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Monte Carlo Simulations of Adsorbed Random Copolymers

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ABSTRACT: A Monte Carlo method is described for simulating the conformations of random copolymers at the solid/solvent interface. The effects of solvency, preferential adsorption, chain length, and coverage are considered. The effects of varying the point of attachment, the chain composition, and the cell boundary are discussed. Volume fraction profiles normal and parallel to the surface are calculated and comparisons are made with experimental data from small-angle neutron scattering (SANS).

Introduction

Copolymers are used widely in many commercial applications as stabilizers and flocculating agents for particulate dispersions. The advantage of copolymers over homopolymers in these systems is that monomers with different solubilities and adsorption properties can be incorporated into a single chain. However, the choice of the chemical and statistical composition of a copolymer required for a specific application is not a straightforward one. For copolymers it is important to assess the effects of varying the structure of the chain as this will strongly influence the extent of the adsorption and the preference of one chain to adsorb over another. For example, in a polydisperse system it may well work out that a lower molecular weight chain will adsorb preferentially to a higher one given that one type of segment (the adsorbing one say) occurs more frequently at one molecular weight than another.[1,2]

To this end, a computer simulation has been developed that predicts the volume fraction layer thickness (δ) and bound fraction (p) of an adsorbed copolymer for various cases of interest.

The simulation of adsorbed polymers requires a statistical mechanical model that includes the segment contact energies and an evaluation of the number of internal conformations of the system. For copolymers there are added difficulties. First, there are several different interaction terms to take into account: the Flory–Huggins solution parameters χ_a, χ_b, and χ_{ab} for two different monomers a and b and the net segment adsorption energies χ_{sa} and χ_{sb}. Second, the conformational statistics are more complex, as the internal conformations of the chain with respect to the two segment types must also be evaluated. Several approaches have been suggested for simulating polymer conformations, but it is the lattice based models that have been most widely used.[3] In this paper we use a Monte Carlo method with a periodic boundary condition[4] to evaluate the conformations of chains on a cubic lattice. The advantages of this technique over mean-field approaches[5] include the ability to generate profiles of segment density parallel to the interface and to explicitly include the excluded volume of the polymer chains. A limitation of the present simulation is the necessity to anchor at least one chain segment at the interface, though this segment may be chosen at random along the chain. A consequence of this anchoring is that the equilibrium between the surface and bulk polymer concentrations is not considered.

Finally, we present experimentally determined volume fraction profiles for adsorbed random copolymers of differing sequence distributions, along with model calculations.

The Monte Carlo Procedure

Chains of up to 141 segments have been generated on a site-centered cubic lattice by using the Rosenbluth sampling criterion.[6] The surface coverage of the adsorbed layer has been modeled by using the periodic boundary condition, which necessarily limits the numerical values of the surface coverage to $r/(2k + 1)$,[2] where r is the number of segments in the chain and k an integer. In this context, the surface coverage is defined as the number of adsorbed segments per surface lattice site. The limitations of a single-chain/boundary model are discussed more fully in the Results and Discussion. Each conformation is a self-avoiding random walk attached at the interface. Segments are added sequentially to the initial point of attachment in such a way that the chain grows bidirectionally. The choice of the initial attachment point of the chain is determined by a Gaussian weighted selection. The consequence of this procedure is that the ensemble generated favors medially attached chains over terminally attached ones. The probability of each conformation in the ensemble is then calculated from its conformational probability and the number and energy of each nearest-neighbor interaction. Each conformation generated is weighted by a set of factors w of the form

$$w_a = \exp^{(-\chi_a n_a/z)} \exp^{(\chi_{sa} n_{sa})} \qquad (1)$$

where χ_a is the Flory–Huggins solution parameter for type a segments, z is the coordination number of the lattice, and χ_{sa} is the net segment adsorption energy for type a segments. n_a is either the number of segment–solvent contacts for that particular segment type, counted for a single random sequence, or the average number of contacts for all sequences given by

