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Brownian Dynamics Simulation Studies on Radical Capture in Emulsion Polymerization

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Summary: A computer simulation method based on the solution of the equations of Brownian motion is used to study the process of radical capture in emulsion polymerization. The effect of the size of the radical was studied, showing that as the radical grows its mobility is reduced (its diffusion coefficient decreases), and this leads to lower collision rates. The distance between the radicals and the surface of the particles at the moment of radical generation was found to be a very important factor in radical capture, with an increase of several orders of magnitude in the collision rate as the radical is generated closer to the particle surface. The effect of process temperature and interfacial barriers to radical capture on the collision rate and on the collision efficiency, defined as the ratio of successful radical captures to the total number of radical-particle collisions, is also analyzed. In the presence of an energy barrier, multiple collisions are observed, having an important effect on capture kinetics. The results obtained evidence the complexity involved in emulsion polymerization and demonstrates the capability of Brownian Dynamics simulation as a powerful tool for the study and understanding of such complex systems.

Keywords: brownian dynamics simulation; colloids; diffusion; emulsion polymerization; monte carlo simulation

Introduction

Emulsion polymerization is a widely used technique for the synthesis of high molecular weight, low viscosity, environmentally friendly polymer-based materials with applications ranging from coatings and adhesives to biomedical applications.[1,2]

Two very important processes involved in emulsion polymerization are particle nucleation and particle growth. Their balance during an emulsion polymerization determines the particle size distribution and the particle morphology of the polymer latex, and therefore, most of the physical properties of interest for its intended application. Furthermore, the balance between nucleation and growth is determined by the interplay of simultaneous (and some times competitive) physical, chemical and colloidal events such as initiation, propagation, chain transfer and termination reactions in the aqueous and polymer phases, transfer of radicals, monomer and polymers between the particles and the aqueous phase, and particle aggregation and coalescence. Thus, the control of the kinetics of these events allows the synthesis of polymer particles with the desired characteristics. An illustrative example of this competition is the synthesis of structured composite polymer particles. Structured polymer particles are industrially important because of their improved (synergistic) performance in applications such as film forming materials, impact modifiers and medical diagnosis.[3–6] Structured polymer particles are usually prepared by seeded emulsion polymerization techniques,[7,8] and as can be seen in the example presented in Figure 1, their

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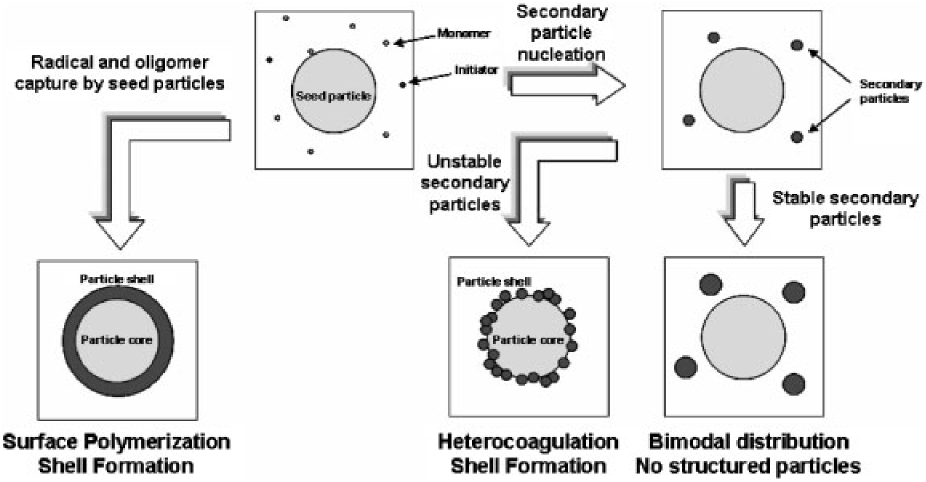

Figure 1.
Example of possible outcomes in seeded emulsion polymerization. A more complete description of possible particle morphologies can be found elsewhere.[4]

final morphology and particle size distribution strongly depend, among many other important factors,[4] on the competition between the capture of radicals, oligomers and oligomeric aggregates by seed particles, and secondary particle nucleation. It also becomes clear that the successful synthesis of structured polymer particles (no bimodal particle size distribution) may be achieved by: 1) the suppression of secondary nucleation (increasing the ratio of the capture rate of radicals and oligomers to the rate of secondary nucleation) or 2) the promotion of secondary particles coagulation on the surface of seed particles (increasing the ratio of secondary particle coagulation rate to secondary particle growth rate). In this paper, the focus will be placed only on the study of the rate of capture of primary and oligomeric radicals by seed particles in emulsion polymerization.

