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Influence of Long-Range Interactions on the End-to-End Distance Distribution and Cyclization Probability of Short Chains

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ABSTRACT: The end-to-end distribution of several different short polymer molecules (represented by a rotational isomeric state model that includes long-range interactions through a hard-sphere potential) has been calculated by means of a Monte Carlo method. The results and their comparison with those calculated in the absence of the long-range potential allow us to discern the influence of these interactions in the whole form of the distribution and, especially, in the range of the smallest values of R, which determines the cyclization probability. The model predictions for this property are contrasted with experimental data of the equilibrium cyclization constants.

Introduction

The intramolecular long-range interactions have a crucial role in the conformational properties of flexible polymers. Thus, an adequate description of the excluded-volume effects is capital in the theoretical description of the behavior of long chains diluted in good solvents.[1] However, the long-range interactions are generally thought to have a reduced importance in the case of shorter flexible chains as *n*-alkanes or siloxane oligomers. In fact, calculations for mean dimensions or hydrodynamic properties[2,3] have been accomplished in the past, and the introduction of long-range interactions have been shown to cause only marginal changes. Nevertheless, these interactions can generate the well-known hole correlation effect,[1,4] which effectively affects the shape of the end-to-end distance distribution function of long polymers. Whether this effect is still present in shorter (though still flexible) chains has not yet been systematically investigated.

In this work, we carry out a study on the correlation hole effect by analyzing the cyclization (or ring-closure) probabilities obtained from end-to-end distribution functions of several different types of short chains, obtained with and without long-range interactions through appropriate numerical calculations, based on the rotational isomeric state (RIS) model. Since this effect is shown to be very remarkable even for chains with a reduced number of units, we describe its influence on some properties that are especially interesting for these chains as the cyclization constant. Illustrations on how the theoretical values for this constant, derived from the realistic distribution function calculations, compare with experimental data[4] are also included.

It should be mentioned that the ring-closure probability of short stiff chains has been extensively studied. Thus, analytical expressions have been derived for wormlike chains,[5-7] while simulations for chains composed of cylinders have been also performed, with explicit consideration of excluded volume.[8] However, since both stiffness and excluded-volume effects tend to decrease the cyclization probability, it is desirable to know whether the excluded-volume effects alone are able to exert a great influence on short chains, which otherwise would exhibit a Gaussian behavior. This is the case of our realistic RIS chains (at least in a part of the range of lengths covered by the present work for the different polymers).

Methods

The chains are represented by means of the RIS model,[9] with chain units, bond lengths, bond angles, sets of rotational angles, and statistical weights previously established for the different molecules: polymethylene[10] (PM), poly(dimethylsiloxane)[11] (PDMS), and atactic poly(methylphenylsiloxane)[12] (PMPS), the latter with an intermediate replication probability (p_r = 0.5), which characterizes its tacticity. A Gaussian fluctuation of the rotational angles, defined by its rms deviation around the mean values ($\delta\varphi$ = 15°), is introduced in the PMPS chains, since it is shown to give a considerably more realistic description of the conformational sample for stiff chains,[13] i.e. when a particular conformation is clearly predominant (in the PMPS chain, this is the case of the "all-trans"[14,15] conformation). For the sake of comparison, we have performed calculations both with long-range interactions and without such interactions. In the latter case (referred hereafter as the unperturbed chain) we have the possibility of using two alternative methods. One of them is a quasianalytical procedure detailed elsewhere,[14,15] based on the inference of the end-to-end distance distribution function, $F(R)$, from higher moments of the type $\langle R^{2p}\rangle$, which are exactly evaluated through iterative formulas. In this case the cyclization probability is defined as $F(0)$. However, the iterative formulas are no longer applicable when the long-range interactions are introduced, and, then, we are also using a more general Monte Carlo sampling of conformations,[16-18] which is shown to yield results very similar to the quasianalytical values for unperturbed chains, but it allows us to introduce properly the long-range potential. In this Monte Carlo method, the distribution functions are obtained by dividing the range of possible values of R into grids and calculating the number of conformations that belong to each one of these grids (with an appropriate normalization that takes into account the grid interval). The cyclization probability is then defined as the value of $F(R)$ in the grid corresponding to the smallest R or, equivalently, as the fraction of conformations for which R is smaller than a given value R_0 (the upper limit of this grid).