$$n_a = n_t x_a \qquad (2)$$

where n_t is the total number of segment–solvent contacts for that conformation and x_a is the fraction of segment type a in the chain. Similarly n_{sa} is either the observed number of segment–surface contacts for segment type a or the weighted average number of contacts. Segment–segment interactions are included through a factor analogous to that used for the segment–solvent contacts

$$w_{ab} = \exp^{(-\chi_{ab} n_{ab}/z)} \qquad (3)$$

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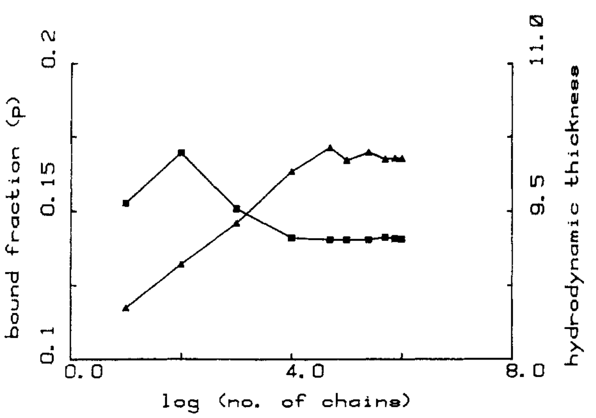

Figure 1. Convergence tests for a 101 segment random copolymer. (■) p and (▲) δ_H as a function of the number of conformations generated: $\chi_{sa} = 1.0$; $\chi_{sb} = 0.1$; $\chi_{ab} = 0$; $\chi_a = 0$; $\chi_b = 0.5$; $\Gamma = 2.06$.

The average number of contacts is given by

$$n_{ab} = 2n_t x_a x_b \tag{4}$$

An alternative approach (and indeed more usual in the simulation of ensembles of small molecules with a low degree of internal freedom) is to use importance sampling. In this procedure new chain conformations are generated by bond flips and rotations; each new conformation is then either accepted or rejected on the basis of a Boltzmann criterion.[4] The disadvantage of this method, however, is that depending on the flips sequences chosen the ensemble generated may not be ergodic.[7] However, a breaking and healing procedure is ergodic, though this had not been widely noted.[7] The present procedure though somewhat computationally intensive does sample the ensemble correctly and the results do converge satisfactorily. The estimate of the required number of iterations can easily be done by evaluating averages of the volume fraction profile. These are typically the bound fraction, p (the fraction of segments of an adsorbed chain in the interfacial plane), the hydrodynamic thickness δ_H[3] and the root mean square thickness δ_{rms}. These parameters can be calculated explicitly from the volume fraction profile by summation.[3] Figure 1 is a convergence test for a 101 segment copolymer showing the variation of p and δ_H, as a function of the number of conformations generated. The adsorbed amount is 2.06 segments per lattice site; the χ parameters are given in the legend. δ_H can be seen to be a more sensitive test of convergence than p. This is to be expected as fluctuations in volume fraction at the edge of the adsorbed layer, which determine δ_H, will be proportionately larger than those in the high-concentration zone near the interface.

Experimental Section

Two (dimethylamino)ethyl methacrylate (DMAEMA) monomethyl methacrylate (MMA) random copolymers were provided by I.C.I. and had mole fractions of DMAEMA of 1 and 5% (CPN1 and CPN5). The molecular weights determined by GPC were both 150 000 with a polydispersity ($\bar{M}_w/\bar{M}_n$) of 1.6.

The silica particles made following the Stober method[8] had a diameter of 197 ± 20 nm, estimated by electron microscopy.

The adsorbed copolymer samples for the SANS experiments were prepared by repeatedly spinning down and redispersing the silica in redistilled MMA. Finally the particles were redispersed in an MMA copolymer solution whose solvent composition (45.0% by weight deuterated MMA) was calculated to be at contrast match with the silica. Since the scattering length densities of the solvent and particle are equal at contrast match, the majority of the observed specular scattering is attributable to the adsorbed polymer layer.[9] The samples, which had a solids content of 2.5% w/w, were tumbled for 24 h at 15 °C. The full coverage pseudoplateau adsorbed amounts of these dispersions were determined by microanalysis and are given in Table II.

