Confinement Effect in Diffusion-Controlled Stepwise Polymerization by Monte Carlo Simulation

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Diffusion-controlled stepwise polymerization of a linear polymer confined in nanoscopic slits is simulated through a Monte Carlo approach. A noticeable influence of the confinement on the kinetics is found. The confinement modifies both the spatial pair distribution function and the diffusive properties of the polymers. As a consequence, the confined system can show either faster or slower reaction kinetics with respect to the bulk system, depending on the strength of intermolecular interactions. The predicted polydispersity of the polymer is in agreement with recent theories of diffusion-controlled stepwise polymerization, and can be slightly affected by the confinement.

Introduction

Polymerization in confined situations, such as mesoporous materials or organoclay substrates, has received increasing attention during the last years due to the interesting properties of both the hybrid organic−inorganic material obtained and the polymer formed in such confinement.[1,2] Even industrially relevant processes, such as solid state radical polymerization in porous isotactic polypropylene, are carried out by polymerizing a monomer in a "confined" situation.[3−6] Consistent changes in polymer characteristics such as average molecular weight and molecular weight distribution,[7] degree of branching,[8] and glass transition temperature[9] have been reported for chain-growth and step-growth polymerizations performed in confined media. Along with this experimental evidence, there is still a lack of theoretical interpretation separating and studying the role of the different interactions taking place in confined polymerization. A first point in devising a suitable theoretical interpretation is understanding the relative importance of the two main aspects arising from confinement in mesoporous materials. The first one is the change in diffusional and conformational properties induced in a polymer system by a nanoscopic geometrical confinement alone, which can affect the kinetics of diffusion-controlled polymerizations.[10−12] The second one is the catalytic action of the surface of the walls of the mesoscopic substrate on which the polymerization is carried out. In this work, only the first aspect will be considered.

For what concerns the confinement alone, narrow boundaries can modify the polymer kinetics for three different reasons:

(1) The number of allowed conformations of each chain in the system is suppressed near the wall surfaces by the presence of geometric confinement, and thus, the conformational entropy of the overall system is lowered by the presence of boundaries.

As a possible consequence of this reduction of allowed states, the diffusivity of the polymer can be lowered.[13,14] On the other hand, in a polydisperse polymer melt, the entropic losses can cause an inhomogeneous distribution of polymer (with respect to their molecular weight) in the vicinity of the walls. The shorter chains, which are more likely to be found close to the walls, can act then as lubricants enhancing the diffusivity near the walls.

(2) The density of the system is no longer uniform but has a damped oscillating behavior as a function of distance from the boundaries whose amplitude is enhanced as the boundaries are approached. The overall diffusion coefficient can be enhanced by the buildup of such marked density gradients as a direct effect of Fick's law.[15]

(3) The buildup of a strongly nonhomogeneous density gives, as a direct consequence, a position-dependent pair distribution function, $\psi(r_i, r_j)$, for the two reactants.

From what was said above, in a confined polymer system, the probability that two reactive monomers situated in particular positions along the chain (in the case of step-growth polymerization, for example, two chain ends) can collide is thus modified in a nontrivial way with respect to the bulk situation. Hence, even the qualitative behavior of the diffusion-controlled polymer reactivity under confinement may not be correctly predicted with simple arguments. On the other hand, the theory of diffusion-controlled reactions in polymer[10,11] has been developed for the isotropic (bulk) situation and an extension for nonisotropic systems may be not straightforward.

In this work, we studied, with Monte Carlo techniques, the linear and diffusion-controlled stepwise polymerization for a system confined in a bidimensional slab of variable thickness with no interactions with the confining boundaries. The initial system was already a linear polymer in which only chain ends can give chemical association and form new bonds. Our study focused on the kinetics of the polymerization and on the molecular weight distribution obtained, to assess if and to what extent simple geometric confinement is able to affect the stepwise polymerization kinetics.

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Models and Methods

I. Polymer Modelization. The polymer has been simulated in the framework of the bond fluctuation (BF) model,[16,17] which has been tested to be adequate for describing the static and dynamic properties of polymer melts[15] and has already been utilized in simulating the polymerization process.[18] In the three-dimensional BF model, a polymer chain is represented by a set of effective monomers on a cubic lattice, each represented by eight occupied vertices of the elementary cube on the lattice, and every two consecutive monomers are connected by an effective bond. Effective monomers can be visualized as occupied sites of a reduced ("dual") lattice, in which each site is given by an elementary cube on the original lattice. The position of a monomer is thus defined through the position of the cube formed by its eight corners. At every step, each monomer is tentatively moved on the *x*, *y*, or *z* direction; if one of the sites in the new position of the monomer is already occupied, the move is rejected according to the excluded volume (EV) condition. By choosing a restricted set of possible allowed bonds (with length 2, $\sqrt{5}$, $\sqrt{6}$, 3, $\sqrt{10}$), two chains cannot intersect each other with a Monte Carlo (MC) move as a direct consequence of the EV condition. A MC step is completed when each monomer has undergone one attempted MC move. A harmonic elastic energy is associated with the bond length in the form:

$$U_{\text{bond}} = \frac{1}{2} k_{\text{B}} T K l^2 \tag{1}$$

where K is the entropic elastic constant expressed as[19]

$$K = 2/(l^*)^2 \tag{2}$$

and $l^* = (\frac{1}{2})(l_{\min} + l_{\max}) = 2.581\ 13$ is chosen as the most probable bond length value.

Attractive interactions between both bonded and nonbonded sites have been modeled through a distance-independent attractive potential between effective monomers:

$$U_{\text{nonbond}} = -\sum_{i}^{F} \epsilon_i \tag{3}$$

where the sum runs only on the first possible occupation shell of each monomer (given by the 98 sites constituting the second cubic shell around each monomer; no effective monomer can occupy the first cubic shell around any other effective monomer due to excluded volume conditions). Repulsive interactions were taken into account only by excluded volume conditions. Two different values have been chosen for the attractive potential; in the first case, $\epsilon_i = 0$ was chosen (only excluded volume conditions present, system A), while, in the second case (system B), the interaction parameter takes the value $\epsilon_i = 0.2$.