Recently, the capture of primary radicals by polymer particles in emulsion polymerization was studied by means of the simulation of Brownian motion (Brownian Dynamics simulation).[9] The rates of radical capture obtained from the Brownian Dynamics simulations of dilute dispersions (volume fractions below 0.1%) in the absence of interaction potentials and in the absence of energy barriers for radical capture, were in very good agreement with the values predicted using the analytical solution derived by Smoluchowski[10] (Equation 1). On the other hand, a significant effect of volume fraction on radical capture rates was observed in systems above 0.1% volume fraction, where most polymer dispersions with any practical interest are found. As a result, a corrected expression of the capture rate coefficient for diluted as well as concentrated dispersions was developed (Equation 2), which is in good agreement with experimental data under very different conditions.[9]

$$k_c = 2\pi N_A D_r d_p \tag{1}$$

$$k_c = 2\pi N_A D_r d_p (1 + \upsilon\phi_p) \tag{2}$$

In these equations, k_c is the radical capture rate coefficient in $m^3/mol \cdot s$, N_A is Avogadro's number, D_r is the diffusion coefficient of the radical in water in m^2/s, d_p is the diameter of the polymer particle in m, ϕ_p is the volume fraction of particles in the dispersion and υ is a geometric constant with a value of 17.95 for the system considered.

One main advantage of Brownian Dynamics simulation is that the capture rate coefficients can be easily determined based on the well-established mechanistic equations of Brownian motion,[11–13] while these rate coefficients are very difficult to measure experimentally in a reliable way especially without the interference of competitive events such as radical desorption, propagation, termination and additional radical reactions. In the present work, the Brownian Dynamics simulation method is used to study additional factors influencing the rates of radical and oligomer capture in emulsion polymerization.

Model and Simulation

Brownian Dynamics (BD) simulation is a computer simulation method based on the numerical solution of Langevin's equation for Brownian motion:[11,12]

$$\begin{aligned} m\frac{d^2x}{dt^2} &= -6\pi\eta a\frac{dx}{dt} + X \\ &= -\frac{kT}{D}\frac{dx}{dt} + X \end{aligned} \qquad (3)$$

where m is the mass of the Brownian entity (particle or molecule), a is its hydrodynamic radius, x is its position at a given time t, η is the viscosity of the continuous phase, X is a random fluctuating force which is the result of the collisions of the Brownian entity with the surrounding molecules of the continuous phase, T is the absolute temperature of the system, k is Boltzmann's constant and D is the diffusion coefficient of the Brownian entity. For spherical particles, the diffusion coefficient can be related to the size of the molecule or particle, the temperature of the system and the viscosity of the continuous medium by means of the Stokes-Einstein equation:[13]

$$D = \frac{kT}{6\pi\eta a} \qquad (4)$$

There are several techniques for the numerical solution of Langevin's equation.[12] In the present work, a Monte Carlo random flight method with a variable time-step[9,14] is used for the simulation of 3-dimensional trajectories of primary and oligomer radicals in water. The simulation is restricted to a cubic simulation cell containing only one polymer particle. However, periodic boundary conditions are applied to take into account the effect of neighbor particles. The graphical representation of the simulation cell for a given set of simulation conditions is presented in Figure 2, where N is the particle number concentration and d_r is the radical molecule diameter.