The SANS data were obtained at the Institut Laue Langevin, Grenoble, on the D17 instrument using a sample detector distance of 2.8 m, a detector angle of 5°, and a neutron wavelength of 1.2 nm.

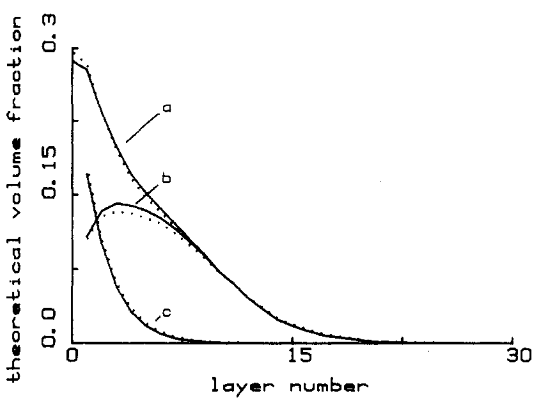

Figure 2. Volume fraction profiles for an adsorbed random copolymer of 10% "a" segments. A single random sequence (···) and a sequence weighted by the probability of a given segment type occurring by using the Flory method (—). (a) Total, (b) tail, and (c) loop volume fraction profiles. The other parameters are the same as for Figure 1.

Table I
Statistical Occurrence of *n*-mers in a Single Random Sequence Found from the Monte Carlo Simulation and also Calculated ( ) from the Method of Flory[10] for a 101 Segment Chain at Various Chain Compositions

	fractn of "a" segments		
n-mer	0.089	0.257	0.505
singlets	4 (7)	16 (14)	12 (12)
dimers	1 (1)	3 (4)	6 (6)
trimers	1	(1)	3 (3)
tetramers		1	2 (2)
pentamers			2 (1)

Results and Discussion

(1) Monte Carlo Simulation. In this discussion we first describe the effects of various limitations and improvements in the Monte Carlo model and in particular the problems of sequence generation and attachment points. For copolymers, one important consideration is the internal structure of the chain. In Figure 2 we compare volume fraction profiles calculated for a single random sequence and a uniformly weighted sequence of monomers. In Table I we compare the statistics of a single computer-generated random sequence and an ideal random chain. The occurrence of singlets dimers etc. as a function of the composition of the chains was found from the Monte Carlo simulation by simply counting segments. The numbers in brackets were obtained by using Flory's method[10] and assuming equal monomer reactivity ratios. As can be seen a correctly sampled single sequence gives almost the same result as a uniformly weighted sequence. For the particular fixed sequence chosen the full profile, a, shows a higher bound fraction. The fixed sequence also underestimates the density of tails (b profiles), while overestimating the role of loops (c profiles).

In previous simulations of adsorbed polymers by the Monte Carlo method,[11,12] invariably terminally attached chains have been used. This is a serious limitation as regards modeling physically adsorbed polymers, as it pre-

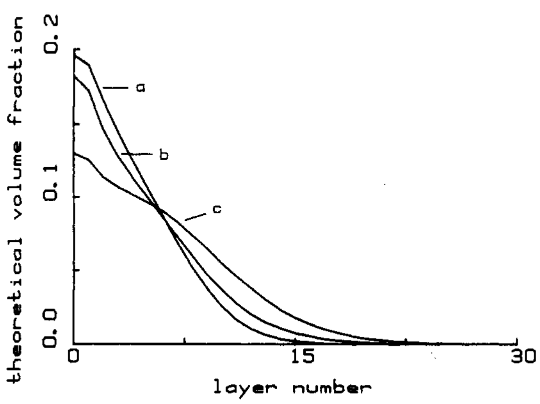

Figure 3. Volume fraction profiles for (a) medially attached chain, (b) Gaussian weighted attachment, and (c) terminal attachment. The other parameters are the same as for Figure 1.