The acceptance probability for a move is expressed in terms of the energy change associated with each move through the Metropolis sampling:[20]

$$P = \min[1, \exp[-\Delta E/k_{\text{B}}T]] \tag{4}$$

Periodic boundary conditions were applied in directions *x* and *y*, while two hard walls perpendicular to the *z* direction were simulated by situating two slabs at *z* boundaries in which each elementary cube is occupied by an effective monomer, to avoid trespassing of *z* boundaries. When attractive interactions are present (system B), the wall then exerts an attractive force over the nearest monomers.

Two different values for the confinement spacing (with the distance between walls being $Z = 10$ and $Z = 30$, respectively) have been studied; for comparison, a bulk system with periodic boundary conditions in the *x*, *y*, and *z* directions has been studied also.

II. Chemical Reaction. A chemical reaction between two reactive units, like the formation of a chemical bond, is given by two consecutive events. First, the two reactants diffuse one toward the other until the distance is small enough to allow the reaction; second, the potential energy activation barrier between the reacted and unreacted state is overcome by the kinetic energy of the reacting species and the reaction occurs. This process can be schematized in the following way:

$$A + A \leftrightarrow AA^* \rightarrow A{-}A$$

The reaction rate of a second-order reaction (e.g., a homopolycondensation of an A monomer) can be written as

$$\frac{d[A(t)]}{dt} = k[A(t)]^2 \tag{5}$$

where the kinetic constant, if the stationary state assumption is valid, is

$$k = \frac{k_a k_d}{k_a + k_d'} \tag{6}$$

In this equation, the term k_a accounts for the probability that the two reactant units, once put at a suitable distance for reaction to take place, effectively give the reaction; the terms k_d and k_d' account for the volume spanned by the reactive monomers by diffusive motion. It is straightforward to see that if $k_d' \gg k_a$ (that is, diffusion is fast compared to reaction) then

$$k = \frac{k_a k_d}{k_a + k_d'} \approx \frac{k_a k_d}{k_d'} \tag{7}$$

while if $k_d' \ll k_a$ (diffusion is slow compared to reaction) then

$$k = \frac{k_a k_d}{k_a + k_d'} \approx k_d$$

and the overall reaction is diffusion-controlled. Thus, diffusion-controlled reactions are encountered when either the reaction taking place is very fast (e.g., in free radical polymerization or catalyzed polycondensation) or the diffusion of reacting units becomes very slow (as expected in high molecular weight polymers).

If reaction takes place in a polydisperse system, the above representation is no more adequate; each pair of polymers with different chain lengths will have a different kinetic constant, due to their values of diffusivities. Thus, for a pair of macromolecules with chain length *i*,*j*, we can write

$$k = \frac{k_a k_d(i,j)}{k_a + k_d'(i,j)} \tag{8}$$

where the diffusive kinetic constant now depends on the molecular weight of both species, on the motional regime (entangled or nonentangled), and on the reaction time scale. The appearance of a chain-dependent rate constant then in principle invalidates the "equal reactivity assumption"[24] which states that all polymer chains terminating with the same functional group are equally reactive. This is able in principle

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to cause strong departures from the molecular weight distribution (MWD) expected from the equal reactivity assumption if the reaction is diffusion-controlled[12] (if the reaction is not diffusion-controlled, then the molecular weight dependencies are canceled out and the assumption is still valid).

According to theory,[12] each macromolecule has a different kinetic constant depending on its dimension; in the long time limit (when the overall reaction time is greater than the time required for one chain to completely lose its initial conformation), the kinetic constant can be approximated by

$$k_d(i,i) \propto R_i D_i \qquad (9)$$

where R_i and D_i are the gyration radius and diffusivity of a chain composed by i monomers, respectively.

In the short time limit, that is, when the overall reaction time is much shorter than the longest relaxation time of the chain, a different relation holds in which the kinetic constant is a function of time:

$$k_d(i,i) \propto [x_i(t)][D_i^{eff}(t)] \qquad (10)$$

where $x_i(t)$ is the mean displacement of the reactive monomer at a given time and $D_i^{eff}(t)$ is an effective diffusion constant whose value depends on the number of monomers, Δn, able to move cooperatively with the reactant monomer during a time interval, t. This regime of motion, referred in the original paper by de Gennes as *compact exploration* due to its efficiency in sampling the space, is dictated principally by the high-order Rouse modes of the chain[23] and is, at short times, almost independent from the molecular weight.

Thus, different reaction time scales will have different dependencies on molecular weight: for long time scales (if compared with the polymer relaxation time), the diffusional kinetic constant depends strongly on molecular weight, and for times shorter than the relaxation time, the same constant can be almost unaffected by the length of the reacting chain.

(It must be borne in mind that the treatment presented is valid only for chains in the bulk state; in confined situations, some differences can be revealed. As an example, pairs of macromolecules having a gyration radius respectively lower and higher than the extent of confinement are expected to display quite different behaviors even qualitatively, from both diffusional and conformational properties.)

In our simulation, the activation barrier has been thought to be present, and k_a was expressed through the probability k_a' for two reactive monomers to react if placed at a suitable distance. The value of k_a' was fixed to 0.01; this choice has been made to limit the contribution of compact exploration to the reactivity of the system within a still acceptable amount of computer time.

