Multiscale stochastic simulation of emulsion polymerization

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Abstract

Heterophase polymerization is a highly complex dynamic process in which several simultaneous and usually competitive chemical (radical generation, propagation, termination, chain transfer) and physical events (diffusion, absorption, desorption, nucleation, coagulation) occur at very different time scales and dimensions. These events take place in a typical free-radical emulsion polymerization at rates ranging from about 10^0 to 10^9 s^{-1} and involving entities of very different length scales, such as ions and molecules (< 1 nm), macromolecules (1 – 10 nm), polymer particles (10 nm – 1 μm) and monomer droplets (>1 μm). A precise quantitative model of the kinetics of emulsion polymerization requires the detailed knowledge of the kinetics of all these physical and chemical processes.

In the present work, different events are investigated at different time and length scales using suitable simulation methods such as Molecular Dynamics (MD) simulation,[1,2] Brownian Dynamics (BD) simulation[3] and kinetic Monte Carlo (kMC) simulation.[4] The use of simulation techniques with spatial resolution such as MD and BD is advantageous when dealing with systems of increased geometrical complexity. This is the case of non-spherical polymer particles, structured polymer particles (e.g. core-shell, multilayered, etc.), non-uniform polymer particles (e.g. gradient in radial monomer composition), polydisperse particles and many others.

Molecular Dynamics simulation is used to estimate the diffusion coefficients of a given molecular species under very specific conditions. These diffusion coefficients are then used by the Brownian Dynamics simulation method to describe the molecular motion at a much larger time and length scale. The BD simulation of radicals in emulsion polymerization is used to determine the rate of radical capture by polymer particles,[5,6] as well as the rate of radical desorption from the particles to the continuous phase.[7] Similarly, the BD method can be used to simulate the absorption and desorption of monomer molecules by polymer particles, and therefore, to obtain a description of the monomer swelling dynamics.[8] The simulation of polymerization reactions under diffusion control, which usually takes place inside the polymer particles at low monomer volume fraction, is performed using a new modified version[9] of the stochastic simulation algorithm developed by Gillespie.[4] Finally, the integration of all these multi-scale processes into one single simulation is performed using a kinetic Monte Carlo (kMC) algorithm.

Introduction

The basic definition of heterogeneous polymerization is the presence of more than one phase at some moment during the polymerization process. In a typical emulsion polymerization the following phases may be found: an aqueous phase (continuous phase) which may contain dissolved ions and molecules, a monomer phase segregated as droplets in a wide range of sizes, micelles or surfactant aggregates, polymer particles and eventually, polymer clusters inside the particles. The size of each segregated phase in a typical emulsion polymerization may vary from a few angstroms (molecular aggregates) to some millimeters (macroscopic monomer drops). All these separate phases are clusters or

aggregates of molecules, and all of them are correspondingly subjected to the processes of diffusion, aggregation (including absorption) and dissociation (including desorption), in addition to the corresponding polymerization reactions. This is graphically presented in Figure 1.

