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Registry No. Poly(α-methylstyrene), 25014-31-7.

Cyclization Dynamics of Flexible Polymers. Numerical Results from Brownian Trajectories

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ABSTRACT: Brownian trajectories of Gaussian chains of different lengths, generated with fluctuating hydrodynamic interactions in previous work, have been analyzed to study the rate constants of cyclization processes. The cyclization constants are compared with those previously calculated by Perico and Cuniberti through the approximate Wilemski–Fixman theory (in which hydrodynamic interactions are preaveraged). A significant disagreement is found between these theoretical and simulation values. The disagreement increases for increasingly stiffer chains and does not seem to be mainly caused by the preaveraging approximation. The simulation values for cyclization are in agreement with rate constants obtained from experimental work, but our decyclization constants are considerably higher than the experimental data.

Introduction

The kinetics of intrachain reactions under conditions of diffusion control is an interesting problem directly connected with the intramolecular dynamics of polymer chains in solution.[1] A theoretical description of this problem has been provided by Wilemski and Fixman[2] (WF). This theory can be applied to polymer models as the popular Rouse–Zimm model[3,4] (i.e., the bead-and-spring model with preaveraged hydrodynamic interactions). Detailed calculations for this model have been reported by Perico and Cuniberti[5] (PC). However, the WF theory includes some additional approximations since it is based on the use of a nonconservative perturbation in the time distribution function of the chain. WF consider that the distribution function of the polymer in the reaction region is in equilibrium. This approximation has been checked by Doi[6] for a harmonic dumbbell and he found that the exact results deviate from the WF prediction by up to 20%. Also, there has been further theoretical work[7–10] that points out different problems related with the WF approach.

Given this situation, it seems desirable to check the theory with simulation results. In this work we report calculations performed from Brownian dynamics trajectories previously obtained for linear chains of different lengths. These trajectories were used elsewhere to study other equilibrium and dynamic properties.[11] The trajectories were generated according to a bead-and-spring model consistent with the PC calculations. However, we introduced in this model an adequate nonpreaveraged description of hydrodynamic interactions. This way, our results are free of the different approximations contained in the WF theory. The discussion of differences between the simulation and theoretical values and the comparison with some experimental data are also included.

Model, Methods, and Numerical Results

We model the polymer molecules as bead-and-spring chains composed of $N + 1$ identical beads. Then, the intramolecular force $\mathbf{F}_j$ exerted by the neighbors of bead j is given by

$$\mathbf{F}_j = (3k_BT/b^2)(\mathbf{AR})_j \tag{1}$$

where k_BT is the Boltzmann factor, b is the bead statistical length, $\mathbf{R}$ contains the position vectors of the different units, $\mathbf{R}_i$, and $\mathbf{A}$ is the Rouse connectivity matrix.[3,4] Excluded-volume forces are not considered so that the chain equilibrium properties are consistent with the Gaussian chain model.

The Stokes radius of the beads, σ, that determines the frictional force associated with their motions is given in terms of the parameter h^*

$$h^* = (3/\pi)^{1/2}(\sigma/b) \tag{2}$$

for which we have set the value $h^* = 0.25$. Hydrodynamic interactions are described by means of the Rotne–Prager[12]–Yamakawa[13] tensor

$$\mathbf{D}_{ii} = (k_BT/\xi)\mathbf{I}$$

($\mathbf{I}$ is a 3×3 unit tensor)

$$\mathbf{D}_{ij} = (3k_BT/4\xi)(\sigma/R_{ij})[\mathbf{I} + \mathbf{R}_{ij}\mathbf{R}_{ij}/R_{ij}^2 + (2\sigma^2/3R_{ij}^2)(\mathbf{I} - 3\mathbf{R}_{ij}\mathbf{R}_{ij}/R_{ij}^2)] \quad \text{if } R_{ij} \geq 2\sigma$$

