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Molecular Versus Conventional Kinetics of Emulsion Polymerization

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Summary: Experimental data are discussed challenging the deterministic kinetics of emulsion polymerization. Examples are given for the overall rate of polymerization, in-situ stabilizer formation, and swelling of latex particles. Improving the deterministic view on emulsion polymerization kinetics requires the consideration of results of molecular modelling and the application of multiscale integration techniques.

Keywords: emulsion polymerization; kinetics and mechanism; molecular modelling; multiscale modelling

Introduction

This contribution is a plea not only to look at the kinetics and mechanism of emulsion polymerization through the eyes of conventional deterministic kinetics but alternatively to take advantage of a molecular attitude considering chemical reactions and physical processes as local events with single molecules or particles as acting species. The authors believe that due to the heterogeneous nature of emulsion polymerization both deterministic and molecular attempts are needed and should be developed complementary.

Within the frame of deterministic kinetics the rate of radical emulsion polymerization (r_p) is expressed by the quite simple Equation (1) where t is the time, k_p the propagation rate constant, $\bar{n}$ the average number of growing radicals per particle, C_M and N_P the monomer and particle concentration, respectively.

$$r_p = -\frac{dC_M}{dt} = k_p \cdot C_M \cdot \bar{n} \cdot N_P \qquad (1)$$

Though formally correct this equation should be handled with care as recently discussed.[1] The main issue is that both concentrations refer to different volumes which are the swollen polymer phase and the water or overall dispersion volume for C_M and N_P, respectively.

Experimental Part

Styrene (Aldrich) and tert-butyl acrylate (tBuA, Acros) were purified by distillation under reduced pressure. Sodium styrene sulfonate (Aldrich), sodium dodecyl sulfate (SDS, ultrapure, Roth), potassium peroxydisulfate (KPS, Fluka), disodium tetraborate (Fluka), 1,3 diisopropenylbenzene (Aldrich), and ethyl benzene (Aldrich) were used as received. The water was taken from a Seral purification system (PURELAB Plus) with a conductivity of 0.06 μS/cm. Emulsion polymerization of styrene was carried out batchwise in a ChemiSens CPA202 reaction calorimeter with the following recipe 83 g of water (overall), 6.77 g of styrene, 0.237 g of SDS, 0.058 g of borax buffer, 0.045 g of KPS dissolved in 3 g of water added after thermal equilibration, variable temperature between 60 and 70 °C. After polymerization the coagulum was removed by filtration and then the solids content was determined with a HR73 moisture analyzer (Mettler Toledo) which was used to calculate the polymer content of the latex and the monomer conversion (X does not consider the coagulum).

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Crosslinked polystyrene particles were made by emulsion polymerization in an overall glass reactor with the following recipe 184.65 g of water, 56.76 g of styrene, 0.412 g of SSS, 1.135 g of DIPB, 0.358 g of KPS, temperature 65 °C, duration 26 hours. Before characterization and use, the dispersion was dialysed (membrane type 36/32 Roth, cut-off 14 kD) until the conductivity of the external water reached a constant value. The lyophilized solid was sulfonated with acetyl sulfate in 1,2-dichloroethane according to standard procedure.[2] tBuA (3.717 g) and styrene (0.75 g) were thermally copolymerized in 50 g of water at 100 °C in sealed glass vials in a rotational thermostat (VLM GmbH). Mixing was achieved by head-over-head rotation with a frequency of 30 revolutions min^{-1} and polymerization was conducted for minimum 48 hours. The coagulum was removed by filtration and the latex phase was dialysed.

Particle morphology was observed with transmission electron microscopy (TEM, Zeiss EM 912 Omega microscope operating at 100 kV, suspension preparation) and scanning electron microscopy (SEM, LEO1550 Gemini operating at 3 kV). Intensity weighted average particle sizes were determined with dynamic light scattering (NICOMP 370). The behavior of latex particles in contact with ethyl benzene was followed by light microscopy (VHX digital microscope, Keyence Corporation, Osaka, Japan).

Experimental Results Challenging Conventional Deterministic Kinetics

Results of three experimental studies will be discussed representing different aspects of this issue. The first considers the whole process by means of a calorimetric study of ab-initio batch polymerization, the second focuses on the precipitation of products generated by heating only water and monomers, and the third discusses the influence of the surface chemistry on swelling of latex particles.

