.0$, in excellent agreement with the experiments. Although the rigid-body simulation treatment is not completely rigorous for flexible chains,[15] it seems to have a good predictive capability.

It is reasonable to suspect that the calculations of Bloomfield and Zimm for cyclic polymers could be appreciably affected by hydrodynamic approximations like preaveraging. On the other hand, various experimental studies have been recently published. These considerations motivated the Monte Carlo calculations for cyclic polymers reported in this paper. We restrict ourselves to the case of $\Theta$, or nearly ideal conditions at which excluded-volume effects can be neglected. The study will be elsewhere extended to the case of good solvents.

## Recall of Experimental Data

In this section we use the following notation for the $M$ dependence of $\langle s^2\rangle$, $[\eta]$, and $f$:

$$R_G\ (\text{cm}) = \langle s^2\rangle^{1/2} = K_s M^{a_s} \tag{6}$$

$$f/\eta_0\ (\text{cm}) = K_f M^{a_f} \tag{7}$$

$$[\eta]\ (\text{dL/g}) = K_\eta M^{a_\eta} \tag{8}$$

**Polystyrene in Cyclohexane.** Following the synthesis of cyclic polystyrene,[16] Roovers[17] reported a detailed study of polystyrene (hereafter PS) in cyclohexane (hereafter CH) at nearly ideal conditions. It is well-known that the $\Theta$ temperature of linear PS in CH is 35 °C. Under this condition the second virial coefficient is $A_2 \cong 0$. However, for cyclic PS, $A_2 \cong 0$ at about 28 °C, while the exponents in eqs 6–8 take values close to $^1/_2$ at 35–40 °C. A discrepancy of this type, which is also observed for branched polymers, should be due to the nonlinear chain topology. A theoretical explanation has been given.[18,19] We shall adopt here the criterion that the ring polymer is nearly ideal at a temperature such that the exponents are close to $^1/_2$.

**Table I**
**Recall of Experimental Data for Polystyrene in Cyclohexane at Nearly Ideal Conditions**

| | Roovers,[16] 35 °C | | Lutz et al.,[19-21] 34.5 °C | |
|---|---|---|---|---|
| | linear | cyclic | linear | cyclic |
| $K_r \times 10^8$ | 0.281 | 0.205 | 0.276 | 0.204 |
| $a_r$ | 0.5 | 0.5 | 0.5 | 0.5 |
| $K_\eta \times 10^4$ | 7.51 | 5.89 | 8.3 | 3.8 |
| $a_\eta$ | 0.51 | 0.49 | 0.5 | 0.53 |
| $K_f \times 10^8$ | 4.24 | 4.29 | 4.28 (35°C) | 3.81 (28°C) |
| $a_f$ | 0.5 | 0.49 | 0.50 (35°C) | 0.49 (28°C) |
| $\Phi \times 10^{-23}$ | 2.64 | 4.1 | 2.69 | 4.2 |
| $P$ | 6.16 | 7.44 | 6.33 | 7.5 |
| $q_f$ | 0.88 | | 0.89 | |
| $q_\eta$ | 0.59 | | 0.68 | |

Values for the constants in eqs 6–8 either have been taken directly from refs 16 and 17 or obtained by fitting data reported therein and are listed in Table I. In order to circumvent slight differences in the exponents that would result in $M$-dependent values for the dimensionless quantities ($P$, $\Phi$, and the $q$'s), we used eqs 6–8 to estimate the properties of linear and cyclic PS with $M = 10^6$ in CH at nearly 35 °C. Combining the properties, we obtain the quantities reported in Table I. We note that the values of $P$ and $\Phi$ for linear PS are very similar to those obtained for ideal chains both theoretically and experimentally (vide supra).

Another set of data for PS in CH near 35 °C is that reported by Lutz et al.[19-21] As their data were determined for $M < 2 \times 10^5$, the reference $M$ taken for the estimation of $P$, $\Phi$, and the q's is now $10^5$. There are slight differences in the $R_G$ data of these authors: while from Figure 1 in ref 20 we obtain $R_G = 0.209M^{1/2}$, from Table I in ref 21 we calculate $R_G = 0.199M^{1/2}$. We take for our subsequent analysis the mean, i.e., $0.204M^{1/2}$, which is nearly coincident with Roovers' result. The set of intrinsic viscosity data reported in ref 20 has been extended and improved later by McKenna et al.,[22] whose list of $[\eta]$–$M$ values (Strasbourg samples) gives the parameters listed in our Table I.