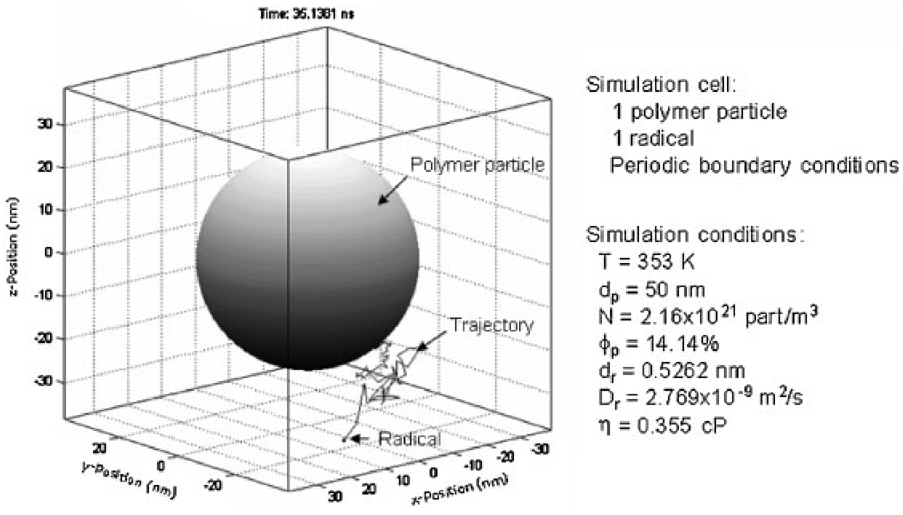

Figure 2.
Simulation cell and simulation conditions.

During the simulation, the capture time τ, defined as the time elapsed between the radical generation and its capture by the particle, is determined for each radical generated in the simulation cell. Then, the capture rate coefficient and the rate of capture are calculated using Equation 5 and 6, respectively:[9]

$$k_c = \frac{N_A}{N\langle\tau\rangle} \tag{5}$$

$$r_c = k_c[R^\bullet]\frac{N}{N_A} = \frac{[R^\bullet]}{\langle\tau\rangle} \tag{6}$$

where r_c is the rate of radical capture in mol/m^{3}s, N is the number concentration of particles in the dispersion in particles/m^3, $\langle\tau\rangle$ is the average capture time in seconds, and $[R^\bullet]$ is the molar concentration of radical species in the dispersion in mol/m^3.

The basic assumptions considered during the simulation of radical capture using Brownian Dynamics are summarized as follows:

- The polymer particles are monodisperse and arranged in a simple cubic structure. These conditions are given by the definition of the simulation cell containing only one polymer particle. If a larger simulation cell is defined containing many polymer particles, then it is possible to use BD simulation to investigate polydisperse systems. However, only the simulation of a monodisperse system allows the discrimination of the effect of particle size on radical capture kinetics.
- No interaction forces involving polymer particles, radicals and water molecules are present in the system. In principle, this model is best suited for dispersions of hydrophilic particles since in this case the interaction forces can safely be neglected. This assumption facilitates the comparison of the simulation results with the established model described by Smoluchowski equation. It is possible to consider interaction forces during BD simulations either by incorporating additional forces in Langevin's Equation (eq. 3), or by considering energy barriers for capture as described in a next section.
- The capture process is irreversible and is the only event considered during the simulation. This assumption is very important because it allows the determination of *actual* capture rate coefficients and not *net* or *apparent* capture rate coefficients which are the case when additional competitive events such as radical desorption, propagation or termination are present.
- Unless an energy barrier for capture is present, the absorption of radicals by polymer particles is determined by the collision between a radical and a particle.
- Radicals are assumed spherical and the diffusion of radicals in water is assumed to follow the Stokes-Einstein Equation (eq. 4).
- The temperature and the volume of the system remain constant during each simulation run.

Using the simulation method described in this section, it is possible to analyze the effect of different variables on radical capture kinetics. Simulation results for some variables of interest in emulsion polymerization are presented in the following section. These variables are: 1) the size of the growing oligomer radicals, 2) the distance between the radical and its closest particle at the moment of radical generation, 3) the system temperature, and 4) the magnitude of an energy barrier for radical capture.

Results and Discussion

During the course of an emulsion polymerization, radicals generated in the aqueous phase may react with dissolved monomer molecules to form oligomeric radicals which increase their size after each monomer addition. A larger size implies a higher collision probability (increased surface area) but also a lower diffusion coefficient (Equation 4), and therefore, the rate of radicals capture will be influenced by these opposing effects. BD simulations were run under the conditions presented in Figure 2, varying only the size of the radicals in the range 0.24 to 1.58 nm. Calculated capture rate coefficients plotted against radical size are presented in Figure 3.