Classical Styrene Emulsion Polymerization

Equation (1) suggests that knowing the values of kp, CM, $\bar{n}$, and N_P at any given time, allows the prediction of r_p for the following period of time (dt). In other words, for isothermal conditions and given recipe just one r_p – t profile does exist. The data of Figure 1 obviously contradict this paradigm. For the particular recipe the individual heat flow - time curves as obtained for five repeats of the polymerization at 70 °C can still quite nicely represented by a single average curve supposing the observed scatter is 'common' for ab-initio batch procedure.

However, the corresponding curves at 60 °C show a much stronger scatter in shape and regarding the period of time it takes until emulsion polymerization sets in after initiator addition (lag time). This behavior

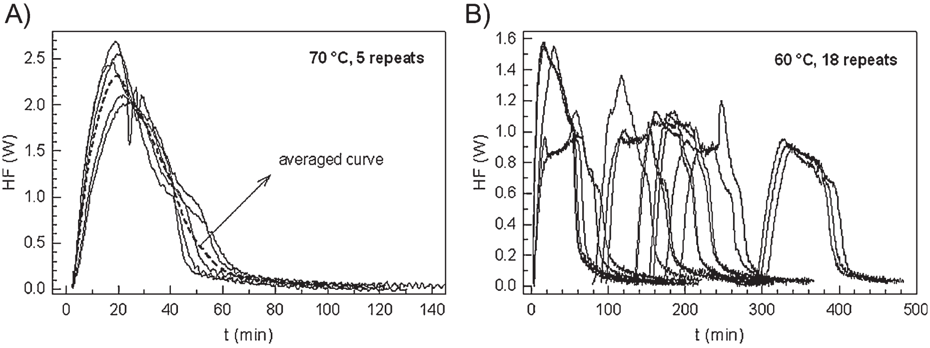

Figure 1.

Heat flow (HF)– time curves of styrene emulsion polymerization at 70 °C (A) and 60 °C (B) illustrating the huge influence of the polymerization temperature on the reproducibility for the particular polymerization recipe (83 g of water, 6.77 g of styrene, 0.237 g of SDS, 0.058 g of borax buffer, 0.045 g of KPS).

is quite surprising as it is observed with a standard emulsion polymerization recipe comprising styrene, SDS above the critical micelle concentration, and KPS. The overall duration of the polymerization at 60 °C varies up to a factor of 4 and the lag time between a few minutes and 3 hours.

It should be mentioned that the data of Figure 1–3 were obtained under as good as possible experimental control by a single experimenter, however, also other experimenters got similar results. Scatter in radical polymerization is frequently associated with different traces of oxygen. Note, oxygen's role is ambivalent as both retardation and acceleration can happen.[3–7] Thus, it is common practice to maintain an inert atmosphere in the system in order to keep the concentration of oxygen as low as possible. The significant dependence of the lag time on the temperature (graph B of Figure 2) supports the idea that the scatter is caused by oxygen as it is used up faster at higher temperature. However, against this hypothesis speaks the huge scatter at each temperature between 60 or 68 °C. Moreover, the oxygen concentration changes in either phase (water and monomer) only little between 60 and 70 °C and it even may increase in the organic phase.[8] Another, more likely explanation will be discussed below.

The data of Figure 2 and 3 illustrate the properties of the final latex and the reaction behavior in the temperature range between

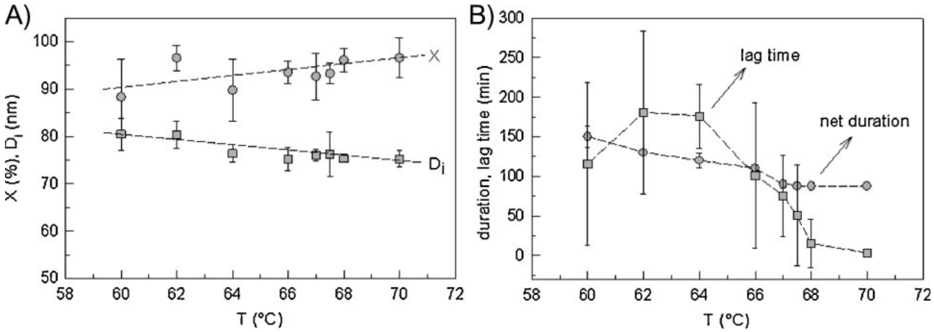

Figure 2.
Average properties of final latexes (A) and net duration and lag time of the polymerization (B) in dependence on the temperature of styrene emulsion polymerization; recipe: 83 g of water, 6.77 g of styrene, 0.237 g of SDS, 0.058 g of borax buffer, 0.045 g of KPS, the number of repeats varies between 4 and 18.