McKenna et al.[22] have also determined $[\eta]$–M data for what they call Akron samples of cyclic PS (at their individual $\Theta$ temperatures) and their linear counterparts in CH. By linear regression of their data we find $[\eta]$ (dL/g) $= 1.15 \times 10^{-3}M^{0.46}$ for rings and $5.38 \times 10^{-4}M^{0.534}$ for linear chains. For $M = 10^5$ this yields $q_\eta = 0.93$. These authors realized already that this value is abnormally high and discussed in detail the possible reasons. We will disregard this value in the forthcoming discussion.

Other experimental data for PS in CH are those of Huang et al.[23] These authors give $a_\eta = 0.5$ for both cyclic and linear PS, with $K_\eta = 5.3 \times 10^{-4}$ for the former and 0.085 for the latter. Both measurements are at 34.5 °C, and their combination yields $q_\eta = 0.62$.

**Polysiloxanes.** Several studies of solution properties of cyclic polysiloxanes and their linear counterparts have been reported by Semlyen and co-workers. Thus, Higgins et al.[24] reported data for poly(dimethylsiloxane) (PDMS) with $M$ between 1000 and 15 000 in benzene at 20 °C. They give $q_f = 0.84 \pm 0.02$, $P_l = 6.3 \pm 1.0$, and $P_c = 6.8 \pm 1.2$. It is noteworthy that the exponents $a_s$ and $a_f$ obtained from their data deviate remarkably from 0.5. In a subsequent paper,[25] they report $q_s = 0.48 \pm 0.07$. Later[26] intrinsic viscosities were measured for $M = (2\text{–}20) \times 10^3$ in bromocyclohexane at 28 °C, which is the reported

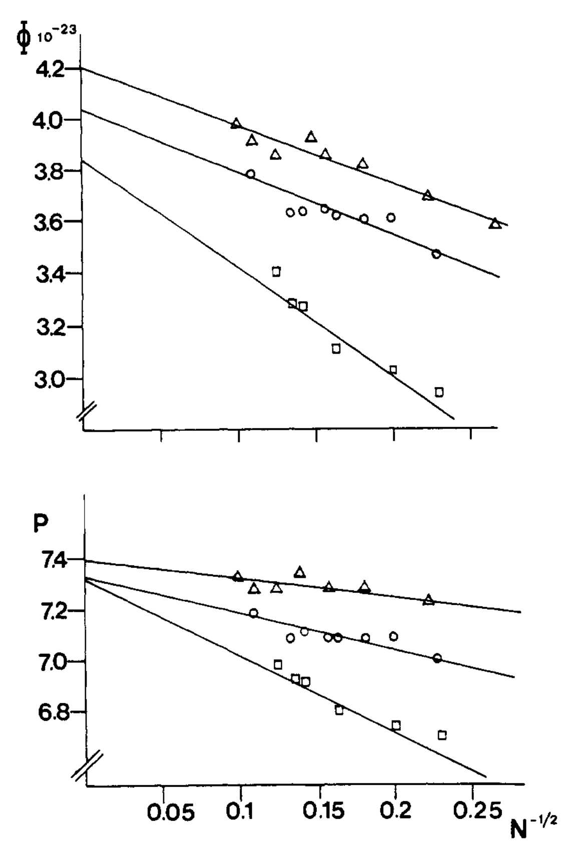

**Figure 1.** Extrapolations of the $P$ and $\Phi$ parameters to the $N \rightarrow \infty$ ($N^{-1/2} = 0$) limit: (△), FJ rings; (○), GB rings; (□), GB-LJ rings. The extrapolation takes into account the error bars of the data points (see Table I), which are not shown for clarity.

$\Theta$ temperature for linear PDMS in that solvent. It was found that $q_\eta$ = 0.64–0.67. However, the $a_\eta$ exponents were 0.70 and 0.68 for linear and ring polymers, respectively, indicating a clear deviation from what we take here as ideal behavior.