Chemical reaction (stepwise polymerization) has then been simulated by first evaluating the minimum image distance between the moved end and all other chain ends after each elementary move of one chain end. If this distance was equal to the minimum allowed distance (2) a random number, nr, with uniform distribution in the interval [0,1] was extracted and compared with k_a': if $nr < k_a'$, then a new bond was created between the two ends if they were belonging to two different chains (cyclization reaction was not allowed). Bonds are created immediately after the elementary MC move, and not at the end of the whole MC step; it must be recognized that this procedure might introduce some artificial correlation between subsequent events (elementary moves), and we intend to investigate the

TABLE 1: Parameters for the Three Different Systems Studied[a]

system	I	II	III
Z	10	30	bulk
X,Y	133	75	55

[a] Z is the spacing between walls (number of cell sites in the z direction), and X,Y, the cell dimension in the x,y direction. In the bulk system, the cell is isotropic.

consequences of this choice in a subsequent paper. The reaction is irreversible, so that no bond breaking can occur during the simulation.

III. Simulation Details. The simulation is performed starting with a system constituted by a fixed number ($n = 1000$) of chains of length $N = 10$. For our purposes, we chose to simulate systems with the same density at a reduced temperature of $T = 1$. Two different densities can be defined in the BF model,[25] based, respectively, on the number of monomers, ϕ, or on the number of occupied lattice sites, ρ. The system particle density (fraction of occupied unit cells in the dual lattice, defined as $\phi = nN/V$, where n is the number of chains, N is the initial polymerization degree, and V is the number of lattice sites[25]) has an ideal reference value of $\phi = 0.062$, equivalent to a volume fraction (ratio of occupied sites in the original lattice) of $\rho = 8\phi = 0.496$. This choice ensures that the polymer has a meltlike density.[15] All of the systems simulated are described in detail in Table 1. Under the chosen conditions, the starting system of chains (in the bulk state) is nonentangled.[21] For each situation, acceptable independent starting configurations have been obtained by generating random walk in the simulation box with no EV constraints and then removing multiple-occupied sites and X-traps (which can affect the dynamics of chains and the ergodicity of the system[21]) by a reptation algorithm.[22] Each configuration has then been equilibrated for 10 000 MC steps with chemical reaction option switched off after obtaining an acceptable (with no overlap) starting configuration; then, reaction has been switched on and the system has been evolved until the polymerization degree ($p = (n(0) - n(t))/n(0)$, where $n(t)$ is the number of chains at time t) had reached the value $p = 0.9$, equivalent to 100 chains remaining in the system. For each system, the results have been averaged over 50 independent runs.

Results and Discussion

In Figure 1, the number of molecules is plotted as a function of time for systems labeled with A (excluded volume interactions only); clearly, the presence of confinement slightly enhances the reaction rate, and the acceleration of kinetics is more consistent for the strongly confined case ($Z = 10$). To understand the reason for such behavior, an accurate study has been performed on the diffusive and conformational properties of the initial system of chain length $N = 10$ where the reaction option has been switched off.

To check which of the two motional regimes (chain diffusion or compact exploration) is responsible for the diffusive formation of the activated complex, we measure center-of-mass and chain end mean square displacement as a function of time. Due to the presence of the wall boundaries for systems different from bulk, diffusivities have been calculated only in directions parallel to the walls. In addition, we calculate the time correlation function of the end-to-end vector to estimate the terminal relaxation time of the polymer and to compare it with the time scale of the reaction.
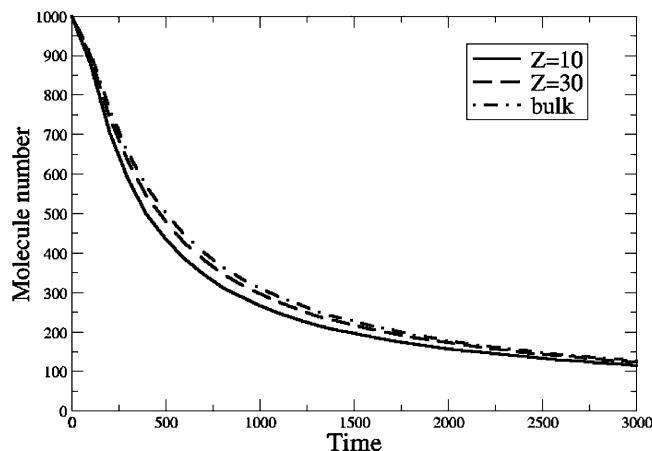
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Figure 1. Evolution of the number of molecules for a step-growth polymerization with respect to time (expressed in MC step number) for system A. The system has initially $n = 1000$ molecules.
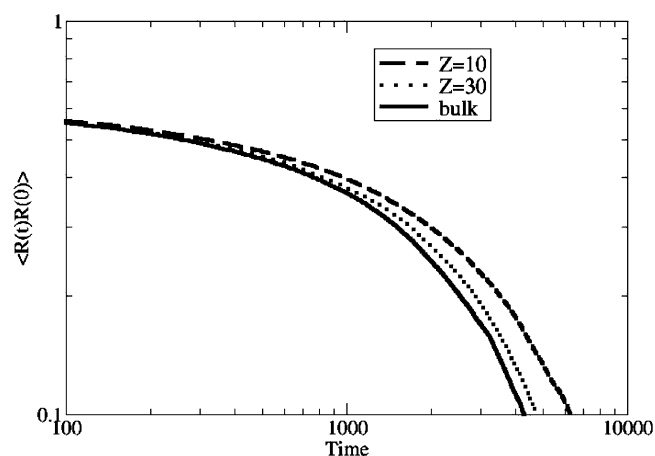

Figure 2. End-to-end vector time correlation function for system A with reaction switched off.

Figure 3. Mean square displacements in directions parallel to the walls (x,y) (in lattice units) as a function of time (in MC step number) for system A with reaction switched off: (a) mean square displacement of the center of mass; (b) mean square displacement of the chain ends.

In Figure 2, the relaxation time of the polymer is reported. The value of the relaxation time, for all systems, is situated between $4000 < \tau_R < 6000$, while the reaction has reached a polymerization degree of 0.9 at times of $t \approx 3000$. From this, we can conclude that the reaction proceeds in the short time scale and thus is governed principally by compact exploration. This conclusion is supported by the analysis of the center-of-mass mean square displacement in the direction parallel to the wall (x) (Figure 3a), which shows that at time scales comparable to the reaction time scale each molecule on average has traveled a distance of less than one radius of gyration (for the bulk system, the square radius of gyration is $R_g^2 = 13.08$).