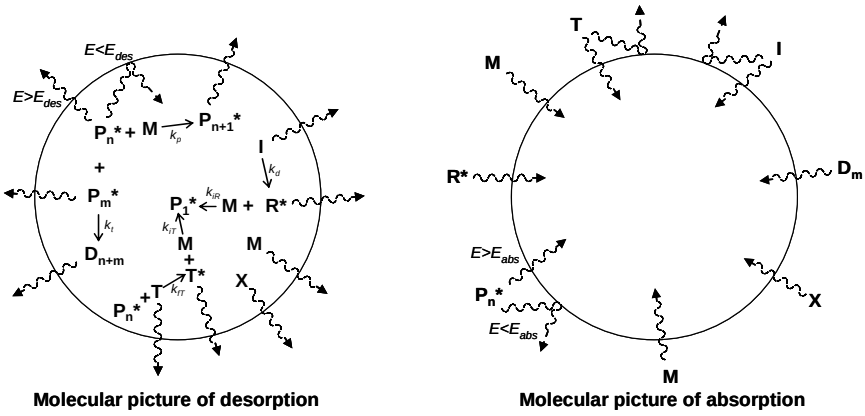

Figure **1** Molecular picture of the processes of reaction, desorption and absorption of molecules for a segregated phase. The transfer of any molecule through the interface is possible only if the energy (E) of the molecule is higher than the barrier for transfer (E_{des} for desorption, E_{abs} for absorption). M: Monomer, I: Initiator, R*: Primary radical, T: Chain transfer agent, T*: Transfer-derived radical, P_n*: Polymer radical, D_m: Dead polymer, X: Any other molecule.

The main factors determining the diffusion, dissociation and aggregation of clusters and individual molecules are the magnitude and direction of intermolecular forces acting between neighboring molecules. Because of this, it would be possible to get a comprehensive picture of heterophase polymerization using molecular dynamics simulation; however, the computational requirement for performing such a simulation for reasonable time and length-scales is extremely high and at present, it is practically impossible. Much larger time and length scales can be reached using Brownian Dynamics for many different processes taking place in emulsion polymerization. However, these methods are not enough to simulate processes at an industrial scale. For these purposes, stochastic kinetic Monte Carlo or deterministic numerical integration of differential equations can be used. Although deterministic methods offer fast estimations of average values, stochastic methods can handle the variability of the process.

In general, polymeric systems are difficult to simulate because of the wide spectrum of time and length scales characterizing their dynamics and structure.[10] If the scale of the simulation is increased in order to observe slower dynamics, the fast dynamics at lower scales must be either neglected or approximated. Depending on the type of approximation and its accuracy, the results obtained in the simulation can or cannot represent the real process. In this sense, a suitable multi-scale simulation algorithm capable of simultaneously considering all relevant dynamics would be desirable.

Multiscale simulation

In order to obtain a more complete picture of emulsion polymerization, the most relevant physical and chemical processes were investigated using different modeling strategies at their corresponding scales. These processes include: diffusion, chemical

reaction under diffusion control, particle formation, radical capture, radical absorption, monomer swelling and particle aggregation.

Molecular diffusion was investigated using Molecular Dynamics simulation, considering Buckingham-type interatomic pair interaction potentials.[11] MD simulation is a numerical method used to solve Newton's classical equations of motion at the molecular level. Considering an initial configuration of a representative ensemble of molecules, and assuming a particular description of the interaction energy between different molecules it is possible to determine the positions and velocities of the molecules at any given future time. The results obtained from MD simulation were used to obtain an analytic expression for calculating the diffusion coefficient of the molecules. The diffusion coefficient was found to be proportional to the square root of the absolute temperature of the system, to be inversely proportional to the molecular mass, to depend exponentially on the density of system (in agreement with the free-volume theory)[12] and to decrease almost linearly with the steepness of the repulsive forces.

For the investigation of diffusion-controlled polymerization reactions, a modified stochastic simulation algorithm has been developed[9] which is able to incorporate imperfect mixing effects into the kinetic Monte Carlo scheme.[4] In the kMC method, all physical and chemical processes take place according to a certain probability distribution, usually a Poisson distribution, characterized by the corresponding rate of each process. In the traditional kMC algorithm, a small finite but representative volume is defined, which is assumed to be perfectly mixed and to remain constant during the whole simulation. In the modified algorithm, the perfectly mixed volume is not defined as an arbitrary and constant input parameter, but it is calculated at every simulation step as a function of the diffusivity of the reacting species. By means of this modified stochastic simulation algorithm, it was possible to describe mass transfer limitation effects (cage effect, gel effect and glass effect) in a typical bulk polymerization of methyl methacrylate, considering constant polymerization kinetics during the whole process.[9]