For the PMPS chains with different stereochemical configurations, the quasianalytical method includes a sampling over randomly generated sequences of stereochemical diads, from which the higher moments $\langle R^{2p}\rangle$ are evaluated, whereas both the conformational and stereochemical samplings are simultaneously carried out in the general Monte Carlo procedure. This sampling has been also detailed previously,[16-18] but we believe it is

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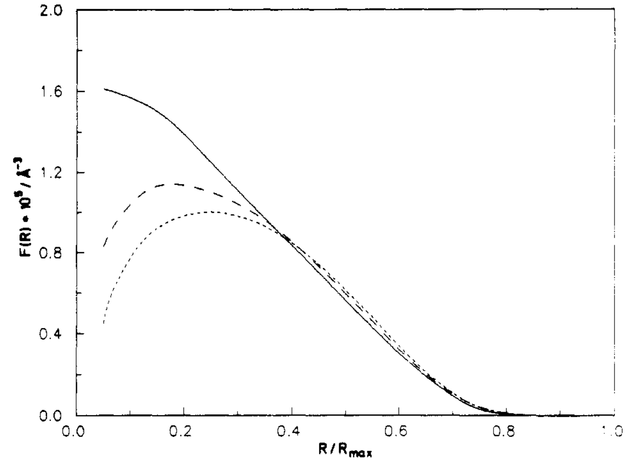

Figure 1. $F(R)$ for a PM chain with $N = 40$ vs R/R_{max}, where $R_{max} = 50.7$ Å: (—) unperturbed chain; long-range interactions with (– –) $\sigma = 2$ Å and (- - -) $\sigma = 3$ Å.

worthwhile to repeat here its most significant features: we generate sequences of rotational angles according to appropriate conditional probabilities, calculated through the use of statistical weight matrices.[16] Then, we build the conformations, obtaining the coordinates of the different units, and, finally, we evaluate the properties of interest (in the present calculations, we assign the conformation to a given grid interval). Long-range interactions are introduced by means of a hard-sphere potential so that, if the distance between two inner units separated by more than four of the skeleton bonds is smaller than the hard-sphere diameter, σ, the conformation is rejected and its properties are not considered. The final results are given as arithmetic means (hence, they correspond to the fraction of conformations included in each grid interval).

It should be remarked that this simple Monte Carlo method is very efficient for short or moderately long chains, where the fraction of rejected conformations is relatively small. Then, more complicated importance samplings, which require the definition of elementary stochastic processes, are not necessary.

Results

The molecular parameters of the chains have been detailed in previous papers[14,16,17] and were assigned by Yoon and Flory[10] (PM). Flory and Chang[11] (PDMS), and Mark and Ko[12] (PMPS). The values for temperatures have been fixed according to those used more commonly in the referenced previous work: 140° for PM and 110° for the siloxane chains. The Monte Carlo calculations have been carried out by sampling 200 000 conformations for each given chain.

Figures 1 and 2 show the distribution functions obtained for PM and PDMS chains of 40 skeleton bonds ($N = 40$), both with and without long-range interactions (defined by two different values of parameter σ). The curves of unperturbed chains adopt shapes very close to the Gaussian distribution, whereas the correlation hole effect[1,4] is clearly manifested in the curves calculated with long-range interactions (and increases for the higher values of σ). It should be considered that the hard-sphere potential is not imposed on the end units so that the depression of $F(R)$ for the smallest values of R cannot be caused by a model artifact. R_{max} is taken as the "all-trans" value of R for PM and is defined as Nl for siloxane chains, with $l = 1.64$ Å (skeleton both length).

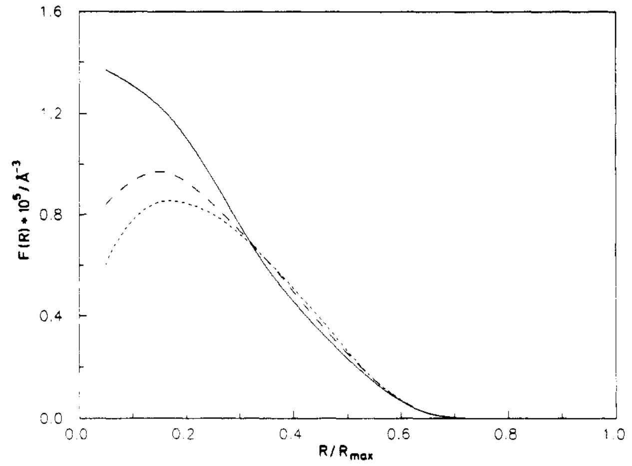

Figure 2. $F(R)$ vs R/R_{max} for a PDMS chain with $N = 40$. Same notation as in Figure 1.