## Models and Theories

We have considered different models that are assumed to represent adequately chain polymers at ideal conditions. The Monte Carlo procedures are quite similar to those used for linear chains but with a modification that accounts for ring closure.

**Freely Jointed Rings (FJ).** FJ rings have $N$ beads joined by $N$ rigid bonds of fixed length $b$. For the Monte Carlo generation of this type of rings we first followed the dimerization procedure of Chen[27] in which the ends of two linear chains with rms end-to-end distance differing in less than one bond length are put together to form a cyclic chain. We followed the procedure proposed by this author to assign statistical weights to the rings so formed. The resulting $\langle s^2 \rangle$ values (not show here) for high $N$ were found to be 10% over the expected values, $Nb^2/12$. Owing to this systematic bias, the procedure of Chen was quit. Alternatively, we used the kink-jump procedure of Baumgartner,[28] in which bead $i$ is rotated a random angle around the line joining beads $i - 1$ and $i + 1$ (for a ring $i + 1$ is 1 for $i = N$ and $i - 1$ is $N$ for $i = 1$). The rotation angle was actually a random number between 0 and $2\pi$. Typically, we generated 180 000 conformations of the ring. Each conformation was obtained from the previous one moving sequentially the $N$ beads. The first 30 000 conformations were rejected to forget the initial conformation. We assume that this is much more than required for the relaxation of the initial condition. Of the remaining 150 000 conformations, about 15 000 were taken for the calculation of $\langle s^2 \rangle$ and between 700 and 1500, depending on the value of $N$, were taken for the calculation of hydrodynamic properties. The samples were divided into five subsamples for which we obtained the averages of each properties. The five subsample averages showed no definite trend, which confirms their statistical independence. The mean of the five values is the final result, and the standard deviation is taken as a measure of the statistical uncertainty.

**Rings with Gaussian Bonds (GB).** In this model the bond lengths are gaussianly distributed with root mean square $b$. We first attempted a simulation procedure based on spontaneous cyclation.[29] A linear chain is generated adding bond vectors with Gaussian distribution. If the end-to-end distance is close to $b$ (say, $0.8 < b^2 < 1.2$), the chain is accepted as a ring. After some preliminary calculations we found that this procedure is rather inefficient, mostly for high $N$. Then we adopted another method in which the beads in the ring are moved, following an algorithm described previously.[30] In this method a new position is assigned to bead $i$ so that the difference vector $\mathbf{b}_{i-1}-\mathbf{b}_i$ obeys a Gaussian distribution with variance $2b^2/3$. The initial ring was produced by spontaneous cyclization as described above. Generation of conformations and the statistical samples was done with the same protocol as for FJ rings. We verified that this procedure is indeed much faster than spontaneous cyclization: if $N = 37$, for instance, the generation of a sample containing a given number of practically independent conformations requires a CPU time that is 10 times longer for spontaneous cyclization.

**Rings with Gaussian Bonds and Intramolecular Lennard-Jones Interactions (GB–LJ).** In previous work we[30,31] have shown that the properties of polymers at ideal conditions may require in some instances the inclusion of attractive and repulsive interactions. This can be done with a Lennard-Jones potential, with well depth $\epsilon$ and zero-potential distance $\sigma$. It was shown[30] that an ideal linear chain ($a_s = {}^1/_2$) is obtained for $\sigma/b = 0.8$ and $\epsilon/kT = 0.3$. We have adopted this model for cyclic polymers with the same microscopic parameters. We anticipate that $a_s$ is practically ${}^1/_2$ for rings also. In the Monte Carlo simulation, the beads are moved sequentially as in the other methods. After a bead move, the Metropolis criterion is used to decide whether the new position is accepted or the old one is counted again. The number of conformations and the size of the subsamples is the same as in the other procedures.