From the analysis of the diffusion, as well as from the behavior of the autocorrelation function, it is clear that the overall dynamics of the system is slightly slowed by the confinement. This is true even for the chain end diffusion (Figure 3b), which we thought is worth studying because reactive units are nevertheless attached at chain ends; thus, the enhancement of reaction rate (which is controlled by compact exploration and thus by the diffusion of chain ends) under confinement cannot be explained by the diffusion behavior, which would lead to the opposite result.

An explanation for the acceleration of kinetics as the confinement gets more pronounced can be given from the analysis of the conformational properties. In the framework of the theory by de Gennes,[10] the kinetics of the process depends on the pair distribution function
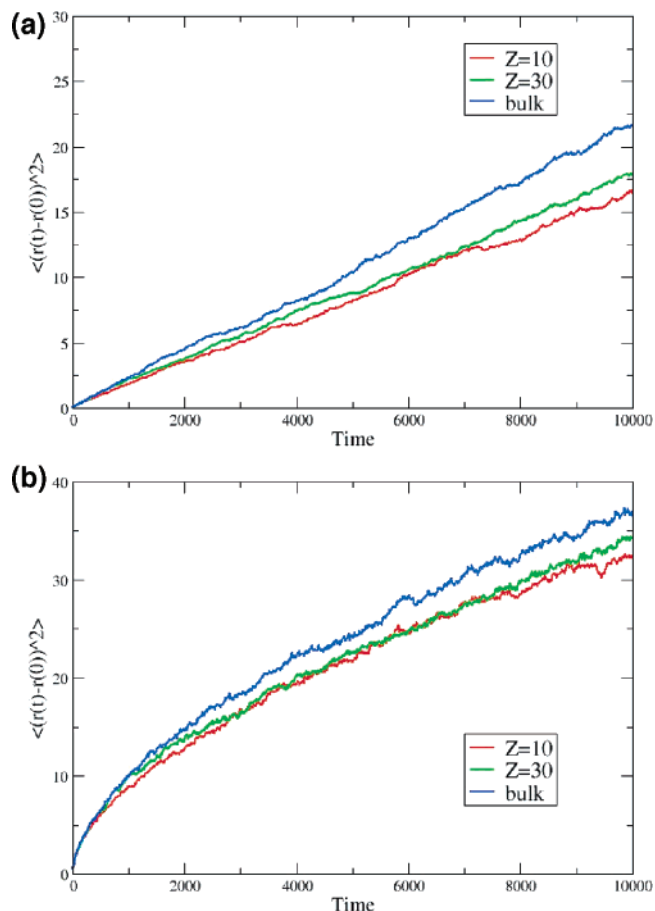
$$\psi(\mathbf{r}_1,\mathbf{r}_2) = \sum_{i,j}^{\text{ends}} \delta(\mathbf{r}_1 - \mathbf{r}_j)\, \delta(\mathbf{r}_2 - \mathbf{r}_i) \qquad (11)$$

through the following integral equation:

$$\psi(\mathbf{r}_1,\mathbf{r}_2) =$$
$$\psi(\mathbf{r}_1^0,\mathbf{r}_2^0) + \int_0^t dt' \int d\mathbf{r}_1^0\, d\mathbf{r}_2^0 \frac{d\psi(\mathbf{r}_1,\mathbf{r}_2)}{dt}\Gamma(\mathbf{r}_1^0,\mathbf{r}_2^0|\mathbf{r}_1,\mathbf{r}_2)\ (12)$$

where $\psi(\mathbf{r}_1^0,\mathbf{r}_2^0)$ is the pair distribution function at $t = 0$ and $\Gamma(\mathbf{r}_1^0,\mathbf{r}_2^0|\mathbf{r}_1,\mathbf{r}_2)$ is the probability of finding reacting sites 1 and 2 at the positions $(\mathbf{r}_1,\mathbf{r}_2)$ at time t, knowing that they were, respectively, in positions $(\mathbf{r}_1^0,\mathbf{r}_2^0)$ at zero time. This equation states that the reactants lacking at time t in location $(\mathbf{r}_1,\mathbf{r}_2)$ were destroyed by a reactive event at an earlier time, t', in positions $(\mathbf{r}_1^0,\mathbf{r}_2^0)$.

The reaction rate between polymer ends depends then on the probability that two reacting monomers (two chain ends) come together at a distance suitable for reaction to occur. Such a probability can be expressed in terms of the pair distribution function for end monomers by measuring or calculating the value

$$P_{\text{reac}} = \int d\mathbf{r}_1\, d\mathbf{r}_2\, \psi(\mathbf{r}_1,\mathbf{r}_2)\, \delta(|\mathbf{r}_1 - \mathbf{r}_2| - 2) \qquad (13)$$
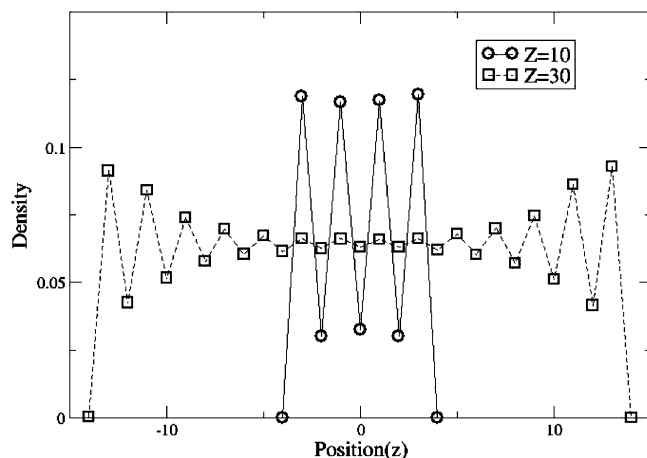
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Figure 4. Particle density profiles, ϕ, in the z direction for system A with reaction switched off, $Z = 10$ (circles) and $Z = 30$ (squares).