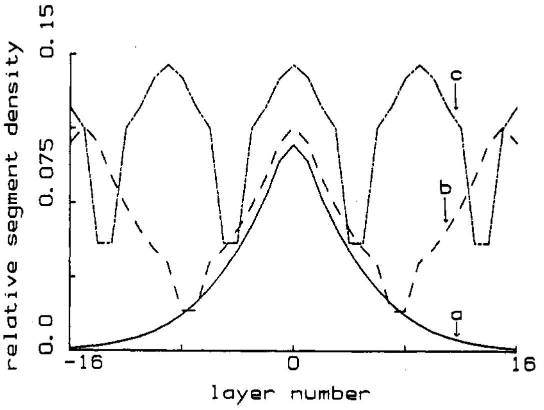

Figure 4. Transverse relative segment density profiles for a randomly attached 101 segment chain at three coverages: (a) isolated and (b) 0.45 and (c) 1.24 segments/lattice site. The other parameters are the same as for Figure 1.

cludes the formation of two tails per chain and hence overestimates the layer thickness. These effects are illustrated in Figure 3, which shows volume fraction profiles for terminally, medially, and randomly attached chains. The random attachment is in fact a weighted selection based on a Gaussian distribution about the chain center; i.e., conformations with medial attachment are most likely whereas end attachment is least likely. The medially attached case can be seen to be a rather better approximation than the terminally attached, but it still overestimates p and underestimates the layer thickness compared to the random case. The random attachment procedure has been used in all of the subsequent simulations.

Another consideration in a simulation of adsorbed polymers is the incorporation of interchain interactions, i.e., surface coverage. In a mean-field approach[5] these effects are accounted for by using the mean volume fraction in each layer as a weighting factor. This method necessarily loses information about polymer density fluctuations across the interface. Although this approach is a good approximation above c^*, the critical overlap concentrations, it is less appropriate at lower coverages. In the Monte Carlo simulation we use a periodic boundary to represent coverage, and by virtue of the fact that all chain segment coordinates are stored it is also possible to calculate the segment density across the interface. These "transverse" profiles are shown in Figure 4 for various adsorbed amounts. For isolated chains the profile is smooth and unlike polymer coils in solution is not Gaussian. At higher coverages (Γ = 1.24 and 0.45), for the selected thermodynamic parameters, there is only a limited degree of coil/coil interpenetration evident and individual chains still retain some features of the free coil profile. It should be noted, however, that this simulation requires that all adsorbed chains be uniformly distributed over the interface and hence overestimates the periodicity of the structure. Multichain models are also possible with the Monte Carlo scheme,[12,13] though computationally the time taken for long chains (>50) may be prohibitive. The effects of a single chain confined by a periodic boundary have been compared with a five-chain simulation also confined in such a boundary and on the cubic lattice.[13] In this extended model, only the central chain conformations were used to calculate the final volume fractions, and only small qualitative differences were found compared with the single-chain model. This comparison gives further credence to the simple single-chain approach.

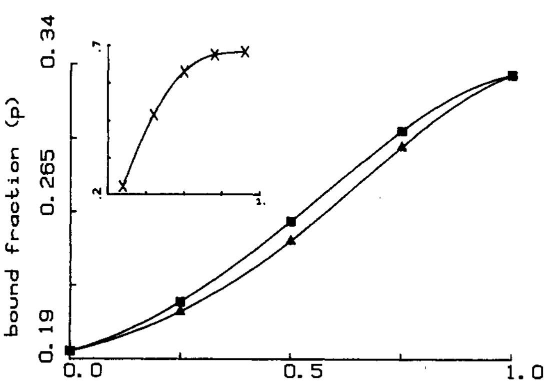

Figure 5. Effect of χ_{ab} on p as a function of the fraction of "a" segments in the chain: χ_{sa} = 1.0, χ_{sb} = 0.1; (■) χ_{ab} = 0, (▲) χ_{ab} = 1.0. Inset: χ_{sa} = 2.0; χ_{sb} = 0.1; χ_{ab} = 0.