Another important mechanism in emulsion polymerization is the formation of polymer particles. Polymer particles formation is an aggregation process which involves not only the polymer chains but also monomer molecules and monomer droplets and any other molecule or molecular aggregate with a certain affinity with the polymer (e.g. surfactant molecules). It is for this reason that the most probable source of polymer particle formation comes from the interaction between growing polymer chains and small monomer droplets formed by the process of spontaneous emulsification.[13] However, given that the propagation of the radicals is a highly exothermic reaction, the chain length of the growing radical and the size of the aggregate are the limiting factors for the proper formation of a polymer particle. If the radical is too small, as well as the polymer-monomer aggregate, the energy released during a propagation step can be large enough to promote the desorption of the radical into the continuous phase.[14] For longer chains and larger aggregates, the thermal dissipation of the energy avoids the propagation-induced desorption of the radical. For these reasons, a new model of particle formation based on the propagation-induced desorption of the radicals has been developed. [11] According to this model, if the chain length of a growing radical is below a certain critical value, the energy released during propagation overcomes the energy barrier for desorption and the chain will return to the continuous phase. Only if the critical chain length is reached in the continuous phase and not inside an already existent particle, a new polymer particle is obtained.

The investigation of radical dynamics (absorption-desorption) in emulsion polymerization was performed using Brownian Dynamics simulation, achieving a precision

which cannot be matched with the available experimental methods. BD simulation is a numerical technique used to solve Langevin's stochastic differential equation of Brownian motion. By means of this method, it is possible to determine the paths followed by Brownian entities (molecules, colloidal particles) as a result of the random collisions against the molecules in the medium. In the case of radical absorption or radical capture, it has been found that for very dilute polymer dispersions the rate of capture is in excellent agreement with the classical Smoluchowski's equation. However, for concentrated dispersions (>0.1%) the rate of radical capture deviates significantly this expression.[5] This deviation is represented by the dimensionless Smoluchowski number, and it has been found to increase almost linearly with respect to the volume fraction of the particles. According to these results, the dependence of the capture rate coefficient on the particle size ranges from a linear to a fourth order dependence depending on the volume fraction of particles in the system. This explains why different models of radical capture have been satisfactorily validated using experimental data.

In the case of radical desorption, BD simulation allowed a more precise determination of the desorption rate coefficient in excellent agreement with theoretical expressions. From the BD simulation of radicals in homogeneous spherical polymer particles, the rate coefficient of radical desorption was found to be: $k_0 \approx 60 D_r/d_p^2$, where D_r is the diffusion coefficient of the radical inside the particles and d_p is the particle diameter. Although this equation was found to be 5 to 30 times larger than the values previously reported, the correctness of the new expression was confirmed by a precise theoretical model.[7] BD simulation has been shown to be a very useful method for the determination of radical desorption kinetics especially when more complex but also more realistic situations are considered, like for example, in core-shell particles, in particles with radial monomer gradients, or for non-spherical polymer particles.[15]

It has been also evidenced that absorption/desorption dynamics and equilibrium are strongly affected by the presence of energy barriers for the mass transfer across the surface of the particles. Furthermore, the behavior described by BD simulation is not exclusive of the radicals but can be extended to all the molecules present in the system, including for example, the monomer molecules. Therefore, the swelling dynamics and equilibrium of polymer particles by monomer can also be described by this approach.[8]

Simulation Example

In this section, an approximation to the modeling of secondary particle nucleation in emulsion polymerization based on multi-scale simulation is presented. The system considered the semi-batch surfactant-free emulsion polymerization of vinyl acetate (VAc) in the presence of monodisperse polystyrene (PS) seed latex. This particular system is very interesting to investigate because:

- Vinyl acetate and styrene do not copolymerize. In fact, the presence of free styrene monomer inhibits the polymerization of vinyl acetate.
- These monomers have very different solubility in water. Vinyl acetate is hydrophilic (0.5 M) while styrene is hydrophobic (4.3×10^{-3} M).
- Their polymers are incompatible. Therefore, polymer phase separation is expected.