Figure 5. Reactive events per chain as a function of time for system A with reaction switched off: (a) intermolecular reactive events; (b) intramolecular reactive events.

where 2 is the minimum allowed distance. This probability is then simply the nonnormalized value of the pair distribution function, $\psi(\mathbf{r}_1,\mathbf{r}_2)$, for $|\mathbf{r}_1 - \mathbf{r}_2| = 2$.

The pair distribution function between two polymer ends is a function of the conformational properties of the polymer; such a quantity, as emerges clearly from eq 11, depends on the local behavior of density.

In strongly confined systems, the density is not homogeneous. In Figure 4, the density as a function of position along the z axis is reported. The density exhibits a damped oscillatory structure with a high monomer concentration at the wall; the amplitude of these oscillations becomes more pronounced as the distance between walls is reduced, and for sufficient distances between walls, the density value approaches the bulk one. As a consequence, we expect the pair distribution function (see eq 11) (and thus P_{reac}) to be affected by the modification of the density function. The reaction kinetics, according to eq 13, should be in turn modified by such a modification. (In the framework of the BF model, the qualitative and quantitative behavior of the overall pair distribution function in confined polymeric melts has already been found to depart from the bulk behavior in recent simulations.[26]) To test this expectation, the number of reactive collisions with the reaction option switched off (number of monomer chain end pairs positioned at a suitable distance) has been counted as a function of time and reported in Figure 5. In Figure 5a, the number of (effectively reactive) collisions between different chains is shown, while, in Figure 5b, the number of collisions between chain ends belonging to the same chain (eventually leading to cyclization, which is not allowed all through the work) is reported. Evidently, the confinement leads to an increase in the number of collisions: this increase is greater for the strongly confined system ($Z = 10$).

The acceleration of reaction rate under confinement for system A can then be explained in terms of the modification of the liquid structure of the polymer, leading to a different pair distribution function, $\psi(\mathbf{r}_1,\mathbf{r}_2)$, for reactive monomers. From eq 12, it is evident that a modification of $\psi(\mathbf{r}_1,\mathbf{r}_2)$ directly affects the reaction probability, P_{reac}, and thus the overall reaction rate. Even if such a modification is nontrivial, due to the oscillating nature of the density, the confinement is found to raise the value of $\psi(\mathbf{r}_1,\mathbf{r}_2)$ when $(\mathbf{r}_1 - \mathbf{r}_2) = 2$.

From the analysis of the collision numbers between chain ends attached to the same chain, we can see that the cyclization probability (in the initial stage) is more than 1 order of
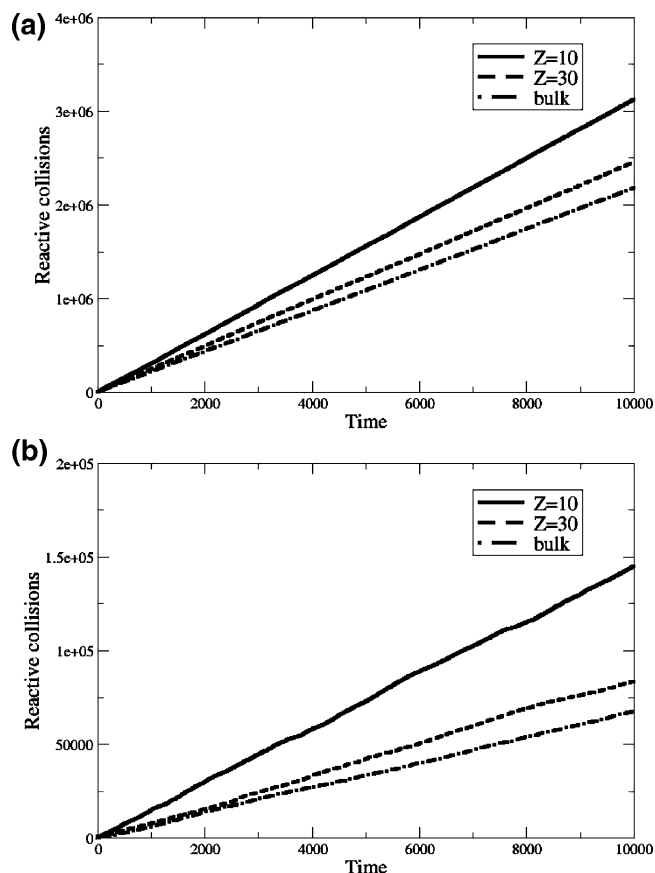
magnitude lower than the corresponding heterochain reaction, somewhat justifying our assumption to neglect the cyclization process in this study. It may be interesting to note, by simple inspection, that the ratio cyclization/heterochain reaction is higher in the strongly confined system than in the bulk system. This behavior can be induced, in principle, by a shorter end-to-end distance with respect to the bulk value in a strongly confined situation, or by a change in sampling possible conformations induced by the quasi two-dimensional system resulting in an increased frequency of collisions for both ends of the same chain. A detailed inspection of the bond length distribution function, reported in Figure 6, shows that the strong confinement enhances the contribution of the shorter bonds (1,2) and lowers the contribution of the longer ones. The chains appears thus to be shorter in the confined situation than in the bulk one, and then, a possible explanation of the augmented cyclization/heterochain reaction ratio in a strongly confined system may be principally given in terms of a reduced end-to-end distance.

For what was said above, in the interplay between diffusion and liquid structure in system A, the reaction rate up to the stage examined ($p = 0.9$) seems to be ruled mainly by the last factor.

