Mechanism and Modeling of Emulsion Polymerization: New Ideas and Concepts – 2. Modeling Strategies

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Summary: Molecular modeling strategies offer new insights into the mechanism of heterophase polymerization. The capabilities of Brownian dynamic simulations are illustrated by means of studies regarding radical entry and exist as essential steps in emulsion polymerization. Interestingly, the results allow certain generalizations which were not possible with macroscopic deterministic modeling strategies.

Keywords: Brownian dynamic simulation; emulsion polymerization; radical entry; radical exit

Introduction

Emulsion polymerization (EP) is highly complex. It comprises several steps proceeding on very different time and length scales. Particles grow throughout the whole polymerization reaction and hence, their volume growth can be easily studied and subsequently modeled. However, some important reactions such as particle nucleation or transfer of matter between segregated phases and the continuous phase have much smaller characteristic time constants. Exchange of matter happens randomly across the interface and its on-line investigation is experimentally extremely challenging.

Also, the number of active species is quite heterogeneously distributed across the reaction volume. The concentration of hydrophobic monomers such as styrene in the aqueous phase is during the entire reaction orders of magnitude lower than inside the particles. The monomer concentration in the particles corresponds to that in the aqueous phase only at a monomer volume fraction of about 10^{-4} that means 99.99% monomer conversion per particle. Inside particles at low conversion the radical exists in a bath of monomer and polymer molecules until it meets a second radical and terminates.

In the aqueous phase, however, radicals are surrounded by water molecules. 10^{12} to 10^{14} radicals per liter water face about $3 \cdot 10^{25}$ water molecules but only 10^{20}–10^{22} molecules of styrene, initiator, or surfactant and still a lower number of polymer particles (about 10^{16} to 10^{18}). In other words, a radical is in average more than 100 nm apart from a monomer molecule. Now, two conclusions are straightforward. Firstly, there is a certain probability that a radical reacts with water causing the formation of other end groups than that stemming from initiator radicals. Indeed, there is experimental evidence that this happens for both peroxodisulfate[1] and 2,2′-azobisisobutyronitrile.[2] Secondly, the fate of a primary radical depends on its birth place, either far away or in the vicinity of a partner (monomer or particle).

Not every contact must lead to reaction but the reactants may bounce back and diffuse away again. Thus, in the continuous phase and inside the particles (here especially the growing radicals but at lower monomer volume fraction also the monomer molecules) the concentration of reactants is so low that stochastic fluctuations can be important and deterministic kinetics fails. Consequently, the heterogeneous

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nature of the reaction system requires other modeling strategies than homogeneous processes where an average concentration on small enough reaction volume can be safely defined. Molecular- and multiscale dynamic modeling approaches correspond to the heterogeneous nature much better than macroscopic averaging strategies.[3] The former offers new insights into the mechanism of heterophase polymerization.

Preliminary Note

The overall rate of radical polymerization (r_p in L/(mol · s)) for batch ab-initio emulsion polymerization is the sum of the rate of monomer consumption in all phases (i), cf. equation (1). d[M]/dt is the overall monomer consumption rate that can be subdivided to take place in the continuous water phase (i: w) and in the segregated phases of monomer swollen particles (i: p), monomer droplets (i: d), or monomer swollen micelles (i: m) (1).

$$-\frac{d[M]}{dt} = \sum_i r_{p,i} \tag{1}$$

The polymerization rates in the individual phases are given by equation (2).

$$r_{p,i} = k_{pi} \cdot [M]_i \cdot [P]_i \tag{2}$$

In equation (2) the $[M]_i$'s denote the monomer concentration in mol/L, the $k_{p,i}$'s the propagation rate constant in mole/(L · s), and the $[P]_i$'s are the concentrations of growing radicals in mol/L in the corresponding phases where monomer consumption has to be considered.