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while for overlapping situations, $R_{ij} < 2\sigma$

$$\mathbf{D}_{ij} = (k_B T/\xi)[(1 - 9\mathbf{R}_{ij}\mathbf{R}_{ij}/R_{ij}^2 + (3/32\sigma)\mathbf{R}_{ij}\mathbf{R}_{ij}/R_{ij}] \quad (3)$$

for $i \neq j$, where $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$ and ξ is the friction coefficient of the beads, calculated from σ and the solvent viscosity η_0, $\xi = 6\pi\eta_0\sigma$. We have also performed some calculations neglecting hydrodynamic interactions (i.e., neglecting the nondiagonal terms of $\mathbf{D}_{ij}$).

The polymer dynamics is simulated by solving the stochastic differential equation of Langevin, where $\mathbf{F}_j$, the frictional force, and a stochastic force are balanced. According to Ermak and McCammon,[14] we calculate $\mathbf{R}_i$ after a simulation step from

$$\mathbf{R}_i(t + \Delta t) = \mathbf{R}_i(t) + (\Delta t/k_B T)\sum_j^{N+1} \mathbf{D}_{ij}^0 \mathbf{F}_j^0 + \rho_i^0(\Delta t) \quad i,j = 1, ..., N+1 \quad (4)$$

where the superscript 0 refers to the beginning of the time step and ρ_i^0 is chosen from a sample of Gaussian random vectors generated with zero mean and with a variance–covariance matrix given by

$$\langle \rho_i^0(\Delta t)\rho_j^0(\Delta t)\rangle = 2\Delta t \mathbf{D}_{ij}^0 \quad (5)$$

We obtain results for scaled or reduced quantities based on the following units: b for length, $k_B T$ for energy, and $\xi b^2/k_B T$ for time. We have employed $\Delta t^* = 0.01$ for the time-step interval, generating three independent trajectories of 40 000 steps. More details on the model and simulation procedures are given in ref 11.

Assuming that two reactive groups are attached to both ends of the chain, we calculate $\Phi(\tau)$, defined as the probability that the groups are active over the time period τ. This probability is calculated as an average over the trajectory of the number of conformations for which the ends have not yet reacted at time $t + \tau$ provided that they are already active at time t. We define that the groups have reacted if the distance between them in a given trajectory point is smaller than a fixed value of the reactive radius R_0. Therefore, we check over the trajectory whether the distance between ends is greater or smaller than R_0 and calculate $\Phi(\tau)$ by counting the different situations in a way consistent with the definitions described above. Thus, an array variable with counters for $\tau = 0, \Delta t, 2\Delta t, ...$ is used. Once an open conformation is generated at time t, we increase in one unit the counters for $\tau = n\Delta t$. n runs from $n = 0$ to the value of n describing time $t - \tau$ at which the trajectory point immediately after the last cycled conformation was generated. $\Phi(\tau)$ is, therefore, obtained as the final values of these counters, normalized according to value obtained for $\tau = 0$. Consequently, all the open conformations are considered in the statistical ensemble of starting times. Our trajectories reproduce the equilibrium properties of a Gaussian chain[11] and, therefore, we believe that this ensemble is close to equilibrium since the number of cycled conformations is small compared with the total number of trajectory points. A discussion on the starting time ensemble characteristics of the cyclization problem can be found in the theoretical work of Perico and Battezzati[9] and Weiss.[10]

The different values of $\Phi(\tau)$ so obtained are then numerically fitted to a single-exponential function. These fittings are satisfactory in all the different cases. Fitting to the sum of two exponentials do not improve significantly the quadratic deviations. Consequently, the fitted exponents allow us to identify first-order constants k_1

$$k_1 = -(d\Phi/d\tau)/\Phi(\tau) \quad (6)$$

The final values of k_1 are reported in the form of statistical means and deviations over samples composed of the values corresponding to the three different trajectories considered as independent data. These results for k_1 (denoted as k^*_1 since they are expressed in reduced units) are shown in Table I.