**Hydrodynamics.** In the context of the rigid-body treatment, instantaneous conformations are regarded as rigid bodies, and their hydrodynamic properties are obtained using the hydrodynamic theory of rigid macromolecules whose details have been presented elsewhere.[14,32,33]

## Results

The numerical values of the calculated properties are listed in Table II in the following dimensionless forms:

$$\langle s^2 \rangle^* = \langle s^2 \rangle / b^2 \tag{9}$$

$$f^* = f/6\pi\eta b \tag{10}$$

$$[\eta]^* = [\eta]M/N_A b^3 \tag{11}$$

In terms of these quantities, the parameters $P$ and $\Phi$ are given by

$$P = 6^{1/2}\pi f^* / \langle s^2 \rangle^{*1/2} \tag{12}$$

**Table II**
**Reduced Values of the Dimensionless Hydrodynamic Properties and Cyclic-to-Linear Ratios**

| $N$ | $\langle s^2\rangle^*$ | $f^*$ | $[\eta]^*$ | $P$ | $\Phi \times 10^{-23}$ | $q_s$ | $q_f$ | $q_\eta$ |
|---|---|---|---|---|---|---|---|---|
| | | | | Freely Jointed Rings (FJ) | | | | |
| 10 | 0.92 ± 0.04 | 0.885 ± 0.002 | 7.28 ± 0.09 | 7.10 ± 0.17 | 3.4 ± 0.2 | 0.56 ± 0.02 | 0.891 | 0.630 |
| 20 | 1.754 ± 0.011 | 1.242 ± 0.009 | 20.9 ± 0.4 | 7.22 ± 0.08 | 3.69 ± 0.10 | 0.526 ± 0.003 | 0.868 | 0.563 |
| 30 | 2.59 ± 0.05 | 1.522 ± 0.009 | 38.8 ± 0.8 | 7.28 ± 0.11 | 3.81 ± 0.19 | 0.519 ± 0.010 | 0.873 ± 0.010 | 0.57 ± 0.03 |
| 40 | 3.48 ± 0.10 | 1.76 ± 0.02 | 61 ± 2 | 7.28 ± 0.19 | 3.8 ± 0.3 | 0.522 ± 0.015 | 0.865 | 0.569 |
| 50 | 4.25 ± 0.10 | 1.965 ± 0.012 | 84 ± 2 | 7.33 ± 0.13 | 3.9 ± 0.2 | 0.510 ± 0.012 | 0.867 | 0.567 |
| 64 | 5.46 ± 0.13 | 2.208 ± 0.010 | 120 ± 3 | 7.27 ± 0.12 | 3.9 ± 0.2 | 0.512 ± 0.012 | 0.863 ± 0.012 | 0.56 ± 0.03 |
| 80 | 6.8 ± 0.3 | 2.463 ± 0.018 | 169 ± 7 | 7.3 ± 0.2 | 3.9 ± 0.4 | 0.51 ± 0.02 | 0.852 ± 0.014 | 0.54 ± 0.04 |
| | | | | Gaussian Rings (GB) | | | | |
| 8 | 0.662 ± 0.012 | 0.729 ± 0.004 | 4.21 ± 0.09 | 6.89 ± 0.10 | 3.20 ± 0.16 | 0.504 ± 0.009 | 0.869 ± 0.008 | 0.54 ± 0.02 |
| 16 | 1.326 ± 0.019 | 1.047 ± 0.009 | 12.9 ± 0.5 | 7.00 ± 0.11 | 3.5 ± 0.2 | 0.499 ± 0.007 | 0.862 ± 0.007 | 0.55 ± 0.03 |