Given the preceding framework for generating volume fraction profiles, it is now possible to explicitly examine the effects of copolymer composition on macroscopic adsorption parameters such as the adsorbed layer thickness and the bound fraction of segments. In Figure 5 we show the variation of the bound fraction, p, as a function of the fraction of strongly adsorbing "a" segments in the chain (χ_{sa} = 0.5, χ_{sb} = 0.1) for two values of χ_{ab} (0 and 1). Favorable segment–segment interactions (χ_{ab} = 0) lead to a more compact chain configuration and a higher bound fraction. The inset figure shows the effect of increasing the preference for one segment type to adsorb (χ_{sa} = 2.0, χ_{sb} = 0.1, χ_{ab} = 0). As might be expected, the bound fraction is extremely sensitive to chain composition especially when the preferential adsorption energy ($|\chi_{sa} - \chi_{sb}|$) is large.

Figure 6 illustrates the importance of intersegment interactions in controlling the adsorbed layer thickness. As the preference of one segment type for another increases (lower χ_{ab}) the chains adopt more compact conformations, leading to a reduced root mean square (rms) thickness. It can be seen that chain composition strongly influences these χ_{ab} effects, with chains having with mole fractions (x_a and x_b) approaching 0.5 being the most sensitive to the choice of segment type (hence choice of χ_{ab}).

(2) Comparison with SANS Data. Small-angle neutron scattering (SANS) can be used to obtain volume fraction profiles for adsorbed polymers.[3,9] In Figure 7 we show profiles for the 1% and 5% DMAEMA (CPN1 and CPN5) copolymers described earlier. The profiles can be described by two regions, one close to the surface and one extending into the solution. The bound fraction, root mean square thickness, and hydrodynamic thickness obtained from the profiles are given in Table II. The

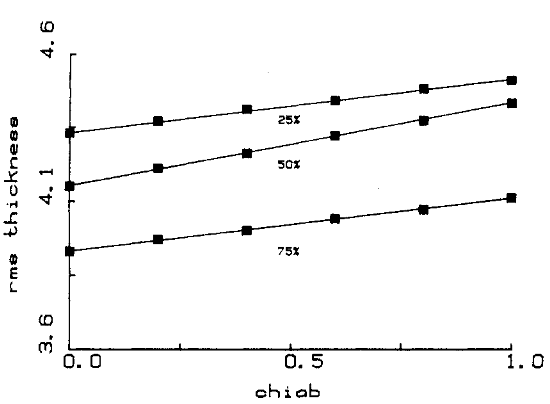

Figure 6. Variation of rms thickness with strength of intersegment interaction for three chain compositions: (1) 25%, (2) 50%, and (3) 75%. "a" segments

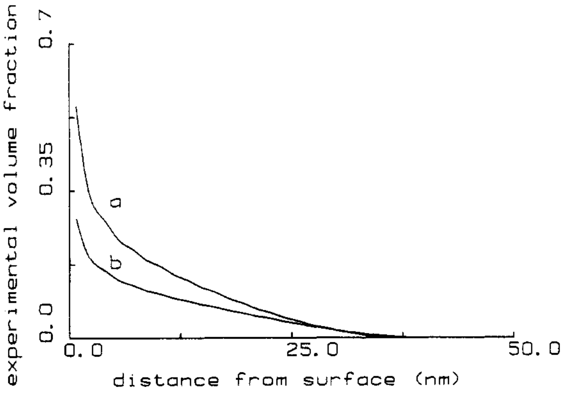

Figure 7. Experimental volume fraction profiles obtained by using SANS for DMAEMA-MMA copolymers adsorbed on silica from MMA: (a) 5% DMAEMA (CPN5); (b) 1% DMAEMA (CPN1).