Table I
Results for k^*_1 and $(k_1^d)^*$ Obtained from Our Brownian Trajectories for $h^* = 0.25$ and for Different Values of N and R_0/b^a

R_0/b	$N+1$	$10^3 k^*_1$	$(k_1^d)^*$	$10^{-7}k_1$, s^{-1}	k_1^{PC}, s^{-1}	k_1^d, s^{-1}
0.50	20	19 ± 2	0.4 ± 0.2	5.5 ± 0.6	8.7	11.8 ± 5.0
	15	33 ± 12	0.67 ± 0.25	9.8 ± 3.5	14.1	20 ± 7
	11	51 ± 6	0.44 ± 0.05	15 ± 2	23.2	13 ± 1.5
	8	114 ± 5	0.43 ± 0.09	34 ± 1.5	39.2	12.6 ± 2.7
	6	163 ± 38	0.34 ± 0.06	48 ± 11	64.2	9.9 ± 1.7
0.25	20	9.1 ± 0.2	1.7 ± 1.7	0.33 ± 0.01	0.62	6 ± 6
	15	13.0 ± 0.2	1.0 ± 0.5	0.47 ± 0.01	0.96	3.8 ± 1.8
	11	15.0 ± 0.1	0.80 ± 0.35	0.54 ± 0.01	1.53	2.8 ± 1.3
	8	28.0 ± 0.2	1.0 ± 0.5	1.01 ± 0.01	2.52	3.7 ± 1.7
	6	42.0 ± 0.5	0.6 ± 0.1	1.53 ± 0.01	4.05	2.3 ± 0.4

[a] Results of k_1 and $(k_1)^d$ for the same values of N, h^*, and $R_0 = 5$ Å and consistent values of b are also included and compared with the PC results[5] for equal N, b, and R_0 and with $\sigma/b = 0.25$.

Furthermore, we have obtained $\Phi_d(\tau)$, defined as the probability that a product group has not yet dissociated after a time period τ. It is obtained as the average over the trajectory of the conformations for which two beads are at a distance closer than R_0 (i.e., they have reacted forming the product) at time t and are still together at time $t + \tau$. In general, we have found that $\Phi_d(\tau)$ decays much faster than $\Phi(\tau)$. Fittings of $\Phi_d(\tau)$ to a single exponential are not as satisfactory as in the case of $\Phi(\tau)$, perhaps as a consequence of numerical uncertainties originating from such fast decays. At any rate, we have calculated a first-order decyclization constant, k_1^d, in a way similar to that used for the calculation of k_1 for the cyclization process. The results are also summarized in Table I (also denoted as $(k_1^d)^*$ in reduced units).

Discussion

The WF theory predicts that $\Phi(\tau)$ can be expressed as

$$\Phi(\tau) = \sum_i \Phi_i \exp(-\delta_i \tau) \quad (7)$$

where the term $i = 1$ accounts for over 99% of $\Phi(\tau)$. This conclusion is confirmed by the single-exponential behavior obtained from our simulation results. Assuming this behavior, $k_1 = \delta_1$ can be evaluated from an integral equation, obtained with the approximate assumption of equilibrium in the reaction volume (sink closure approximation). Following the PC scheme[5]

$$k_1 = kV_{eq}/[1 + kV_{eq}\int_0^\infty [K(t)/K_\infty - 1]\exp(k_1 t)\, dt] \quad (8)$$

where the purely diffusive regime is obtained by assuming that $k \gg k_1$ (k is the intrinsic second-order constant of the chemical reaction).