| 19 | 1.576 ± 0.008 | 1.140 ± 0.005 | 16.7 ± 0.2 | 6.99 ± 0.05 | 3.46 ± 0.06 | 0.499 ± 0.002 | 0.851 ± 0.009 | 0.533 ± 0.018 |
| 25 | 2.07 ± 0.04 | 1.325 ± 0.012 | 26.2 ± 0.9 | 7.08 ± 0.13 | 3.6 ± 0.2 | 0.498 ± 0.010 | 0.844 ± 0.019 | 0.52 ± 0.04 |
| 30 | 2.51 ± 0.04 | 1.458 ± 0.004 | 35.0 ± 0.4 | 7.08 ± 0.08 | 3.61 ± 0.13 | 0.503 ± 0.008 | 0.866 ± 0.007 | 0.56 ± 0.02 |
| 37 | 3.09 ± 0.06 | 1.618 ± 0.016 | 48 ± 1 | 7.08 ± 0.14 | 3.61 ± 0.19 | 0.501 ± 0.010 | 0.85 ± 0.02 | 0.55 ± 0.06 |
| 40 | 3.29 ± 0.03 | 1.669 ± 0.014 | 53 ± 1 | 7.08 ± 0.09 | 3.64 ± 0.15 | 0.494 ± 0.004 | 0.851 ± 0.011 | 0.53 ± 0.02 |
| 49 | 4.08 ± 0.03 | 1.87 ± 0.02 | 73 ± 3 | 7.11 ± 0.11 | 3.63 ± 0.19 | 0.500 ± 0.004 | 0.84 ± 0.03 | 0.51 ± 0.06 |
| 55 | 4.65 ± 0.05 | 1.984 ± 0.012 | 89 ± 2 | 7.08 ± 0.08 | 3.63 ± 0.12 | 0.507 ± 0.005 | 0.84 ± 0.04 | 0.50 ± 0.06 |
| 64 | 5.21 ± 0.09 | 2.15 ± 0.04 | 113 ± 5 | 7.2 ± 0.2 | 3.9 ± 0.3 | 0.489 ± 0.008 | 0.86 ± 0.02 | 0.55 ± 0.04 |
| 80 | 6.640 ± 0.015 | 2.404 ± 0.012 | 158 ± 3 | 7.18 ± 0.04 | 3.78 ± 0.08 | 0.498 ± 0.001 | 0.865 ± 0.011 | 0.56 ± 0.02 |
| | | | | Gaussian Rings (BG–LJ) | | | | |
| 8 | 0.916 ± 0.003 | 0.823 ± 0.003 | 5.92 ± 0.09 | 6.62 ± 0.04 | 2.77 ± 0.06 | 0.569 ± 0.011 | 0.914 ± 0.005 | 0.627 ± 0.015 |
| 19 | 2.354 ± 0.015 | 1.33 ± 0.02 | 25.9 ± 0.2 | 6.69 ± 0.03 | 2.94 ± 0.05 | 0.566 ± 0.014 | 0.902 ± 0.016 | 0.610 ± 0.007 |
| 25 | 3.13 ± 0.03 | 1.550 ± 0.007 | 40.9 ± 0.7 | 6.74 ± 0.06 | 3.03 ± 0.09 | 0.60 ± 0.06 | 0.910 ± 0.006 | 0.631 ± 0.017 |
| 37 | 4.68 ± 0.03 | 1.908 ± 0.007 | 76.9 ± 0.9 | 6.79 ± 0.05 | 3.11 ± 0.07 | 0.60 ± 0.08 | 0.918 ± 0.011 | 0.68 ± 0.04 |
| 49 | 6.09 ± 0.11 | 2.217 ± 0.015 | 120 ± 2 | 6.91 ± 0.11 | 3.27 ± 0.14 | 0.57 ± 0.14 | 0.900 ± 0.019 | 0.62 ± 0.04 |
| 55 | 6.84 ± 0.11 | 2.353 ± 0.011 | 143 ± 3 | 6.92 ± 0.09 | 3.28 ± 0.15 | 0.56 ± 0.04 | 0.870 ± 0.013 | 0.54 ± 0.03 |
| 64 | 7.83 ± 0.19 | 2.538 ± 0.019 | 180 ± 6 | 6.98 ± 0.14 | 3.4 ± 0.2 | 0.56 ± 0.04 | 0.893 ± 0.000 | 0.90 ± 0.03 |