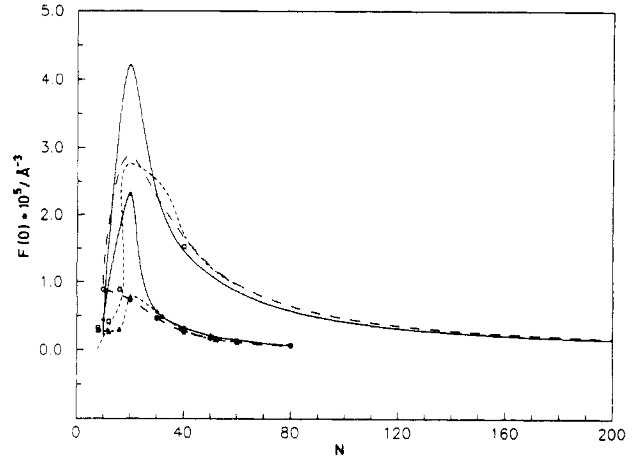

Figure 3. Cyclization probabilities for PDMS (—, ×), PM (– –, ○), and atactic PMPS (- - -, △) chains vs N. The upper set of curves correspond to unperturbed chains (calculated with the quasianalytical method). Points in the lower set represent values obtained with long-range interactions ($\sigma = 3$ Å) through the Monte Carlo method ($R_0 = 4$ Å). Squares represent points obtained through the Monte Carlo method ($R_0 = 4$ Å) for unperturbed PMPS chains.

In Figure 3, we present our values for the cyclization probability, also obtained with and without long-range interactions for the different types of chains as a function of the chain lengths. Results for unperturbed chains obtained from both the quasianalytical and the Monte Carlo method for PMPS are included, and a very good agreement between them can be observed. Since the quasianalytical method is much more efficient for the higher values of N, our results for longer unperturbed chains have been exclusively obtained through this procedure. (For the chains with long-range interactions, only the Monte Carlo method can be applied. Fortunately, the cyclization probability in this range of longer chains is practically null, though a considerable computational effort has been needed to obtain the Monte Carlo results of intermediate lengths.) Three important features can be discussed from the analysis of the curves shown in Figure 3: (a) The long-range interactions cause a remarkable decrease of the cyclization probability through the previously mentioned correlation hole effect. This decrease is already manifested for surprisingly small values of N. (b) In the range of the smallest values of N, significant differences of the cyclization probability are observed, due to the particular characteristics of the different chains (short-range interactions). The qualitative aspect of the curves is not very dependent on the presence or absence of long-range interactions in the siloxane chain, showing a sharp peak for very small N, but the cyclization probability curve of PM becomes smoother (and the peak disappears) when these interactions are included. (c) The curves for the different chains tend to converge as N increases, and the chain becomes more flexible, so that, in the range of high values of N, the shape of the curves are solely determined by the presence or absence of long-range interactions. Thus, according to the central limit theorem, a Gaussian distribution is predicted for long unperturbed chains so that the cyclization probability is given by

$$\lim_{N\to\infty} F(0) = (3/2\pi C)^{3/2}N^{-3/2} \qquad (1)$$

where only the constant $C = \lim_{N\to\infty} \langle R^2\rangle/N$ depends on the particular type of chain. The quantitative differences due to short-range interactions engulfed in C can be considered as marginal (in fact, they are hardly observed in Figure 3) when compared with those due to the introduction of long-range interactions, which cause a depression of the cyclization probability of one or several orders of magnitude. Moreover, the qualitative variation of this probability with N is also substantially modified by the long-range interactions. Thus, the first-order cluster theory predicts[19] the depression in a factor $1 - 4z$, where z is the well-known excluded-volume variable, $z \sim N^{1/2}$. Furthermore, the correlation hole theory, based on renormalization group theory, predicts[1,4,20-22]

$$\lim_{N\to\infty} F(0) \sim N^{-a} \qquad (2)$$

where a is an exponent close to 1.9. Thus, the second-order theory yields $a \simeq 1.98$[20-22] for a ring closure where the two ends of the chain are involved (as those considered in this work) and higher exponents if the rings are formed from inner chain segments. These results have been recently confirmed through an exhaustive computer enumeration method in lattices.[23] Experimental data of particle scattering functions for polymers in good solvents are also consistent with these exponents.[24]

We have performed a log-log linear least-squares regression analysis of the dependence of our results for the cyclization probability versus N. From this analysis, we have obtained estimations of exponent a for the different types of chains. Of course, only numerical values corresponding to the longer chains are useful for this analysis. Nevertheless, our results are clearly dependent on the chosen range of chain lengths, since the long-chain limit is not definitely reached in our calculations. However, all the estimated numerical exponents fluctuate between -1 and -1.5 for the unperturbed chains and between -1.7 and -2.3 for the chains with long-range interactions, whereas the increase in the absolute value of a due to these interactions varies from 0.6 to 1. Then, the main quantitative features of the correlation hole effect are reproduced.