$K(t)$ contains the information on chain dynamics that ultimately depends on the Rouse–Zimm eigenvalues and eigenvectors[3,4] (in the preaveraged treatment) and also

on the variable γ_R defined as

$$\gamma_R = (3/2)^{1/2}(R_0/b)N^{-1/2} \quad (9)$$

k_1 depends very strongly on the concentration of chain units, and, therefore, it exhibits a systematic decrease for increasing values of N. In order to eliminate this large effect, PC studied also the second-order constant $k_2 = k_1/c_{eq}$, where c_{eq} represents the equilibrium concentration of end chains, obtained as

$$c_{eq} = [(4/3)\pi R_0^3]^{-1}K_\infty \quad (10)$$

with

$$K_\infty = \text{erf}(\gamma_R) - (2/\pi^{1/2})\gamma_R e^{-\gamma_R^2} \quad (11)$$

Consequently, the PC results obtained with $R_0 = 5$ Å and different choices for b, (σ/b), and N can be compared with our simulation results that were calculated with different choices for h^*, R_0/b, and N. We have selected values of R_0/b in accordance with some of the PC choices for b and R_0. Moreover, our fixed value $h^* = 0.25$ is in very close agreement with the choice $\sigma/b = 0.25$ used by PC (both values lead to the nondraining limit with a small number of chain units). We have also considered the free-draining situation for which $h^* = 0$.

Our simulation results for k_1 in reduced units contained in Table I can be compared with values reported by PC (in real units) through the relationship

$$k_1 = [6\pi(\eta_0/T)b^3(\sigma/b)/k_B]^{-1}k^*_1 \quad (12)$$

where we adopt $\eta_0/T = 10^{-5}$ pK^{-1} (as PC did).

In Table I we present a comparison between our simulation values of k_1 (now explicitly depending on b through eq 12) and those of PC. Very significant differences between both sets of results can be observed. (Though the accuracy of the simulation results varies with b, being higher for higher values of this variable, they are always clearly smaller than the theoretical ones.) The differences increase with increasing values of b, i.e., for stiffer chains, and can be attributed either to the preaveraging of hydrodynamic interactions or other approximations contained in the WF theory. Since the differences are higher than those caused by preaveraging for the rest of the dynamic properties so far investigated,[11] we believe that these other approximations may contribute significantly to the lack of agreement. Besides the closure approximation, it should be considered that an irreversible reaction is assumed in the PC calculations, while, in our simulations, a cycled conformation is allowed to open again along the trajectory. Moreover, our test to define cycled conformations is equivalent to a Heaviside sink function. However, WF considered a product of a Heaviside and a δ function to evaluate the kernel quadratic in the sink function, for the sake of computational convenience. However, Battezzati and Perico[7] analyzed the different choices for the sink function and they concluded that the influence of the choice on the final results should be small.

In Figure 1 we show a comparison between results for k_2. Of course, the differences between simulation and theoretical values are similar to those found for k_1. However, it can be now observed that the qualitative variation of k_2 with N (changing for different values of N) is adequately predicted by both the WF theory and our simulation results.

The results obtained without considering hydrodynamic interactions have been summarized in Figure 2, where the corresponding theoretical curves have been also

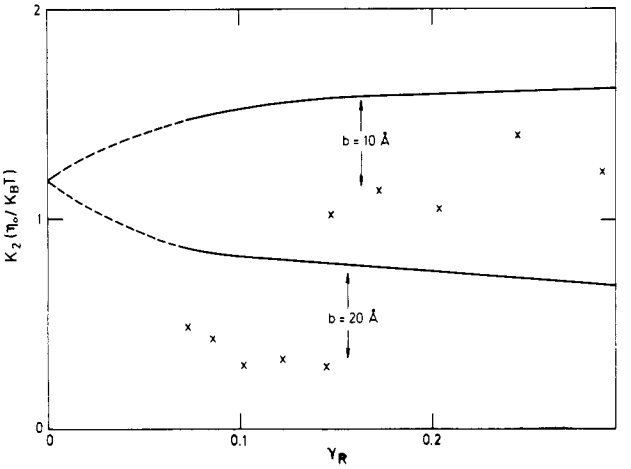

Figure 1. Scaled second-order rate constant versus γ_R from the PC results[5] with $\sigma/b = 0.25$ Å (—) and from the Brownian trajectories for $h^* = 0.25$ (×). $R_0 = 5$ Å; two different values of b are considered.