The final calculated polydispersity index (PDI) values for system A are shown in Table 2. The polydispersity is in the range expected from a diffusion-controlled step-growth polymerization for Rouse chains,[12] in which the reaction rate is much greater than the diffusion-controlled formation of the activated complex. (For a reaction-controlled polymerization (in which every chain end has the same probability to react, no matter which molecular weight is the chain), the
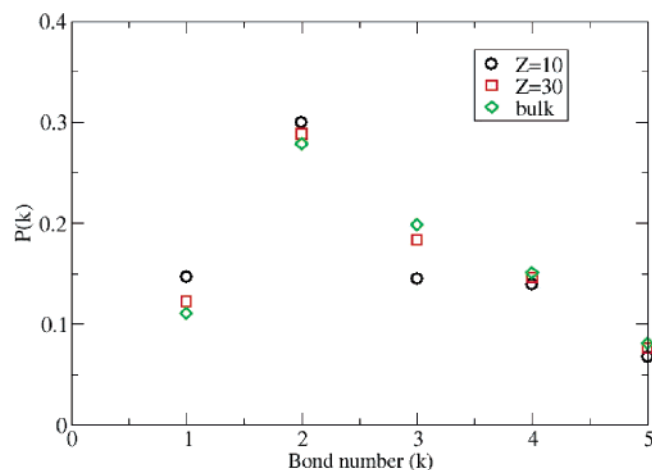
Figure 6. Normalized probability distribution of bond population (the bond lengths are 2, $\sqrt{5}$, $\sqrt{6}$, 3, $\sqrt{10}$, respectively) for system A.

TABLE 2: Polydispersity Index (PDI) for the Systems Studied at a Polymerization Degree of $p = 0.9$

	A	B
I	1.391	1.425
II	1.392	1.456
III	1.367	1.388

polydispersity is given by the Flory expression[24] $w = (1 + p)$, and thus, at this conversion level, the PDI would be expected to be equal to 1.8.)

Nevertheless, no significant differences are found in the polydispersity of the bulk system and of the confined ones: according to eq 8, this can be interpreted as a consequence of the fact that the simple confinement is not able to modify the relative reactivities of macromolecules of different molecular weights in this system. Of course, the PDI cannot fully characterize the molecular weight distribution (MWD) at the present polymerization degree: as will be shown later on, the whole MWD is nevertheless very slightly affected by the presence of confinement.

A rather different behavior, reported in Figure 7, is displayed by system B. Here, we can see that the presence of confinement enhances the reaction rate only for earlier reaction times; after a certain time, situated at about $t = 700$, the reaction rate slows down for the confined systems. The slowing down is more pronounced for the system with $Z = 10$. Here, we can presume
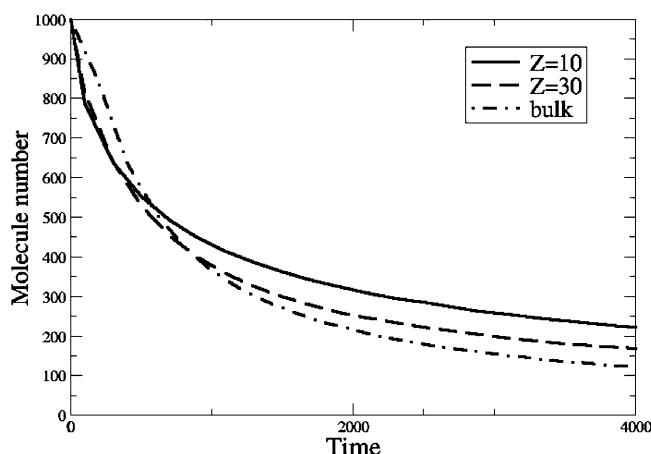

Figure 7. Evolution of the number of molecules for a step-growth polymerization with respect to time (expressed in MC step number) for system B. The system has initially $n = 1000$ molecules.
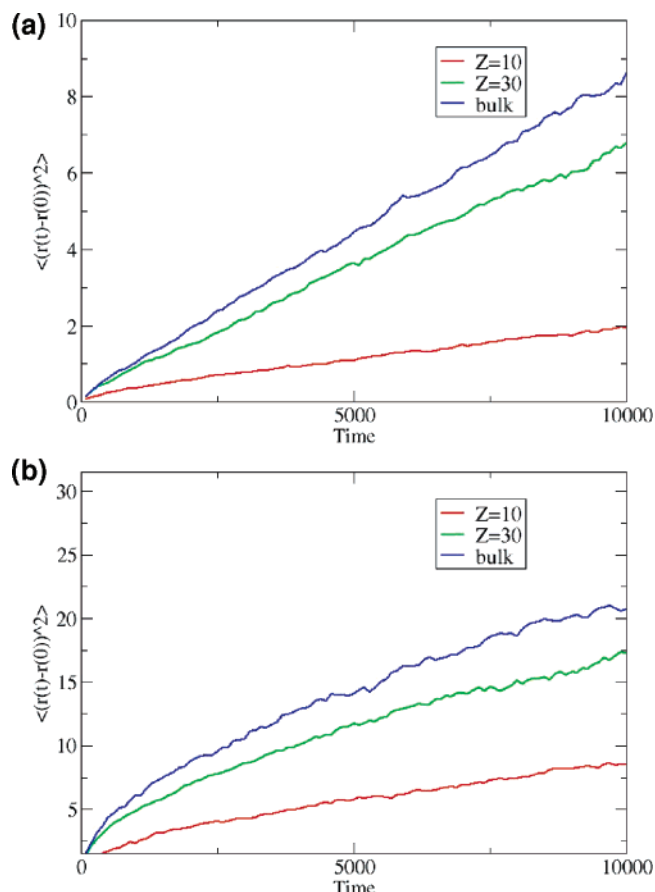

Figure 8. Mean square displacements in directions parallel to the walls (x,y) (in lattice units) as a function of time (in MC step number) for system B with reaction switched off: (a) mean square displacement of the center of mass; (b) mean square displacement of the chain ends.

that the effect of variation of the pair distribution function due to the confinement is present but rules the reaction kinetics only at shorter times; after the crossover time, the kinetics is ruled mainly by diffusion of reactive units.