A remark is necessary regarding the units of measurements in the above equation, particularly regarding those for concentrations. To illustrate the issue, let us assume two identical homogeneous solution polymerizations in two units (i: r1, r2; reaction volumes v_{r1}, v_{r2}) separated by a membrane that allows only exchange of monomer molecules and small radicals. For such scenario equation (1) is correct if the concentrations are related to volume of solvent. Then the equality $[M] = [M]_{r1} + [M]_{r2}$ holds. If, however, [M] is related to the overall reaction volume, $v_r = v_{r1} + v_{r2}$, this equality is not valid anymore and has to be replaced by $[M] = [M]_{r1} \cdot \phi_{r1} + [M]_{r2} \cdot \phi_{r2}$, where the ϕ's are the volume fractions of r1 and r2. This means for heterophase polymerization equations (1) and (2) have to be modified as given by equations (3) and (4).

$$\begin{aligned}-\frac{d[M]}{dt} &= -\sum_i \frac{d[M]_i \cdot \phi_i}{dt} \\ &= -\sum_i \phi_i \frac{d[M]_i}{dt} \\ &\quad -\sum_i [M]_i \frac{d\phi_i}{dt}\end{aligned} \tag{3}$$

$$\begin{aligned}-\frac{d[M]}{dt} &= \sum_i k_{p,i} \\ &\quad \cdot [M]_i \cdot [P]_i \cdot \phi_i - \sum_i [M]_i \frac{d\phi_i}{dt}\end{aligned} \tag{4}$$

Equation (4) is a general description and can be reduced for many practical cases as there are good reasons to assume that polymerization inside very large monomer droplets with tens of micrometers in size is rather unlikely. Moreover, the polymerization inside the continuous water phase and in micelles is frequently negligible compared to the monomer consumption inside the particles.

From equation (4) and an estimation of the monomer concentrations (cf. above) follows immediately, that the rate of monomer consumption is quite different in the phases and that for hydrophobic monomers a dramatic change happens after the appearance of swollen polymer particles. Equations (1)–(4) contain, directly or indirectly, the parameters and processes that are essential for an understanding of emulsion polymerization. These are kinetic events causing monomer consumption (initiation of the chain reaction, its propagation, and termination) and physical changes in the state of the reaction system leading to particle formation and to subsequent transfer of matter between the phases.

For EP the overall monomer consumption is frequently reduced to that inside the particles. Hence, the overall radical concentration [P] is expressed with an average number of radicals per particle ($\overline{n}$) (5a), where N_A is Avogadro's constant and N' the overall number of particles in the reaction volume. However, this approximation is not consistent with (1)–(4) and should be replaced by (5b).

$$[P] \approx \overline{n} \cdot N'/N_A \tag{5a}$$

$$[P] \approx [P]_p \cdot \phi_p \approx \frac{\overline{n} \cdot N'}{N_A} \tag{5b}$$

Another approximation for the overall rate of emulsion polymerization (6), that is often used, must also consider the change in the volume of the reaction system.

$$r_p \approx k_{p,p} \cdot [M]_p \cdot \overline{n} \cdot \frac{N}{N_A} \cdot \phi_w \tag{6}$$

In equation (6) N is the number of particles per volume of water ($N' = N \cdot \phi_w$).

A peculiarity of heterophase polymerization is that the reaction takes place at very different sites. As for any polymerization the volume changes during the reaction due to the density difference monomer - polymer. Hence, the ϕ_i's are changing as well and in order to calculate the conversion from reaction rates (as for instance from calorimetric data) requires to consider their conversion-dependence as described by equations (3)–(6).

On the other hand, these considerations suggest that for the reactions involving the particles a summation similar to that given by equation (1), that is, over all volume elements containing a single particle and all other ingredients, can be carried out. This sets the base for molecular modeling techniques to describe the transfer of matter between the particles and the continuous phase as exemplified in the following chapter.

New Experiments Contributions and Modeling Strategies

Thermodynamics requires an equilibration of the chemical potential of a species in all phases present in the system. Consequently, in emulsion polymerization any species can enter any phase. And indeed, it was shown that even hydrophilic radicals can enter latex particles.[4,5] On the other hand also hydrophobic material can enter latex particles passing through the aqueous phase.[6] Either molecularly dissolved hydrophobic substances or aggregates thereof can enter latex particles. The uptake of matter by latex particles is co-operative in nature causing even polymers such as poly(methyl methacrylate) to enter polystyrene particles dissolved in hydrophobic solvent drops.[7]

In contrast to this thermodynamic consideration, which is path-independent and valid for large systems (based on energy or chemical potential differences) at equilibrium, the behavior of individual species is path- and time-dependent. In addition to the points made in the introduction, this is a strong argument to try molecular modeling techniques in order to learn more about heterophase polymerizations.

The success of these approaches has recently been shown unifying the many models/theories of entry and exit in emulsion polymerization.[8,9] Brownian Dynamics (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 path of individual Brownian entities as a result of the random collisions with the molecules in the medium, as well as the precise time of occurrence of certain physical events such as collision between entities, phase transfer, etc. BD simulation is a powerful tool for describing processes at the colloidal or molecular scale, and for determining the kinetics of different relevant physical processes.