Table **1** Parameters used for the second example of multiscale kMC-BD simulation for the seeded emulsion polymerization of vinyl acetate

Parameter	Value	Parameter	Value
Temperature (°C)	80	Simulation volume (l)	$2x10^{-18}$ - $9x10^{-15}$
Seed volume fraction (%)	5 – 40	Seed particle diameter (nm)	100 – 1000
Particle number concentration (#/l)	$4x10^{14}$ – $4x10^{17}$	Aqueous monomer concentration (mol/l)	0.5
Monomer concentration inside the particles (mol/l)	7.5	Initial initiator concentration (mol/l)	$1x10^{-3}$
Initiator decomposition rate coefficient (s^{-1})	$8.6x10^{-5}$	Propagation rate coefficient (l/mol·s)	$1.29x10^{4}$
Chain transfer to monomer rate coefficient (l/mol·s)	2.32	Termination activation energy (J/mol)	2000
Primary radical diameter (nm)	0.526	Primary radical molar mass (g/mol)	96.16
Monomer unit diameter (nm)	0.664	Monomer unit molar mass (g/mol)	86.09
Energy barrier for desorption (J/mol)	12000	Energy barrier for absorption (J/mol)	8000
Enthalpy of propagation (J/mol)	88000	Minimum chain length for particle formation	18
Radical diffusion coefficient in water (m^2/s)	$1.4\ x10^{-9}$	Radical diffusion coefficient inside the particles (m^2/s)	$1x10^{-11}$
Final simulation time (s)	0.42 – 390		

The dynamics of radicals around or inside a single structured polymer particle are simulated using a kMC-BD multiscale approach, where a BD simulation will be performed around one single particle achieving a spatial resolution of the motion of the radicals, while all other processes are periodically incorporated by means of the kMC approach. Not only radical absorption but also desorption are considered assuming energy barriers determined by non-conservative forces and by the chemical potential difference of the radicals between the particle and the continuous phase. In addition, radical desorption induced by the propagation of the growing chain and chain transfer to monomer are incorporated into the model, and the particles are assumed to be swollen by monomer before starting the polymerization. New particle formation is assumed to take place according to the propagation-induced desorption model, briefly described in the previous section. Since the time-scale that can be covered by BD simulation is relatively short compared to the total polymerization time, the simulation is performed only up to the first 400 seconds of the reaction. In order to investigate secondary particle formation this time is enough given that secondary nucleation, if ever takes place, is observed at the beginning of the process. In fact, since the existing polymer particles are continuously growing, the probability of radical capture increases with polymerization time and thus, the probability of particle formation is reduced. The parameters and conditions used in the simulation are summarized in Table 1. In a first case, the radicals are generated by thermal decomposition of initiator molecules which are assumed to be uniformly distributed in the continuous phase. A second set of simulation data was obtained using the same conditions of Table 1, but assuming that hydrophilic radicals are generated by a redox reaction between one hydrophilic reducing agent located in the continuous phase and one hydrophobic oxidizing agent present inside the polymer particles. In this way, the locus of radical formation can be restricted to the surface of the particles. A third set of simulation data was obtained using the same parameters and assuming that the radicals are generated by the thermal decomposition of

inisurf molecules, that is, initiators with surface activity that are mainly located at the surface of the particles. The simulation results for all three situations are presented in Figure 2.

According to the simulation results, the probability of secondary particle formation decreases by increasing the seed volume fraction of the latex for a given seed particle size, and increases by increasing the seed size for a constant seed volume fraction. This is caused by the increased chain length of the polymers that can be achieved in the continuous phase. On the other hand, it is possible to clearly evidence the influence of the locus of radical generation on the probability of secondary nucleation. When a hydrophilic/hydrophobic redox initiation system is used, it is observed a complete suppression of secondary particle formation for seed volume fractions above 20% for a seed particle size of 500 nm, and for 20% volume fraction seed latexes, secondary nucleation is suppressed for seed particle sizes below 1 μm. In the case of the inisurf, the probability of particle formation is greatly reduced compared to normal initiators. Although both the redox initiator and the inisurf produce radicals close to the surface of the particles, the use of the redox system allowed a larger reduction in secondary particle formation compared to the inisurf. This result can be explained by the fact that the rate of radical generation in the redox system is much higher than for the thermal decomposition of the inisurf, leading to a higher concentration of radicals around the particles and to a larger number of termination events. Even though secondary nucleation is further suppressed with the redox system, the rate of polymerization can also be reduced and shorter chains may be produced. However, this multi-scale simulation approach showed that the control of the locus of radical generation is an excellent strategy for the control of secondary particle formation during the synthesis of structured particles by seeded emulsion polymerization.