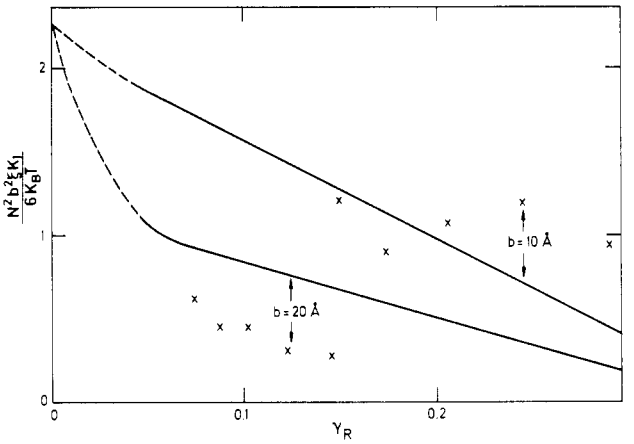

Figure 2. Scaled first-order rate constant versus γ_R for $h^* = 0$ (i.e., free-draining). (—) Curves from the PC results (extrapolated from straight lines for the highest γ_R). (×) Values from our Brownian trajectories. $R_0 = 5$ Å; two different values of b are considered.

plotted. This comparison is interesting because the differences cannot now be attributed to the preaverage approximation. The uncertainties of the simulation results for our smallest choice of b preclude any precise comparison for this case. Moreover, the theoretical curves for the highest values of γ_R are straight-line extrapolations from the curves reported by PC for smaller γ_R, though one can expect that these curves may reach an asymptotic level. However, we find that the differences between simulation and theoretical values are very significant for the highest b, i.e., for the stiffer chain, the simulation values being again smaller than the theoretical ones, in agreement with our previous conclusion obtained from calculations that include hydrodynamic interactions. This way, our remark that the main source of disagreement between theory and simulation values may arise from approximations not related with the treatment of the hydrodynamic interactions (as the closure approximation) is reinforced. (A direct comparison between results obtained with and without hydrodynamic interactions was performed by PC and is not repeated here.)

We have also simulated trajectories with a preaveraged version of the diffusion tensor and have obtained in this way some values of k_1. For $b = 10$ Å, we reproduce the PC results. In this case the differences between the fifth and sixth columns in Table I can be unambig-

uously attributed to preaveraging. For b = 20 Å, nevertheless, the simulation with preaveraging gives values that are intermediate between the theoretical results and those obtained with fluctuating hydrodynamic interactions. Then, it can be concluded that the WF approximations have a stronger influence for more rigid chains.

The results for k_1^d contained in Table I do not seem to show a definite dependence on the chain length (most differences for a given value of b are surely caused by numerical problems of the fitting procedure, vide supra). Both the PC theoretical results and our simulation data for k_1 vary with chain length with a scaling law $k_1 \sim N^{-a}$, where a is always close to 1.5, an exponent that corresponds to the variation predicted for the first relaxation times of the chains according to the Rouse–Zimm theory.[4] Since the equilibrium constant for the cyclization process $K_{cy} = k_1/k_1^d$ has the same type of variation with N for chains that obey Gaussian statistics, one may conclude that k_1^d should not depend on chain length. Experimental results for both k_1 and k_1^d can be calculated from the analysis of fluorescence decay measurements of chains labeled with fluorescent groups at their ends. Recent data reported by Winnik et al. for polystyrene, poly(ethylene oxide), and poly(dimethylsiloxane)[15,16] and for polycarbonate in different solvents[17] do not show a significant variation of k_1^d with varying molecular weight. This may indicate a qualitative agreement with our simulation values. Unfortunately, the quantitative comparison does not support this conclusion. Thus, while the order of magnitude of the experimental results for k_1 is in accordance with our results (a more detailed comparison cannot be accomplished because the experimental data cover a narrow region of small molecular weights corresponding to our smallest values of the number of statistical units, N), the experimental values of $k_1^d \simeq (2\text{–}4) \times 10^6$ s^{-1}, in the range of 50–200 repeating units, are in general smaller than the corresponding values of k_1 and much smaller than our simulation results for k_1^d. This seems to suggest that the decyclization process is under chemical control (the intrinsic rate constant of the decyclization process should be smaller than that of cyclization, since the difference between their respective activation energies corresponds to a high excimer binding enthalpy[18] of about 8 kcal mol^{-1}. Also, a strong variation with temperature for experimental values of decyclization rate constants has been observed.[16] This variation corresponds to an activation energy of about 11 kcal mol^{-1}).