For entry we were able to derive a new dimensionless number, the Smoluchowski number, Sm, that relates the actual entry rate coefficient determined by Brownian dynamics simulations, k_c, to the Smoluchowski rate coefficient (denominator in equation 7a). Numerical experiments show that Sm depends linearly on the polymer volume fraction (equation 7b, υ is a geometrical constant). Note, this is a universal treatment of entry that does not distinguish between radicals or monomers. The discriminating property is basically the size of the entity that determines coefficient diffusion and an energy barrier.

$$\mathrm{Sm} = \frac{k_c}{2\pi D_r d_p N_A} \tag{7a}$$

$$\mathrm{Sm} = 1 + \upsilon\phi_p \tag{7b}$$

With the Smoluchowski number and equation 7b the over decades ongoing discussion with which power radical entry depends on the particle size came to an end as it was clearly shown that this exponent depends on the solid content and can vary between 1 and 4, cf.[8].

Moreover, the k_c depends on the size of the entering species and on their position in relation to the particle's spot. The latter means for radicals that k_c depends on their 'birthplace', that is how distant from the particle surface decomposition of an initiator molecule takes place (Figure 1).

Also for radical desorption different models / theories have been developed over the last decades with quite different conclusions (for a recent summary cf.[9]). Similar as for entry, molecular dynamic calculations can greatly contribute to develop general solution of this important kinetic event during emulsion polymerization.

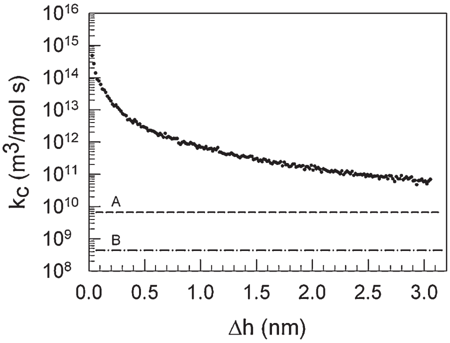

Figure 1.
Dependence of the entry rate coefficient on the distance from the particle surface (Δh); dashed line (A) denotes the value for uniform distribution (average over randomly generated positions) and the dashed-dotted line (B) that resulting from the Smoluchowski equation.

Radical desorption takes place by diffusion of the radical inside the polymer particle towards the interface, and the subsequent transfer to the continuous phase after overcoming the energy barrier at the interface that opposes exit. The rate of radical desorption can be determined theoretically (cf.[9]) for relatively simple cases, such as homogeneous spherical particles, that is particles entirely made of either hard or soft polymer (simple desorption coefficient k_0, equation 8). D_p is the diffusion coefficient of the desorbing species inside particles of diameter d_p.

$$k_0 = \frac{60 \cdot D_p}{d_p^2} \tag{8}$$

For more complex situations, the analytical solution becomes very difficult if not impossible at all. In these cases a numerical approach is much better suited for an estimation of k_0. A Monte Carlo Random Flight (MCRF) algorithm of BD simulation is used for the estimation of k_0 in EP containing particles of increased complexity. Details of the MCRF method have been published elsewhere.[9] The estimations of k_0 in core-shell particles, in particles with a gradient monomer concentration, and in non-spherical particles illustrate impressively the ability of this procedure.

The first example considers particles with hard core and soft shell or vice versa ($d_p = 100$ nm) with varying volume fraction of the soft polymer phase (ϕ_{soft}) and radical generation in both phases. The diffusion coefficients are $D_{hard} = 10^{-12}$ and $D_{soft} = 10^{-9}$ m^2/s. Results are summarized in Figure 2 and compared to the rate coefficients for homogeneous hard or soft particles calculated with (8). It is clear from Figure 1 that the sequence of the hard and soft polymers has a great effect on k_0. A theoretical prediction is not straightforward

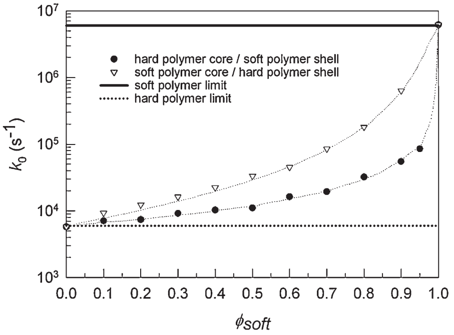

Figure 2.
Simple desorption in core/shell particles. Radicals are generated uniformly in both core and shell phases.