A good fit to the simulation data is obtained using Equation 7, which is derived after combining the corrected Smoluchowski Equation (eq. 2) with the Stokes-Einstein Equation (eq. 4):

$$k_c = \frac{2}{3}\frac{RT}{\eta}\frac{d_p}{d_r}(1+\upsilon\phi_p) = \frac{k*}{d_r} \tag{7}$$

where R is the universal gas constant and k^* is a function of temperature, particle size, particle volume fraction and viscosity of the medium. Although the surface area of the radical is expected to influence the value of the geometric constant υ, its effect is negligible as it is evidenced by the very good agreement between the value of k^* calculated under the simulation conditions presented in Figure 2 ($9.750 \times 10^8\,\mathrm{m}^3 \cdot \mathrm{nm/mol} \cdot \mathrm{s}$) and the value fitted from the BD simulation results ($9.986 \times 10^8\ \mathrm{m}^3 \cdot \mathrm{nm/mol} \cdot \mathrm{s}$). These results indicate that the influence of radical mobility on radical capture is stronger than that of radical surface area.

Another important factor involved in radical capture is the distance between the radical and its closest particle at the moment of its birth or generation. Intuitively, it is easy to imagine that if the radical is generated closer to a particle, the probability of collision will increase and the time required for capture will be reduced. Using the same system conditions as before, primary radicals of the same size were generated at different distances to the surface of the polymer particles (in the range 0.03–3.06 nm) and the capture rate kinetics were determined by BD simulation. Results are presented in Figure 4.

In Figure 4, the corresponding values of the capture rate coefficient obtained by BD simulation of radicals uniformly distributed in the aqueous phase (equivalent to Equation 2) and that predicted by the uncorrected Smoluchowski Equation (eq. 1) are also presented for comparison. A significant increase of several orders of magnitude in the capture rate coefficient is evidenced when the generation of the radical takes place closer to the particle surface. The behavior of the capture rate coefficient is very well represented by Equation 8.

$$k_c = \frac{6D_r' N_A}{N(r+r')^2} \tag{8}$$

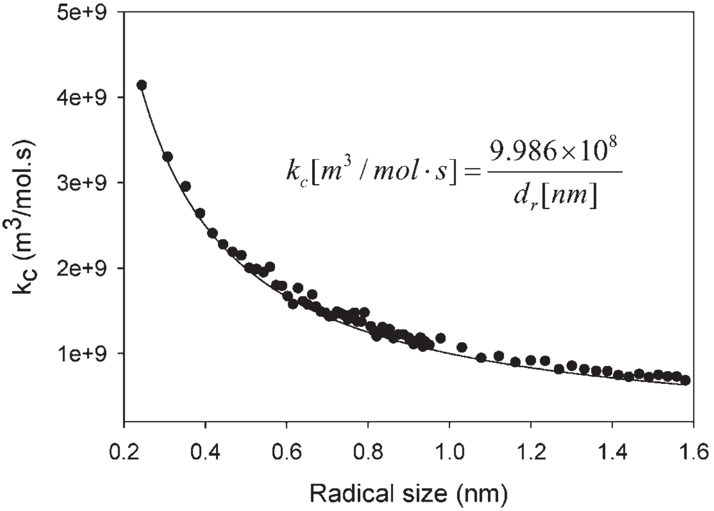

Figure 3.
Effect of radical size on capture kinetics; ● = computer experiments; — = best fit to Equation 7.