An indirect type of comparison can be also performed with the theoretical and simulation results for k_1 and experimental data obtained from fluorescence quenching due to collisional interactions between the fluorescent ends of a chain. PC carried out such comparison with the data reported by the same authors.[19] This comparison is based in the following equation for the quantum yield of the quenching process

$$\Phi/\Phi_0 = (1 + \tau_0 k_1)^{-1} \qquad (13)$$

valid when other processes are not competing. In Figure 3 we have plotted the experimental quantum yields reported in ref 19 for pyrene end labeled poly(ethylene oxide) chains of different molecular weights and also theoretical and simulation values obtained from k_1 corresponding to chains of b = 20 Å (R_0 = 5 Å) whose molecular weights are assumed to be in accordance with the relationship $M = Nb^2/0.413 \times 10^{-16}$, parameters provided for poly(dimethylsiloxane) chains in ref 5. Also following PC, we fix $\tau_0 = 10^{-7}$ s for the lifetime of the

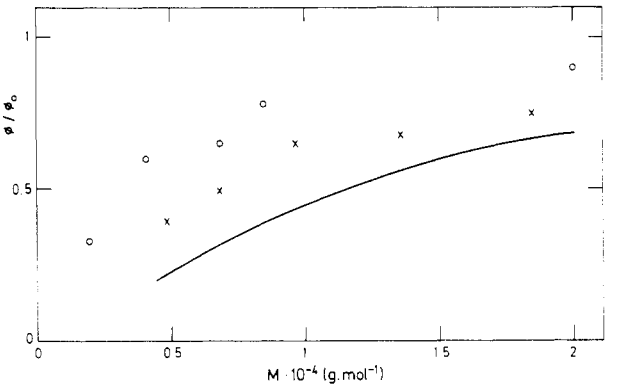

Figure 3. Quantum yield for fluorescence quenching versus molecular weight, obtained according to eq 13 (see text) with $\tau_0 = 10^{-7}$ s and values of k_1 calculated from PC with b = 20 Å, R_0 = 5 Å, and σ/b = 0.25 (—) and from our Brownian trajectories with R_0/b = 0.25, b = 20 Å, and h^* = 0.25 (×). Experimental data for PEO[19] (○).

fluorescent species.

Though the comparison between theoretical and experimental data depends on the particular choice of τ_0 (a change of its value is equivalent to a shift of the theoretical results), our assignment of parameters is rather arbitrary, and eq 13 is only an approximation, we can establish the following conclusions: (a) Both the simulation and theoretical values follow the general trend of the experimental data. Since the measurements were performed in a good solvent where the excluded-volume forces slow down the chain relaxation, an adequate model that includes these forces would move both the theoretical and simulation values close to the experimental data. (b) The quantitative differences between simulation and theoretical results are very significant, even in this indirect form, when both types of results are simultaneously compared to experimental data.

Direct experimental data for k_1 have been obtained from the analysis of spectroscopic decay experiments of end-capped chains of polystyrene with pyrene[20,21] (intramolecular excimer formation) and anthracene[22,23] (intramolecular triplet–triplet annihilation) labels. The PC results with b = 60 Å (value that reproduces the hydrodynamic properties of short polystyrene chains[5]) are in reasonable agreement with the excimer data. Unfortunately, our calculations cannot be extended to this value of b, for which we can only find a few cycles along the whole trajectory. Notwithstanding, our attempts to perform such calculations have shown that the simulation values should be several times smaller than the PC results and, perhaps, in better agreement with the much smaller triplet–triplet annihilation data. In any case, quantitative comparisons of this type should be considered with caution since the rate constant values are strongly dependent on the choice of parameters and other model details.