although an average diffusion coefficient can be defined (9) but its physical relevance is questionable as it does not properly describe the case. Combination of (9) and (10) leads to equation (11) for k_0 which can be used to fit both data sets as proven by the lines connecting the computational data points in Figure 8. The fit gives for the hard core/soft shell particles $a = 6000$, $b = 0$, $c = -0.999$, $d = 0$. In this case, when the diffusion coefficient in the core is small compared to the diffusion coefficient in the shell, the fitted parameters correspond to the values obtained using equation 10, and therefore, the simple desorption rate coefficient can be estimated using a volume fraction averaged diffusion coefficient (9). On the other hand, the parameters obtained for the soft core/hard shell were: $a = 6000$, $b = 2863$, $c = -1.974$, $d = 0.9751$. This case is quite complex and an accurate analytical solution difficult to obtain. Moreover, with BD computer experiments it is easily possible to study the fate of radicals that have been generated only in certain volume elements.

$$\overline{\mathrm{D}}_{\phi} = \frac{1}{\frac{(1-\phi_{\mathrm{soft}})}{\mathrm{D_{hard}}} + \frac{\phi_{\mathrm{soft}}}{\mathrm{D_{soft}}}} \tag{9}$$

$$\mathrm{k_0} = \frac{60}{\mathrm{d_p^2}} \frac{\mathrm{D_{soft}D_{hard}}}{\mathrm{D_{soft}}(1-\phi_{\mathrm{soft}}) + \mathrm{D_{hard}}\phi_{\mathrm{soft}}} \tag{10}$$

$$\mathrm{k_0} = \frac{\mathrm{a} + \mathrm{b}\cdot\phi_{\mathrm{soft}}}{1 + \mathrm{c}\cdot\phi_{\mathrm{soft}} + \mathrm{d}\cdot\phi_{\mathrm{soft}}^2} \tag{11}$$

The greater k_0 for particles with a soft core and hard shell seems at a glance surprising, but is reasonable considering two effects. The first effect is the different geometry between the core and the shell. As a result, the average diffusion path through the hard phase for a radical in a hard core/soft shell is different from the average diffusion path in a soft core/hard shell. It is important to notice that for a given volume fraction of hard polymer, the diffusion path length in a hard core particle will always be larger than for a hard shell particle. The second effect is caused by the diffusion of the radicals in all direction, also towards the core of the particles. When the core is soft, this effect is not significant, but when the core is hard, this leads to an increase in the average desorption time and therefore to a decrease in the rate of radical desorption.

In the former example the radical experienced a sudden change in its diffusion coefficient after crossing the core-shell interface. Now we consider a monomer gradient inside the particles. This means composition-dependent diffusion coefficients inside the particle in a way that it decreases from the surface towards the particle's core. The diffusion coefficients required by the BD simulation algorithm are calculated, for the present example, with the parameters reported in[10] for MMA in poly(methyl methacrylate) using a corresponding free volume model.[11] Particularly, desorption of radicals with non-zero energy barrier (between 600 and 20 kJ/mol) at the particles – water interface is considered. The radicals have been positioned for the start of the simulations at the interface, corresponding either to radical generation in water and subsequent capture by particles or generation at the interface. In the absence of an energy barrier for desorption k_0 is very large because of the high probability of desorption. If that would describe the real case, the capture of radicals from the aqueous phase would not be an effective process contributing significantly to the kinetics of EP. Clearly, a certain energy barrier for desorption should exist and must be considered.[12] The incorporation of the energy barrier into the BD simulation is performed using the Metropolis method traditionally used in Monte Carlo simulation.[13] According to this method, the probability of a successful desorption event (p_{des}) is calculated assuming an Boltzmann or Arrhenius-type exponential function: $p_{des} = \exp(-E_{des}/kT)$. The data in Figure 3a and b illustrate how significantly desorption is reduced by an energy barrier. Figure 3a shows the decay of k_0 observed in the computation experiments with increasing E_{des}.

Figure 3b compares the influence of the temperature on k_0 for zero and non-zero energy barrier. These data reveal an interesting effect of the existence of an energy barrier as at lower temperatures a significant deviation from the Arrhenius' type of behavior (assuming only a single or constant energy barrier) is observed (Figure 3b, lower curve). Obviously, at lower temperature the probability of desorption decreases which means that the radicals must hit the interface many more times before a successful exit event. Now, if the effective number of hits necessary for desorption is higher than the average number of hits, the radical will diffuse towards the center of the particle and desorption times will inevitably increase.