**Table III**
**Constants and Exponents in Equations 14–16 for the Three Models**

| | FJ rings | GB rings | GB-LJ rings |
|---|---|---|---|
| $a_s$ | 0.485 ± 0.002 | 0.499 ± 0.002 | 0.490 ± 0.005 |
| $C_s$ | 0.095 ± 0.004 | 0.084 ± 0.003 | 0.134 ± 0.008 |
| $C_s'$ | 0.088 ± 0.001 | 0.083 ± 0.001 | 0.126 ± 0.001 |
| $a_f$ | 0.493 ± 0.006 | 0.510 ± 0.005 | 0.524 ± 0.007 |
| $C_f$ | 0.284 ± 0.006 | 0.257 ± 0.005 | 0.288 ± 0.007 |
| $C_f'$ | 0.277 ± 0.001 | 0.266 ± 0.001 | 0.313 ± 0.003 |
| $a_\eta$ | 0.509 ± 0.006 | 0.539 ± 0.006 | 0.569 ± 0.006 |
| $C_\eta$ | 0.229 ± 0.018 | 0.186 ± 0.014 | 0.27 ± 0.02 |
| $C_\eta'$ | 0.235 ± 0.002 | 0.213 ± 0.002 | 0.335 ± 0.009 |

$$\Phi = N_A[\eta]^*/(6\langle s^2\rangle^*)^{3/2} \qquad (13)$$

Values of $P$ and $\Phi$ for each chain length are listed in Table II. For very long chains the values of these parameters can be extrapolated to the $N \rightarrow \infty$ limit as the intercepts in linear plots vs $N^{-1/2} = 0$. Although the $N$ dependence of the intrinsic viscosity could be derived from Zimm eigenvalues obtained by Öttinger,[34] the good linearity observed in such extrapolation (see Figure 1) is sufficient for our purpose of estimating the limiting results. The expected dependence of the reduced parameters on $N$ was checked fitting the results to equations similar to eqs 6–8:

$$\langle s^2\rangle^* = C_rN^{2a_r} \qquad (14)$$

$$f^* = C_fN^{a_f} \qquad (15)$$

$$[\eta]^* = C_\eta N^{1+a_\eta} \qquad (16)$$

The constants and the exponents were obtained by linear regression in log–log plots. The results are listed in Table III. The case of the FJ rings is shown in Figure 2. For this case and for GB rings the linearity was excellent. In the plots for the GB-LJ case we observed a slight but systematic curvature, which was more evident in linear plots vs $N^{1/2}$. We attribute this situation to a slower convergence of this model to the limiting behavior specified by eqs 6–8 or 14–16. Indeed, for GB and LJ rings the values of $a_s$, $a_f$, and $a_\eta$ are very close to the theoretical value of $^1/_2$ for ideal conditions. The deviation seen for $a_f$ and $a_\eta$ of GB-LJ rings is probably due to the above-commented facts. We also calculated the constants $C_s'$, $C_f'$, and $C_\eta'$, forcing the exponents to $a_s = a_f = a_\eta = {}^1/_2$. The latter form of the $C$'s is useful to obtain the parameters $P$ and $\Phi$ from the primed constants as

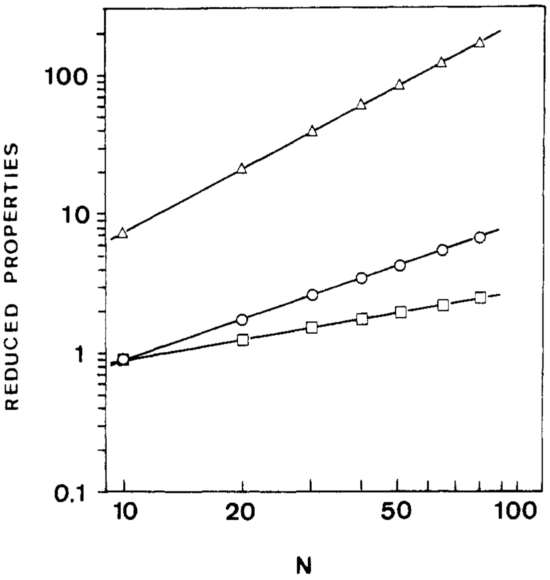

**Figure 2.** log–log plots of $[\eta]^*$ (△), $\langle s^2\rangle^*$ (○), and $f^*$ (□) for FJ rings. The straight lines are least-squares fits. The uncertainties of the data points are smaller than the size of the points in the plot.

$$P = 6^{1/2}\pi C_f'/C_r'^{1/2} \qquad (17)$$

$$\Phi = N_AC_f'/(6C_r')^{3/2} \qquad (18)$$

The $q$ ratios defined in eqs 1–3 were calculated combining the results for rings reported in Table II with others for linear chains that were either taken from the literature or calculated for the present purpose. It seems