Table II
Experimental (CP) and Theoretical (SIM) Adsorption Data for a 5% and a 1% Composition Random Copolymer[a]

	Γ, mg/m^2	δ_H, nm	δ_{RMS}, nm	p	x^b
CPN5	4.3	27.78	12.18	0.21	0.05
CPN1	2.7	28.88	13.58	0.18	0.01
SIM5	4.18	27.37	13.25	0.13	0.05
SIM1	2.72	27.41	12.80	0.10	0.01

[a] The parameters are described in the text. [b] x = mole fraction DMAEMA.

bound fraction for the 5% sample is considerably greater than that for the 1% sample, which reflects the strong adsorption of the DMAEMA moiety and the nonadsorption of the methacrylate segments. Although the adsorbed amount for the 5% sample (4.3 mg m^{-2}) is greater than that for the 1% sample (2.7 mg m^{-2}), the two profiles extend to approximately the same distance (similar values of δ_H). Theoretical predictions for the two cases SIM5 and SIM1 are shown by curves a and b of Figure 8, respectively. The Flory parameters chosen are given in Table III and reflect the known solution properties of the polymer segments. The χ_s parameters are more problematical, at least in an absolute sense, and the values are chosen to reflect the strong surface affinity of the DMAEMA segments (χ_{sa} = 2.5) and the virtual nonadsorbance of the methacrylate segments from solution in their own monomer (χ_{sb} = 0.0). The respective derived parameters are given in Table II. The theoretical data have been scaled to give the best fit to the experimental data. The parameters chosen lead to one lattice site having a length of 1.2 nm and an adsorbed amount of one segment per lattice site equal to 1.6 mg m^{-2}. The other parameters used are given in Table III. The theoretical profiles display the two regions seen experimentally, but the surface region is more extended than in the experimental case leading to lower bound fractions. The ratio of the experimental p values is, however, rather close to that obtained from the simulation. The extended region evident in the profiles is presumably due to tails as predicted by the simulation and as found previously.[14] It is interesting to note that although the 5% sample has a higher Γ (4.3), its hydrodynamic thickness is comparable to that of the 1% sample (Γ = 2.7). It is also apparent that the 5% sample has a higher p value and lower rms thickness than its counterpart.

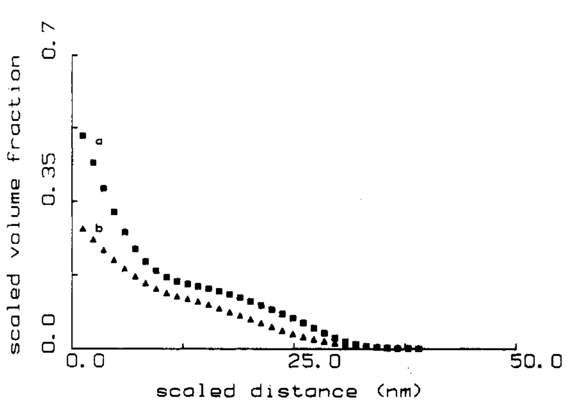

Figure 8. Monte Carlo simulations of adsorbed random copolymers: (a) 5% (■) (SIM5) and (b) 1% (▲) (SIM1) strongly adsorbing segments.

Table III
Simulation Parameters: Mole Fractions of DMAEMA (x_a) and Flory-Huggins Parameters (χ) for DMAEMA (a) and Methacrylate (b)

	x_a	χ_a	χ_b	χ_{ab}	χ_{sa}	χ_{sb}
SIM5	0.05	0.4	0.0	0.4	2.5	0.0
SIM1	0.01	0.4	0.0	0.4	2.5	0.0

Conclusions

The Monte Carlo model has been successfully applied to the simulation of adsorbed random copolymers. Various averages of the adsorption profile can be predicted, which are found to be in good qualitative agreement with experimentally determined parameters obtained by using SANS. The data presented in this paper show that the same effective thickness of an adsorbed layer can be achieved either by a high adsorbed amount or by a low fraction of strongly adsorbing segments and suggest that the equilibrium chain conformation in each of the two cases shown may be similar.

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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 Φ and P, combining $\langle s^2 \rangle$ with, respectively, $[\eta]$ and f, and the ratios q_s, q_f, and q_η 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 Φ 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_η 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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