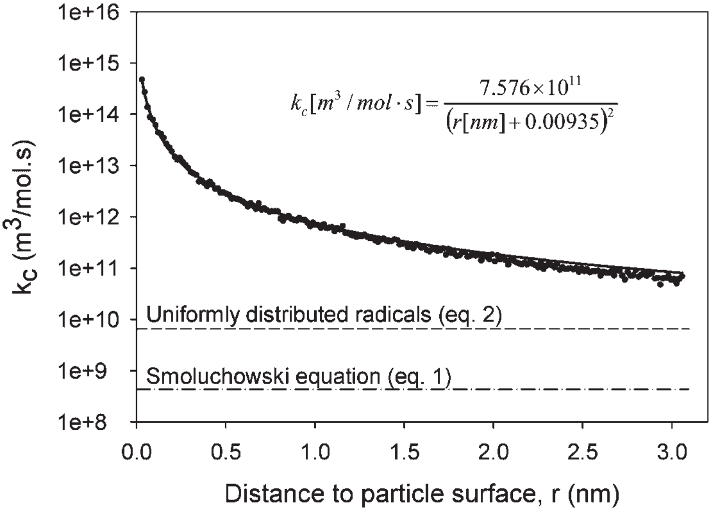

Figure 4.
Effect of the initial position of the radical on capture kinetics; ● = computer experiments; — = best fit to Equation 8; -·- = Equation 1; --- = Equation 2.

r is the distance between the radical and the particle, r' is an effective minimum separation distance and D'_r is an effective diffusion coefficient resulting from the geometry of the radical-particle collision as illustrated in Figure 5. The values of r' and D'_r obtained after fitting the simulation data were 0.00935 nm and 4.529×10^{-10} m^2/s, respectively. Although the magnitude of D'_r would probably be a function of the distance r and the particle diameter d_p, this effect was not taken into account because only very small separation distances (<3 nm) and constant particle diameter were considered.

It is clear that the distance to the particle surface at which a radical is generated is a critical factor determining the capture rate of the radical. Therefore, the generation of radicals close to the particle surface, either by a radical generating redox interfacial system[15,16] or by using surface active

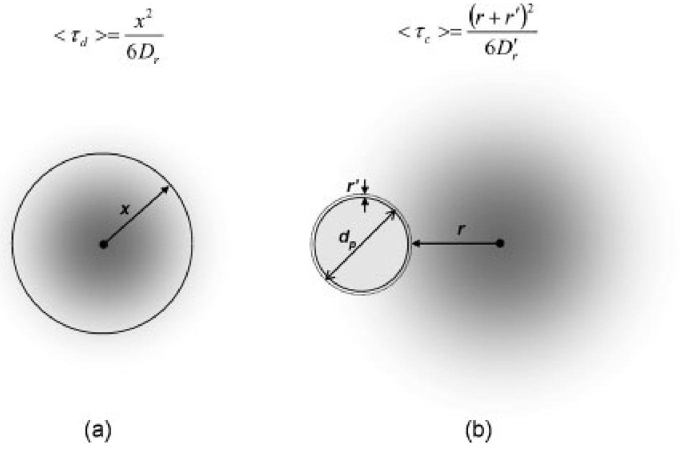

Figure 5.
Geometry of radical diffusion: a) average time $\langle\tau_d\rangle$ required by the radical to diffuse a distance x. b) average time $\langle\tau_c\rangle$ required by the radical to diffuse and hit a particle at a distance r.

initiators (inisurfs),[17,18] will result in increasing radical capture rates and reducing the tendency to form secondary particles.

Up to this point, every radical-particle collision was considered as a successful radical capture. However, interaction forces, interfacial tensions, the presence of stabilizer molecules at the surface of the polymer particles and many other physical and chemical effects may lead to an increase in free energy during radical capture, and thus, to the existence of an energy barrier for radical capture. In these cases, only a fraction of the radicals colliding with the particles will be effectively captured (capture efficiency) and the other will just bounce. Another important conclusion that can be drawn from the results presented in Figure 4, is that when a radical is not captured by a particle because of the energy barrier, the radical will have a very high probability of hitting the same particle again, leading to a series of multiple collisions in a very short time before the radical goes away from the particle surface. BD simulations were performed for the same system, but this time varying the system temperature between 278 and 353 K, and the magnitude of the energy barrier between 0 and 50 kJ/mol. The effect of temperature on the capture rate coefficient is presented in Figure 6, the effect of the magnitude of the energy barrier on the capture efficiency is presented in Figure 7, and the effect of the energy barrier at different temperatures on the capture rate coefficient is presented in Figure 8.

According to the Stokes-Einstein Equation (eq. 4), the system temperature affects the diffusion coefficient directly by the term kT, but also indirectly by the viscosity of the medium. The influence of temperature on viscosity for liquids is usually expressed in the form:[19]

$$\eta = Ae^{B/T} \tag{9}$$

where for pure water, $A = 6.404 \times 10^{-3}$ cP and $B = 1418$ K.