This hypothesis can be confirmed from investigation of the initial system with $N = 10$, analogously with the previous system. In Figure 8, the mean square displacement is reported for the three cases in system B. In this system, the presence of confinement strongly hampers the chain motion, particularly in the case $Z = 10$; the difference in diffusivity is consistent not only for chain center of masses but for chain ends also.

The density distribution along the z direction (Figure 9), as expected, displays now larger oscillations with respect to system A, where attractive interactions were not considered. As a consequence, the modification of the pair distribution function is now more pronounced, as can be checked by inspection of Figure 10. Here, it is evident that both intermolecular and intramolecular reactive collisions are augmented by the presence of the wall, and that a stronger degree of confinement results in an enhancement of reactive collision probability.

Even if the two aspects, namely, the buildup of an adsorption-induced excess density at the walls and the attraction effects in the bulk of the system, cannot be separated neatly in our simulations, some considerations can be made from the direct comparison of the bulk systems with respect to the confined ones. It is interesting to note that, for intermolecular collisions, the switching on of the attractive interactions has practically no effects on the reactive collision probability, as can be checked
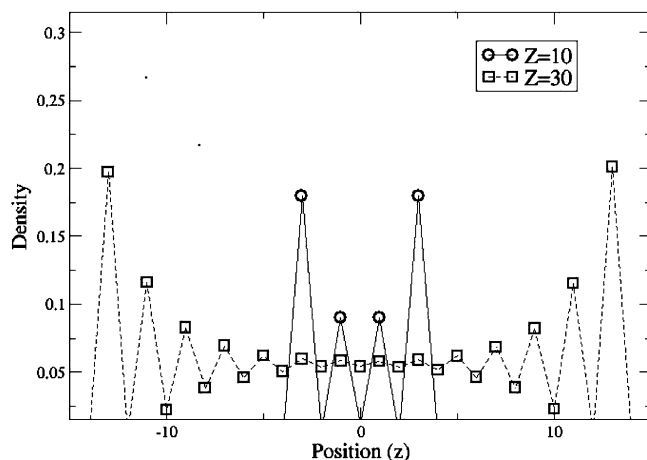
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Figure 9. Particle density profiles, ϕ, in the z direction for system B with reaction switched off, $Z = 10$ (circles) and $Z = 30$ (squares).
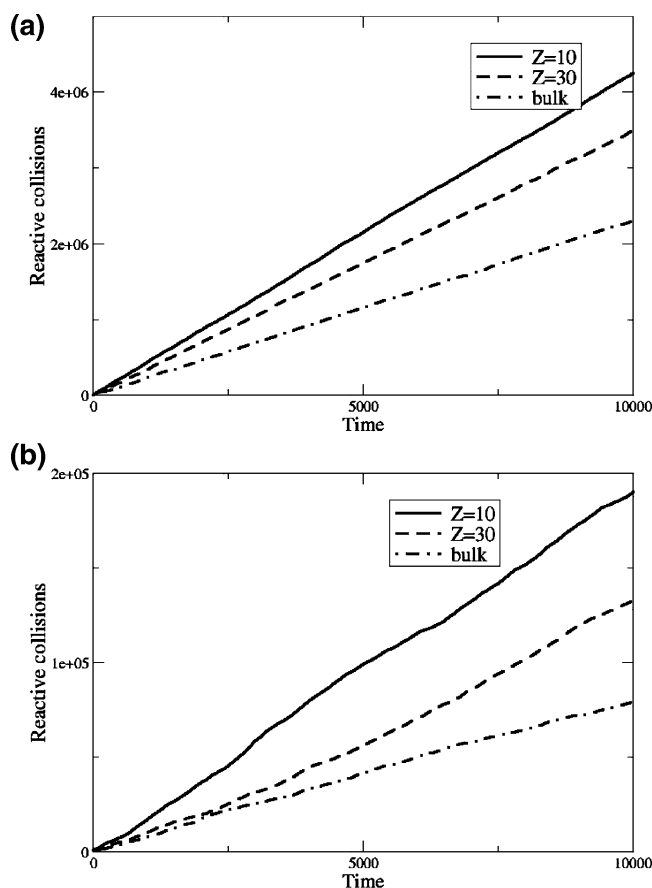

Figure 10. Reactive events per chain as a function of time for system B with reaction switched off: (a) intermolecular reactive events; (b) intramolecular reactive events.

Figure 11. Direct comparison of the evolution of the number of molecules for a step-growth polymerization with respect to time (expressed in MC step number) for system A and for system B: (a) $Z = 10$, case I (top); (b) bulk, case III (bottom). The system has initially $n = 1000$ molecules.