**Table IV**
**Summary of Experimental and Theoretical Results for the Parameters $P$ and $\Phi$ and the Ratios $q_s$, $q_f$, and $q_\eta$**

| | $P$ | $\Phi \times 10^{-23}$ | $q_s$ | $q_f$ | $q_\eta$ |
|---|---|---|---|---|---|
| approximate theories[7,10] | 6.14 | 5.23 | 1/2 | 0.85 | 0.66 |
| exptl | 7.4,[a] 7.5,[b] 6.8[c] | 4.1,[a] 4.2,[b] 4.8[c] | 0.5 | 0.88,[a] 0.89,[b] 0.84[c] | 0.59,[a] 0.68,[b] 0.66,[c] 0.62[d] |
| this work[e] (summary) | 7.2 | 4.0 | 0.5,[f] 0.57[g] | 0.86,[f] 0.90[g] | 0.55,[f] 0.60[g] |
| this work, FJ | 7.4 ± 0.02[h] | 4.2 ± 0.4 | 0.505 ± 0.011 | 0.856 ± 0.006 | 0.553 ± 0.011 |
| | 7.19 ± 0.07[i] | 3.69 ± 0.09 | | | |
| this work, GB | 7.3 ± 0.1[h] | 4.0 ± 0.2 | 0.498 ± 0.011 | 0.859 ± 0.015 | 0.55 ± 0.03 |
| | 7.10 ± 0.07[i] | 3.75 ± 0.09 | | | |
| this work, GB–LJ | 7.1 ± 0.1[h] | 3.8 ± 0.2 | 0.57 ± 0.02 | 0.898 ± 0.006 | 0.601 ± 0.013 |

[a] Roovers, ref 16. [b] Lutz et al., refs 19–21. [c] Higgins et al., refs 24–26. [d] He et al., ref 23. [e] Summary of averages of the results for the three models. [f] GB and FJ rings. [g] GB–LJ rings. [h] Values in this line are from extrapolations to $N \to \infty$. [i] Values in this line are from eqs 17 and 18.

that the three $q$'s for the three models are practically independent of $N$. Although a weighted average could simply be appropriate, we preferred to estimate the limiting values for $N \to \infty$ by linear regression with $N^{-1/2}$ as done for $P$ and $\Phi$.

## Discussion

The values for infinite chain length of the two dimensionless parameters $P$ and $\Phi$, and the ratios $q_s$, $q_f$, and $q_\eta$ for the three kinds of ring models, are listed along with those corresponding to the approximated theories and the experimental results in Table IV to which all the following discussion will be referred.

**Comparison between Chain Models.** Although for the three models $a_s = {}^1/_2$ as shown in Table III, we see that $C_s' = \langle s^2 \rangle / Nb^2$ is equal to the expected value of ${}^1/_{12} = 0.083\,33$, in the case of GB rings, and acceptably close to that value in the case of FJ rings. However, the value for GB–LJ rings is remarkably different. A similar circumstance was observed in our previous simulation for GB–LJ linear chains with the same Lennard-Jones parameters:[30] we obtained $C_s'$ (linear) = 0.22 instead of the well-known value of ${}^1/_6$. Indeed, the ${}^1/_{12}$ coefficient is expected only for the ideal Gaussian chain which does not include intramolecular interaction, while the GB–LJ model includes intramolecular interactions that are compensated at the $\Theta$ temperature. This difference affects also the cyclic to linear ratio. As shown in Table IV, $q_s$ is practically equal to ${}^1/_2$ for both FJ and GB rings while $q_s = 0.57$ for GB–LJ rings.

A similar situation is found for the other properties. We found $q_f = 0.86$ and $q_\eta = 0.55$ for both GB and FJ cycles, while the values for the GB–LJ model are appreciably higher. It seems that rings with Gaussian bonds (GB) and rings with fixed-length bonds (FJ) are practically equivalent, the rings with attractive/repulsive intramolecular interactions (GB–LJ) behave differently. In previous works[30,31] we considered the GB–LJ chain in an attempt to model systematically linear polymers in the collapse region, in $\Theta$ and good solvents, and also to better reproduce the interactions in some particular topologies like stars. The presence of a central core in stars has an influence on the properties in the $\Theta$ region that could be only mimicked through this model (the GB model seemed to underestimate the chain dimensions). The ultimate test of chain models should be the comparison with experimental data, but, as we will discuss below, such a test is not very conclusive for rings.

Looking at the values of the Flory parameters $P$ and $\Phi$ listed in Table IV, we feel a different sensation: for the three models, the values of the parameter are quite close; the differences are within the simulation uncertainties or are sufficiently small to be attributed to computational effects.