If we replace Equation 9 in Equation 2, we obtain the capture rate coefficient as a function of the system temperature:

$$k_c = \frac{2}{3}\frac{d_p}{d_r}\frac{RT}{A}(1 + \upsilon\phi_p)e^{-B/T} \tag{10}$$

For the system conditions used in the BD simulations, Equation 10 becomes:

$$k_c = 2.910 \times 10^8 Te^{-1418/T} \tag{11}$$

with T in K, and k_c in m^3/mol · s. There is a good agreement between the calculated values presented in Equation 11 and the

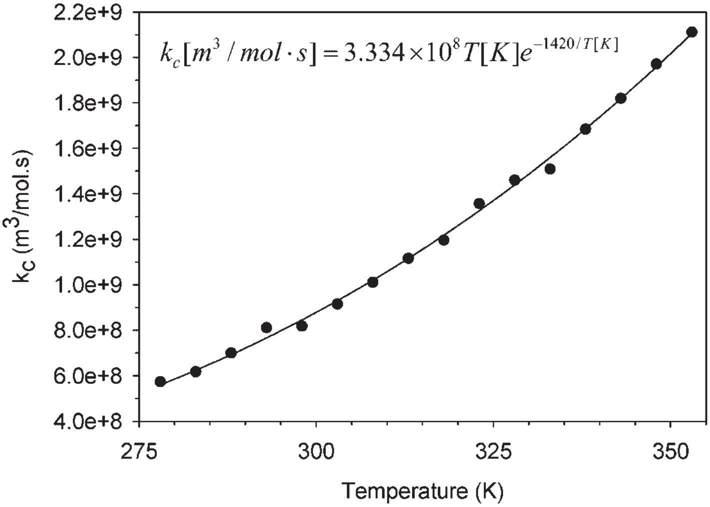

Figure 6.
Effect of temperature on capture kinetics; ● = computer experiments; — = best fit to Equation 10.

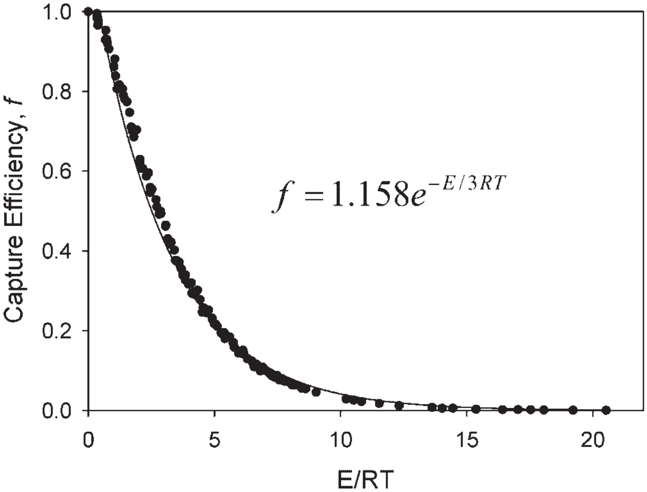

Figure 7.
Effect of energy barrier on capture efficiency; ● = computer experiments; — = best fit to exponential decay.

values obtained after fitting the results from BD simulation presented in Figure 6. It is observed that the radical capture rate increases with temperature in a very similar way as chemical reaction rates do.[20]

Since radicals can react in the aqueous phase, there is a competition between radical reactions and radical capture by particles. In emulsion polymerization, the competition between the aqueous phase propagation reaction and radical capture determines whether new particles are generated or existing particles grow, because a radical propagating in the aqueous phase will eventually either reach a critical size and precipitate[21] or reach a critical supersaturation condition and then nucleation will take place.[22] The ratio between the