In summary, we have obtained results for the end-to-end cyclization and decyclization rate constants of flexible chains through the analysis of previously obtained Brownian trajectories. The cyclization constants are in general agreement with experimental data and show a significant quantitative deviation with respect to the values predicted by the Wilemski–Fixman theory. These differences increase for increasingly stiffer chains (for which the uncertainties in the simulation numerical values decrease in some cases) and may not be mainly caused by the theoretical treatment of hydrodynamic interactions. The decyclization rate constants obtained through the trajectories do not vary much with chain length. This

is in qualitative agreement with the behavior of experimental rate constants, which, nevertheless, are always much smaller.

Acknowledgment. This work has been supported in part by the Grant PB12/86 of the Comisión Interministerial de Ciencia y Tecnologia. A.R. and J.L.G.F. acknowledge fellowships from the Ministerio de Educación y Ciencia (PFPI and Beca-Colaboración).

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Ideal Polymer Chains of Various Architectures at a Surface

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ABSTRACT: We study the macroscopic behavior of ideal polymer chains of various architectures in the vicinity of a surface, by considering that at least one of the units of the chains is in contact with the surface. The probability that any unit will be in contact with the surface is employed and the macroscopic properties are determined as averages over this probability. The present model is an amendment to the model used previously with the one end of a linear chain fixed at the surface, and though it is a simplification to the full problem where the chains can move freely in the whole space, it is free from the necessity to include the volume and the polymer concentration in order to describe chains in the vicinity of the surface. We estimate the mean number of contacts between a chain and the surface for the cases of linear, ring, regular star, and regular comb polymers as the basic quantity for the description of both the thermodynamics of chains at a surface and the degree of adsorption of polymers of various architectures.

1. Introduction

The study of the macroscopic behavior of polymer chains at surface finds applications in numerous fields such as the stabilization of colloid suspensions,[1] chromatography,[2] adhesion,[3] and restriction of flow in capillaries.[4] A number of theoretical[5,6] and experimental[7] works have been done on the subject but they mainly concern the adsorption of linear chains. Only few works deal with polymers of various architectures at an interacting surface,[8-10] though interest in the synthesis[11] and the study of the solution properties[12,13] of such macromolecules is increasing. We present in this work a model capable of describing the role of architecture on the behavior of chains at an interacting surface, and we apply it to the cases of ideal linear, ring, regular star, and regular comb polymers.

In the vicinity of an interacting surface the conformational behavior of a polymer chain in a solvent is governed by two kinds of mean interactions: the two-body interactions between all pairs of units far along the contour length of the chain but close in space and the interactions between the units of the chain and the surface. The probability of a specific configuration determined by the M position vectors ($\mathbf{R}_i$, $i = 1, 2, ..., M$) of the units of the chain can be written as

$$P(\mathbf{R}_i) = P_0(\mathbf{R}_i) \exp\{-u_e \sum_{i=1}^{M} \sum_{\substack{j=1 \\ i \neq j}}^{M} \delta^3(\mathbf{R}_i - \mathbf{R}_j) - u_a \sum_{i=1}^{M} \delta(z_i)\} \tag{1.1}$$

where $P_0(\mathbf{R}_i)$ is the ideal probability representing the connectivity term of the chain. The two δ function pseudopotentials obtain significant values, the first one when two units come close in space and the second one when a unit approaches the surface. The exponential form of these pseudopotentials is realized through its expansion where the terms to all orders in a perturbation theory scheme are produced. The interaction parameters u_e and u_a are proportional to the binary cluster integrals of the two mean potentials in the presence of the solvent, between two units and a unit and the surface, respectively. They express the intensity of the corresponding interactions

0024-9297/90/2223-2061$02.50/0