The equilibrium cyclization rate constant for a chain of N units, K_N, is a experimentally measurable quantity directly related to $F(0)$. According to the well-known Jacobson-Stockmayer theory[25,26]

$$K_N = F(0)/N_A\sigma_N \qquad (3)$$

where σ_N is the cyclic symmetry number, which can be identified with N for the siloxane chains. In Figures 4 and 5 we show a quantitative comparison between the experimental data[26] of K_N for PMDS and PMPS chains and theoretical results obtained from eq 3 and our numerical values for the cyclization probability, obtained with and without long-range interactions. (We should mention previous similar calculations, together with direct and more specialized computational evaluations of K_N for unperturbed RIS models of short PDMS and other chains, summarized in ref 25, which, nevertheless, extend to considerably smaller upper values of N.) Though the experimental values are much higher than the theoretical ones for the shortest cycles, it should be considered that these cycles can only be obtained through sequences of rotational angles, mutually interdependent rotational angles,[25] and bond length and angle distorsions,[13,27] which are given probability weights of zero in the standard RIS model. However, a much closer agreement is found for still very short chains, as also revealed in the previous studies,[25] so that the introduction of realistic cyclization probabilities improves significantly the performance of the Jacobson-Stockmayer theory with respect to its crudest version,[26] where the Gaussian expression for $F(0)$, eq 1, is combined with eq 3. A more detailed analysis of Figures 4 and 5 points out that the experimental results lie generally between the theoretical predictions of the models with and without long-range interactions, but the data seem to agree better with the model with long-range interactions for the shorter chains (within the useful interval for which the usual RIS is applicable) and tend to approach somehow to the unperturbed chain predictions as N increases. The latter trend may reflect the partial or total compensation between polymer-polymer and polymer-solvent interactions, typical of long polymers, while this effect does not seem to be significant for shorter chains. Since the experimental data are not sensitive to the solvent nature, according to Figures 6 and 7 of ref 26, these results could indicate a partial compensation of polymer-polymer effects that may occur before the

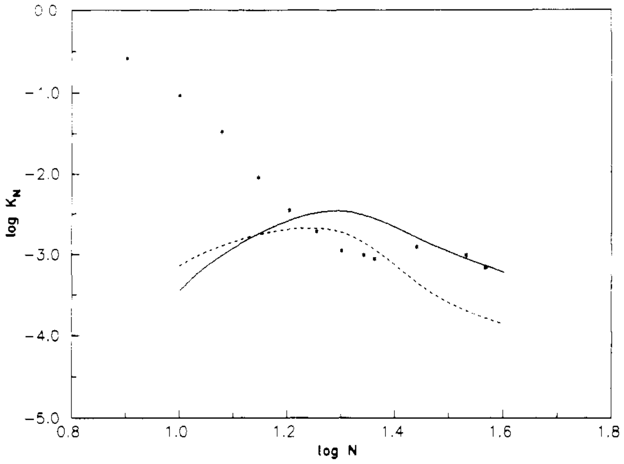

Figure 4. Equilibrium cyclization rate constants vs N for PDMS chains. Solid line: numerical results for unperturbed chains. Broken line: results obtained with long-range interactions (σ = 3 Å, R_0 = 4 Å). (*): experimental data from ref 26.

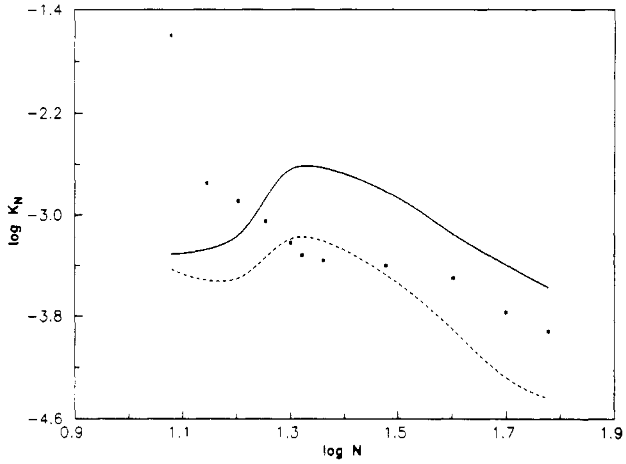

Figure 5. As in Figure 4 but for atactic PMPS chains.

important differences in behavior due to the solvent quality can be noticed. A rather more complex RIS model incorporating attraction wells of varying depths for the long-distance intramolecular interactions could help to clarify this point. In any case, it is clear that the correlation hole should still be present for long polymers in good solvents, as shown clearly by the experimental results for the scattering function previously discussed.[24]

In summary, the contribution of long-range interactions to the end-to-end distance distribution function is important even for surprisingly short chains due to the correlation hole effect. The cyclization probability is especially sensitive to model effects and, as previously established in earlier studies,[25] only the use of realistic models for short chains as the RIS model is able to yield reasonably good predictions for equilibrium cyclization constants, which are now shown to be also greatly influenced by the long-range potential.