**Adequacy of Dimensionless Parameters *P*, $\Phi$, and the *q*'s.** In our recall of experimental data we showed the difficulty of establishing the conditions under which *ideal* ring polymers and *ideal* linear polymers should be compared. The exhaustive presentation of McKenna et al.[22] in their very recent paper deserves a new mention here. Thus, there can be inconsistencies in the experimental values of the cyclic-to-linear ratios $q_s$, $q_f$, and $q_\eta$. On the theoretical side we have shown that these ratios are model dependent.

On the other hand, $P$ and $\Phi$ combine properties of the same polymer in the same solvent and are free of such inconsistencies (their validity depends essentially on their dependence on chain length and that seems to be granted for the present case). Furthermore, our calculations have shown that $P$ and $\Phi$ are practically model independent, when the $q$'s are not. In the field of cyclic polymers it has been customary to express experimental results in the form of $q$ ratios, taking for reference theoretical results like $q_s = 0.5$ (which is model dependent) and $q_\eta = 0.66$ (which in addition is approximate). The conclusion from our analysis is that the parameters $P$ and $\Phi$ are more preferred to characterize the conformation and hydrodynamics of cyclic polymers, and will be helpful to analyze systematic measurements of $\langle s^2 \rangle$, $f$, and $[\eta]$ of these kinds of macromolecules.

**Comparison between Theories and Experimental Data.** In Table IV we present a summary of the results for the various models used in this work, a summary of the experimental data recalled in a previous section of this paper, and the results from the theories of Bloomfield and Zimm[7] and Kurata and Fakatsu.[10] Although there is a remarkable scatter in the experimental data obtained in different polymer/solvent/temperature conditions and different laboratories, it seems clear that our results improve generally those of the older theories. The improvement is really remarkable for the parameters $P$ and $\Phi$, which, as discussed above, are the most significant ones. Although the $q$ ratios present the inconveniences discussed above, we make some further comments about them. Taking $q_s = 0.5$ as the experimental reference, the FJ and GB models seem to be more accurate than GB–LJ. The converse situation is found for $q_f$. Interestingly, this parameter is shown to be rather insensitive to differences in theories and models. Finally, the result of the old Bloomfield–Zimm[7] theory ($q_\eta = 0.66$) agrees better with the experimental result than our supposedly more rigorous values ($q_\eta = 0.55$ or 0.60; see Table I). This circumstance should be valued critically, keeping in mind the preaveraging approximation in that theory and our previous conclusion about the significance of the $q$ ratios. Schaub et al.[36] have recently carried out a renormalization group calculation of the intrinsic viscosity of rings to the lowest order. Their result, $q_\eta =$

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0.486, deviates even more than ours from the Bloomfield-Zimm value.

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# Effect of Swelling on the Fractal Dimension of Branched Silica Polymers Formed near the Sol-Gel Transition[†]

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ABSTRACT: Scaling theories of semidilute branched polymer solutions depend crucially on the notion that diluted clusters swell sufficiently to alter the fractal dimension. This change in dimension gives rise to the concentration scaling $\xi \sim c^{-5/3}$ of the spatial correlation length $\xi$. We report light scattering studies of semidilute solutions of silica branched polymers formed near the sol-gel transition that show that the spatial correlation length scales as $\xi \sim c^{-2.0\pm0.3}$, lending credence to the swelling conjecture. The nonequilibrium nature of chemical gels is then demonstrated by comparing the fractal dimension $D \cong 1.6$ of dilution-induced spatial correlations to the fractal dimension $D \cong 1.9$ found when the gel is grown under dilute conditions. In dilute solutions, cluster growth is exponential in time and the system is well described by reaction-limited aggregation.

## Introduction

Branched polymers formed near the sol-gel transition have remarkable scaling properties that are only just beginning to be widely appreciated. The variety of static and dynamic scaling behaviors exhibited by branched polymers is striking, particularly in the area of dynamics where qualitatively new effects have been observed. However, to date relatively little work has been done on semidilute solutions. Static scaling investigations of the sol-gel transition have focused primarily on *dilute* solutions, using light[1-3] and neutron[4] scattering to determine both the ensemble and single-polymer fractal dimensions and the critical exponents.[5] These static measurements generally support the percolation description

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