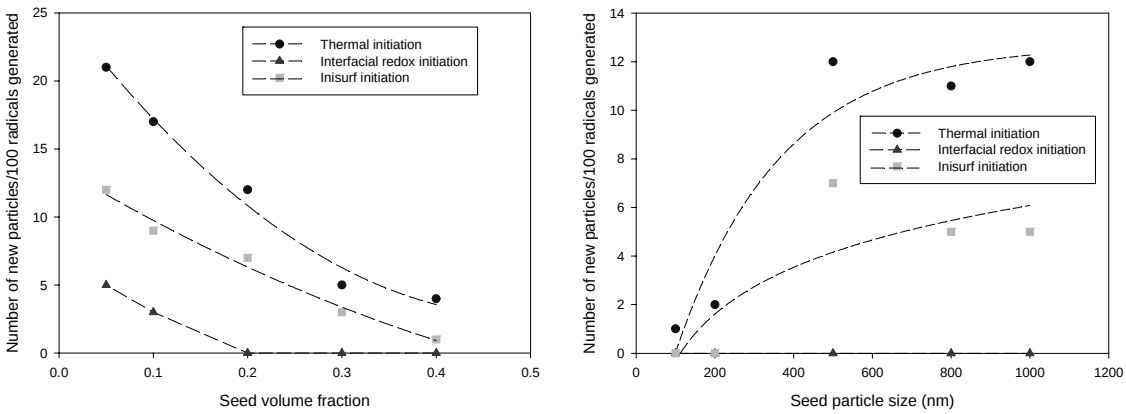

Figure **2** Number of new particles formed per 100 radicals as a function of the seed volume fraction for a seed latex of 500 nm in particle size (left) and as a function of the seed particle size for a seed latex of 20% volume fraction (right). Circles: Generation of radicals by thermal decomposition of water-soluble initiator. Triangles: Radical generation by redox interfacial reaction between a hydrophilic reducing agent and a hydrophobic oxidizer. Squares: Radicals generated by the thermal decomposition of an inisurf. Dashed lines: Fitted curves.

The experimental evidence of the success of this idea was presented by Soltan-Dehghan et al.[16] for the synthesis of structured polystyrene/poly(vinyl acetate) polymer particles. They used a two-stage polymerization process to prepare PS/PVAc nanocomposite polymer particles with a core-shell morphology in an emulsifier-free emulsion polymerization system, employing 2,2-azo bis(2-amidino propane) dihydrochloride as an inisurf initiator. The particle diameter of the polystyrene seed used was around 300-

400 nm, which is clearly beyond the limiting value of 150 nm obtained theoretically by Ferguson et al.[17] for this particular system.

Conclusion

The most important conclusion of the present work is that heterophase polymerization is a complex multi-scale stochastic process. For that reason, a very accurate description of this type of process requires the adequate integration of all these relevant scales, that is, requires the use of suitable multiscale dynamic simulation methods.

It has been shown that multiscale dynamic simulation methods can be successfully used for the investigation of the kinetics of emulsion polymerization. In particular, these methods were used to investigate the synthesis of structured polymer particles by semi-batch seeded emulsion polymerization as a representative case study. The results obtained in the simulation were used to find optimal conditions for the suppression of secondary nucleation in emulsion polymerization. It was demonstrated that by controlling the locus of radical generation at the surface of the particles it is possible to greatly reduce the probability of secondary particle formation in seeded emulsion polymerization systems. These conditions were successfully tested by combining Brownian Dynamics simulation with kinetic Monte Carlo simulation, and they could not be obtained using the traditional modeling techniques used in emulsion polymerization.