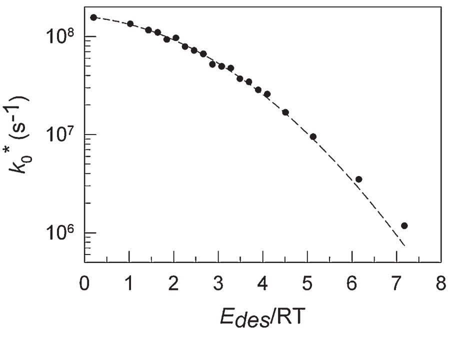

Figure 3a.

k_0 as a function of the energy barrier for desorption; $d_p = 100$ nm, PMMA/MMA linear radial concentration gradient, radicals captured from the aqueous phase $T = 353$ K.

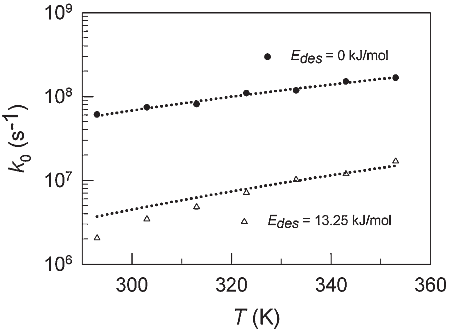

Figure 3b.

k_0 as a function of temperature and E_{des}; $d_p = 100$ nm PMMA/MMA particles with a linear radial concentration gradient, radicals captured from the aqueous phase, lines correspond to the fitted Arrhenius equations.

An additional degree of complexity in real systems is given by the fact that polymer particles may not be perfectly spherical.[14–16] For non-spherical particles, the desorption rate coefficients can be easily determined from BD simulations after a suitable parameterization of the shape of the particle. In the present example, k_0 is determined for various types of ellipsoidal particles (oblate spheroid with $\phi_y = 1$ and $\phi_z > 1$, prolate spheroid with $\phi_y = \phi_z > 1$, thin disk with $\phi_y = 1$ and $\phi_z \gg 1$, needle with $\phi_y = \phi_z \gg 1$). The surface of an ellipsoidal particle is given by (12), where x, y and z represent the Cartesian coordinates, and ϕ_y and ϕ_z are shape parameters and δ_x is the radius of the y-z cross section of the ellipsoid.

$$x^2 + \phi_y^2 y^2 + \phi_z^2 z^2 = \delta_x^2 \tag{12}$$

It is observed that the rate of simple radical desorption in spheroidal particles is lowest (and thus, the effective particle diameter is the largest) when the particles are perfectly spherical (Figure 4). As the shape of the particle deviates from the perfect sphere, k_0 increases with increasing surface-to-volume ratio of the particles. k_0 is determined by the shortest distances required to reach the surface of the particle.

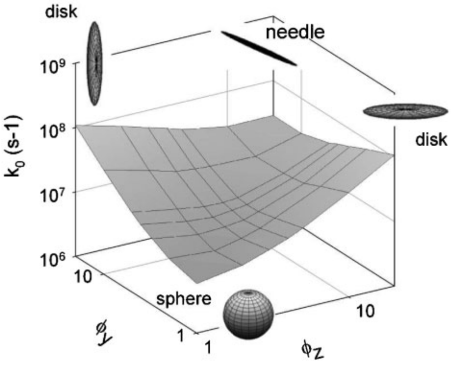

Figure 4.
k_o in ellipsoidal particles as a function of the shape parameters ϕ_y and ϕ_z, the volume of the particles corresponds to that of a sphere with $d_p = 100$ nm and $D_p = 10^{-9}$ m^2/s.

Summary and Conclusions

During the last years progress has been made towards a consistent mechanistic description of *ab-initio* batch emulsion polymerization.[7,17]

The direct experimental observation of the transfer of matter between particles and the continuous phase is extremely challenging but nevertheless it was possible to prove that also hydrophilic species (such as primary radicals) enter latex particles.[4,5] Detailed studies of entry and exit processes are possible using Brownian dynamic simulations. Such computational experiments have shown that the entry rate depends on the overall particle volume fraction with varying size exponent between 1 and 4. Brownian dynamic simulations are extremely useful to study transfer processes in complex particle morphologies and/or non-spherically shaped particles that are experimentally, if so ever, only hardly accessible.

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