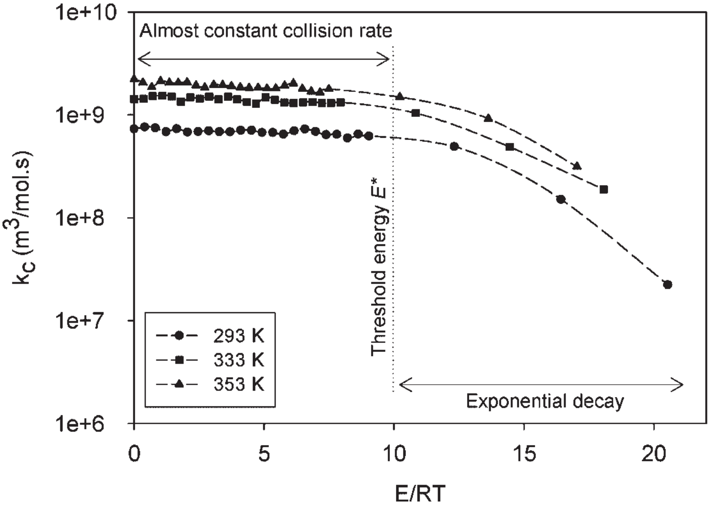

Figure 8.
Effect of temperature and energy barrier on capture kinetics; -●- = computer experiments at 293 K; -■- = at 333 K; -▲- = at 353 K.

corresponding activation energies finally determines which event will be most favored by an increase in the system temperature.

As mentioned before, the radical capture efficiency defined as the fraction of collisions leading to radical capture with respect to the total number of radical-particle collisions depends strongly on the energy barrier that a radical must overcome to get inside a polymer particle. Only if the energy of the collision, calculated as the sum of the kinetic energies of the radical and the particle, is higher than the energy barrier for radical capture, the collision leads to a successful capture. Therefore, the capture efficiency is expected to behave accordingly to a Boltzmann distribution, that is, to show an exponential decay with respect to E/RT, where E is the magnitude of the energy barrier for radical capture.

BD simulation results varying the magnitude of the energy barrier (Figure 7 and 8) clearly evidence that the capture efficiency f decays exponentially with E/RT, while the radical capture coefficient remains almost constant until certain ''apparent'' threshold energy (E^*) is reached, and then it shows the expected exponential decay. As stated before, this behavior is explained by the very high probability of a repeated collision after any radical-particle collision not leading to successful capture. The magnitude of the apparent threshold energy observed under the conditions of the simulation is approximately 10 RT, corresponding to a capture efficiency of about 0.04. This means that a radical hits the same particle on average 25 times before going away unless radical capture occurs. The effect of an energy barrier on the capture rate coefficient can be expressed as:

$$k_c = \begin{cases} k_{c0}, & E < E* \\ k_{c0} e^{-\frac{(E-E*)}{3RT}}, & E \geq E* \end{cases} \qquad (12)$$

where k_{c0}, the capture rate coefficient in the absence of energy barriers, is given by (from Equation 10):

$$k_{c0} = \frac{2}{3} \frac{d_p}{d_r} \frac{RT}{A} (1 + \upsilon \phi_p) e^{-B/T} \qquad (13)$$

and E^* is the magnitude of the apparent threshold energy, which is expected to be a function of the radical and particle diameters. It is also possible to identify the functional dependence of E^* on d_p and d_r by means of BD simulation, but this is out of the scope of the present contribution.

Conclusion

The formation of secondary polymer particles in emulsion polymerization depends on many factors affecting the rates of radical capture and radical propagation in the aqueous phase. If the accumulation of propagating radicals in the continuous phase cannot be avoided, secondary nucleation can be negligible only if the rate of radical capture is much higher than the rate of oligomeric radical accumulation in the aqueous phase. The radical capture rate can be increased by increasing the volume fraction of seed particles (smaller size and higher concentration of seed particles), by generating smaller primary radicals close to the particle surface and by reducing the energy barriers to radical capture. For energy barriers smaller than the activation energy for aqueous phase propagation, lower process temperatures will reduce the probability of formation of secondary particles. These results clearly demonstrate the capability of Brownian Dynamics simulation models for studying and understanding complex processes in colloid and polymer science, such as the capture of radical molecules by polymer particles in emulsion polymerization, especially when reliable experimental techniques are not readily available. The competition between radical capture by polymer particles, radical desorption from polymer particles, and radical termination and propagation reactions in the aqueous phase and inside the polymer particles can be further studied using multiscale modeling combining the Brownian Dynamics simulation method presented in this paper, with complementary simulation techniques such as lattice-Boltzmann or kinetic Monte Carlo stochastic simulation.

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