from comparison of Figures 5a and 10a. Conversely, the attractive interaction raises the collision probability for confined systems, with respect to confined systems where only excluded volume interactions are present (system A-I and A-II); thus, in confined systems with attractive interaction, the collision probability in the initial system is higher than that in the same systems with no attractive interactions. The reaction rate at the very beginning of polymerization should then be higher for system B with respect to system A in the confined situation. This is what actually can be observed from Figure 11a, where the kinetics for the strongly confined ($Z = 10$) cases are
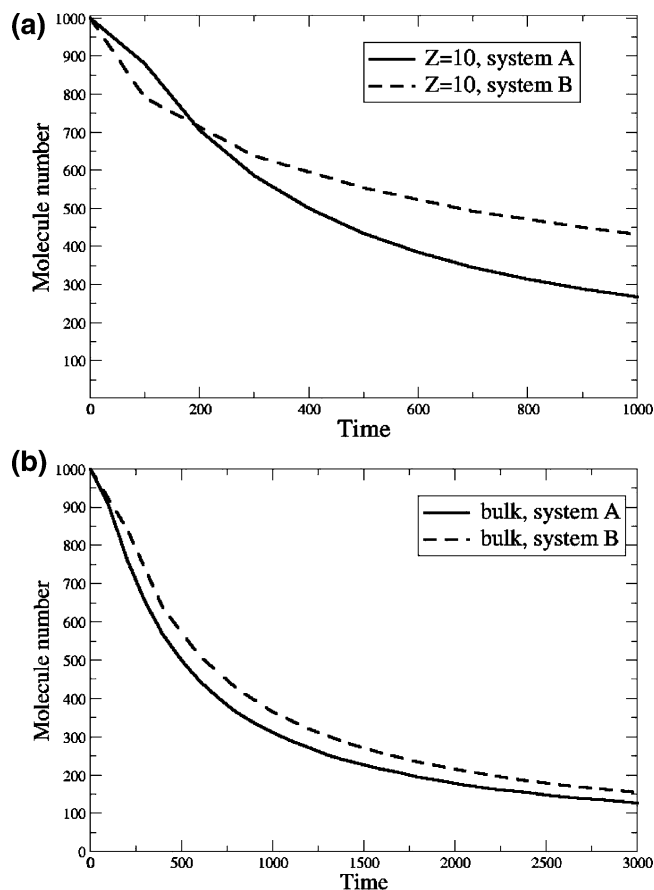
compared for system A and system B. Nevertheless, at long reaction times, diffusion of chain ends begins to rule the kinetics and the overall reaction rate of the system is lowered with respect to system A. On the other hand, on the basis of our interpretation, one would expect that a simple switching on of attractive interactions between monomers without considering the excess density at the walls (as happens in the bulk case) should result simply in a deceleration of the reaction rate due to the lower diffusivity of the system with attractive interactions. This expected behavior indeed reflects the actual one, reported in Figure 11b, in agreement with our previous interpretation.

A final remark concerns the PDI for system B, which is reported in Table 2; here, the most interesting thing to note is the nonmonotonic behavior of the polydispersity index as a function of slab thickness. It is anyway true that the confined polymerization leads to a MWD broader than the corresponding bulk polymerization. It must be noted, however, that the differences in polydispersity are not quite relevant. This could be appreciated better from Figure 12, where the MWDs for all of the systems studied are reported and compared and where the differences in the whole MWD appear to be negligible. This aspect seems to indicate that the effect of confinement, with these starting systems and at these extents of polymerization, is to reduce the differences between the reaction probability of a pair of macromolecules of different molecular weights. The poor importance of diffusion of the whole macromolecule in this study makes perhaps this effect difficult to be appreciated.
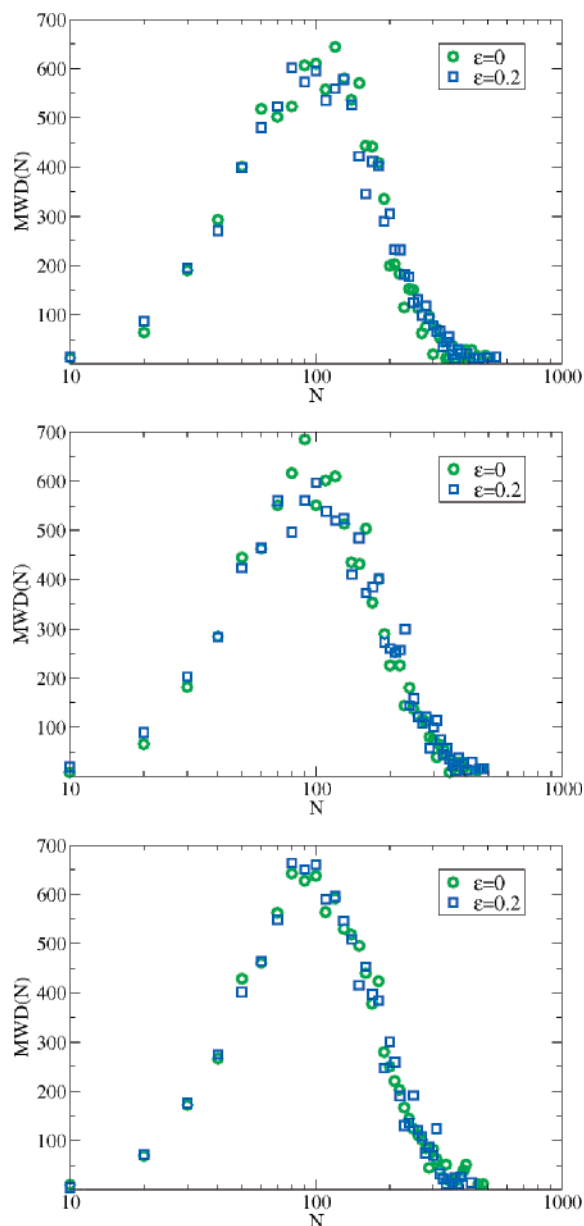
Figure 12. Molecular weight distribution (MWD) for system A ($\epsilon = 0$) and system B ($\epsilon = 0.2$) for $Z = 10$ (top), $Z = 30$ (middle), and bulk system (bottom).

Conclusions

In conclusion, we performed lattice MC simulation to study the diffusion-controlled stepwise linear polymerization kinetics in confined situations. The confinement is found to affect the reaction rate principally through two mechanisms: the modification of the pair distribution function between reactive units, which in these systems is able to accelerate the reaction rate, and the slowing down of diffusive motion for polymer chains, which on the contrary leads to a reduction of reaction rate. The relative importance of these two aspects is dependent on the nature of the system, and the overall reaction rate can result in being either enhanced or reduced depending on the interactions between chain units among themselves and with the wall constituents. A crossover time (or polymerization degree) can exist, separating the polymerization process into two subsequent intervals, the first ruled by the distribution of reactive units and the second by the diffusion of the same units.

The molecular weight distribution of the system, which agrees with the hypothesis of a diffusion-controlled reaction, is only slightly affected by the confinement at this stage.

In the future, we plan to investigate the role of the thermal kinetic constant, k_a, on the polymerization behavior and to perform analogous simulations on the more interesting case of 2-D confinement in narrow channels which can be useful to study polymerization kinetics in mesoporous materials.

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