There are still enormous possibilities for the investigation and exploration of multi-scale integration in heterogeneous polymerization systems, involving different combination of scales ranging from the atomistic to the macroscopic scale. Hopefully, these ideas can be used to obtain an even more complete understanding of all the mechanisms taking place in heterophase polymerization at all relevant length scales, and also, that the fast increase in computational power can allow very soon to perform faster simulations and to span more easily a wider range of time scales.

References

[1] Frenkel, D. and B. Smit. “Understanding molecular simulation”, Academic Press, San Diego 2002.

[2] Chen, J. C. and A. S. Kim. “Brownian Dynamics, Molecular Dynamics and Monte Carlo modeling of colloidal systems”. Adv. Colloid Interf. Sci., 112, 159-173 (2004).

[3] Ermak, D. L. and J. A. McCammon. “Brownian dynamics with hydrodynamic interactions”. J. Chem. Phys., 69, 1352-1360 (1978).

[4] Gillespie, D. T. “A general method for numerically simulating the stochastic time evolution of coupled chemical reactions”. J. Comp. Phys., 22, 403-434 (1976).

[5] Hernández, H. F. and K. Tauer. “Brownian Dynamics Simulation of the capture of primary radicals in dispersions of colloidal polymer particles”. Ind. Eng. Chem. Res., 46, 4480-4485 (2007).

[6] Hernández, H. F. and K. Tauer. “Brownian Dynamics Simulation Studies on Radical Capture in Emulsion Polymerization”. Macromol. Symp., 259, 274-283 (2007).

[7] Hernández, H. F. and K. Tauer. “Radical desorption kinetics in emulsion polymerization 1. Theory and Simulation”. Submitted to Ind. Eng. Chem. Res.

[8] Hernández, H. F. and K. Tauer. “Non-equilibrium molecular uptake by polymer particles in emulsion polymerization”. In preparation.

[9] Hernández, H. F. and K. Tauer. “Stochastic simulation of imperfect mixing in free radical polymerization”. Macromol. Symp. (2008). In press.

[10] Harmandaris, V. A., N. P. Adhikari, N. F. A. van der Vegt, K. Kremer, B. A. Mann, R. Voelkel, H. Weiss and C. C. Liew. “Ethylbenzene diffusion in polystyrene: United atom atomistic/coarse grained simulations and experiments”. Macromolecules, 40, 7026-7035 (2007).

[11] Hernández, H. F. “Multiscale simulation of heterophase polymerization: Application to the synthesis of multicomponent colloidal polymer particles”. Ph.D. Dissertation. Potsdam University. 2008.

[12] Fujita, H. “Diffusion in polymer-diluent systems”. Adv. Polym. Sci., 3, 1-47 (1961).

[13] Tauer, K., H. F. Hernández, S. Kozempel, O. Lazareva and P. Nazaran. “Towards a consistent mechanism of emulsion polymerization – new experimental details”. Colloid Polym. Sci., 286, 499-515 (2008).

[14] Harkins, W. D. “A general theory of the mechanism of emulsion polymerization”. J. Am. Chem. Soc., 69, 1428-1444 (1947).

[15] Hernández, H. F. and K. Tauer. “Radical desorption kinetics in emulsion polymerization 2. Application of Brownian Dynamics Simulation”. Submitted to Ind. Eng. Chem. Res.

[16] Soltan-Dehghan, M., N. Sharifi-Sanjani and N. Naderi. “Preparation of polystyrene/poly(vinyl acetate) nanocomposites with a core-shell structure via emulsifier-free emulsion polymerization”. J. Appl. Polym. Sci., 100, 2409-2414 (2006).

[17] Ferguson, C. J., G. T. Russell and R. G. Gilbert. “Synthesis of latices with polystyrene cores and poly(vinyl acetate) shells. 1. Use of polystyrene seeds”. Polymer, 43, 6371-6382 (2002).