A final caution should be stressed on the calculations for siloxane chains. As previously stated, the present work is based on the conventional RIS model for these chains,[11,12] which is now known to include incorrect statistical weights for the gauche placements and the second-order interactions. A considerable improvement of the description of equilibrium cyclization constants of the shorter chains with respect to previous bibliographic comparisons[25] is achieved with a more complex model, as very recent studies have demonstrated.[28] However, the main conclusion of this work, i.e., the striking differences for the cyclization probability and, consequently, for the cyclization constants, found when long-range interactions are introduced, is very likely to be independent of the model details, as is actually shown here for the upper region of chain lengths, though a more detailed analysis of this point with the new model is desirable.

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References and Notes

(1) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University: Ithaca, NY, 1979.
(2) Garcia de la Torre, J.; Jiménez, A.; Freire, J. J. *Macromolecules* **1982**, *15*, 148.
(3) Rubio, A. M.; Freire, J. J.; Garcia de la Torre, J. *Macromolecules* **1987**, *20*, 1619.
(4) Winnik, M. A. In *Cyclic Polymers*; Semlyen, J. A., Ed.; Elsevier: London, 1986; pp 285–348.
(5) Yamakawa, H.; Stockmayer, W. H. *J. Chem. Phys.* **1972**, *57*, 2843.
(6) Shimada, J.; Yamakawa, H. *Macromolecules* **1984**, *17*, 689.
(7) Yamakawa, H. *Annu. Rev. Phys. Chem.* **1984**, *35*, 23.
(8) Post, C. B. *Biopolymers* **1984**, *23*, 601.
(9) Flory, J. P. *Statistical Mechanics of Chain Molecules*; Wiley: New York, 1969.
(10) Yoon, D. Y.; Flory, P. J. *J. Chem. Phys.* **1974**, *61*, 5366.
(11) Flory, P. J.; Chang, V. W. C. *Macromolecules* **1976**, *9*, 33.
(12) Mark, J. E.; Ko, J. H. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 2221.
(13) Mansfield, M. L. *Macromolecules* **1983**, *16*, 1863.
(14) Freire, J. J.; Rubio, A. M. *J. Chem. Phys.* **1984**, *81*, 2112.
(15) Rubio, A. M.; Freire, J. J. *Macromolecules* **1989**, *22*, 333.
(16) Rubio, A. M.; Freire, J. J. *Macromolecules* **1982**, *15*, 1411.
(17) Rubio, A. M.; Freire, J. J. *Macromolecules* **1985**, *18*, 2225.
(18) Rubio, A. M.; Freire, J. J. *Comput. Polym. Sci.* **1991**, *1*, 63.
(19) Barret, A. J.; Domb, C. *Proc. R. Soc. London A* **1981**, *376*, 361.
(20) de Gennes, P.-G. *Phys. Lett. A.* **1972**, *38*, 339.
(21) des Cloizeaux, J. *J. Phys., Colloq.* **1978**, *C2*, 135.
(22) des Cloizeaux, J. *J. Phys.* **1980**, *41*, 223.
(23) Chan, H. S.; Dill, K. A. *J. Chem. Phys.* **1990**, *92*, 3118.
(24) Tsunashima, Y.; Kurata, M. *J. Chem. Phys.* **1986**, *84*, 6432.
(25) Semlyen, J. A. In *Cyclic Polymers*; Semlyen, J. A., Ed.; Elsevier: London, 1986; pp 1–41.
(26) Wright, P. V.; Beevers, M. S. In *Cyclic Polymers*; Semlyen, J. A., Ed.; Elsevier: London, 1986; pp 85–133.
(27) Horta, A.; Rubio, A. M.; Freire, J. J.; Piérola, I. F. *Macromolecules* **1991**, *24*, 3121.
(28) Bahar, I.; Zúñiga, I.; Dodge, R.; Mattice, W. L. *Macromolecules* **1991**, *24*, 2986, 2993.

Registry No. Poly(methylene) (homopolymer), 25038-57-7.