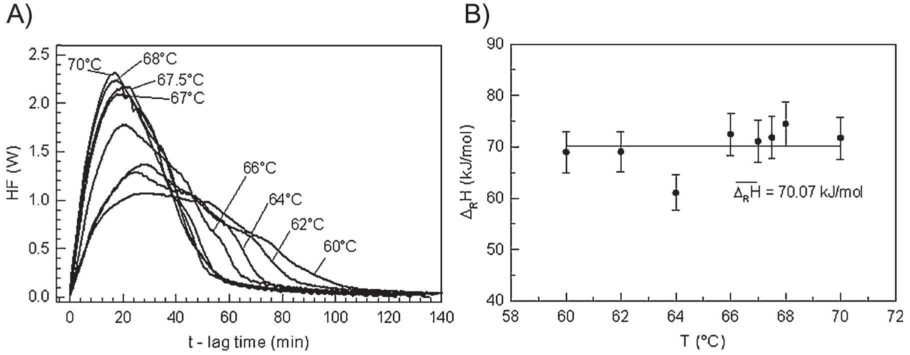

Figure 3.
Averaged heat flow – time curves and average overall heat of reaction for styrene emulsion polymerization in dependence on polymerization temperature; recipe: 83 g of water, 6.77 g of styrene, 0.237 g of SDS, 0.058 g of borax buffer, 0.045 g of KPS, the number of repeats varies between 4 and 18.

60 and 70 °C. Both the monomer conversion (X) and the average particle size (D_i) of the final latexes show a weak dependence on the polymerization temperature (Figure 2A). X increases with T whereas D_i decreases. Figure 2B reveals that the lag time strongly depends on the polymerization temperature with a steep transition between 64 and 68 °C. The net duration of the polymerization, that is the overall time minus the lag time, decreases with increasing T and is almost constant for $T > 67\,^{\circ}C$. Moreover, the experimental scatter of the lag time is much larger than that of the net duration. Also, the shape of the averaged reaction rate profiles (Figure 3A) depends on T showing more or less clearly the appearance of a gel effect at low T and a significant shape transition between 66 and 67 °C. The heat of the reaction ($\Delta_R H$) is, except one outlier, apparently constant and the average value of 70.07 kJ/mol is the expected one for styrene.[9]

Another explanation of these results is possible assuming an energy barrier that must be surmounted during the initial stage before emulsion polymerization can commence. If the internal energy of the reaction mixture or the driving force (Φ) is high the lag time is short and no delay is observed.

By visual inspection of the reaction it is clear that the heat flow increases when the reaction system has changed from whitish emulsion to bluish latex. This observation strongly suggests that the energy barrier is connected with the event of particle nucleation. Indeed, non-micellar nucleation theory, such as classical nucleation theory, that can also be applied for emulsion polymerization[10–12] predicts that the rate of nucleation (r_{nuc}) is an exponential function (Equation 2) of the cube of the interfacial tension nucleus – water (σ), the molar volume of the nucleating species squared, the cube of the thermal energy (k_BT), and the supersaturation (S) squared.

$$r_{nuc} \propto \exp\left(-\frac{\sigma^3 \cdot v^2}{(k_B T)^3 \ln^2 S}\right) \qquad (2)$$

Thus, the nucleation step is particularly sensitive to even tiny changes of the interfacial tension, temperature, supersaturation, and chain length of the nucleating species. Moreover, dissolved gas (either oxygen or nitrogen) that generate bubbles has a strong influence on the nucleation process as experimentally proven[10] and, in general, any interface influences nucleation as the activation free energy is drastically affected.[13,14]

In-Situ Formation of Stabilizer

The adoption of thermal styrene polymerization,[15] that is filling a reactor with water and hydrophobic monomer, sealing, and heating up is the simplest way to perform heterophase polymerization. In fact, doing so in the presence of stabilizer was the technology of the first heterophase polymerization ever.[16] The drawbacks of this procedure might be compensated by the chance to get polymer dispersions containing less foreign material, provided stability can be achieved by the proper choice of monomers. So, hydrophobic and hydrophilic monomer combination such as styrene and styrene sulfonate might be good candidates. Indeed, this particular combination works fine and stable latexes are accessible.[17] Another, not that straightforward monomer is tBuA either alone or in combination with styrene. The use of tBuA is feasible due to the easiness of tert-butylester hydrolysis leading to stabilizing carboxylate groups. As the rate of hydrolysis is finite, thermal tBuA homopolymerization in water results in latexes (cf. Figure 4A). Adding styrene at definite time intervals, thus, mimicking a semibatch procedure, leads to the formation of stable copolymer latexes (cf. Figure 4B). Contrary, the outcome of the batch copolymerization where the same amount of styrene is added from the beginning of the reaction is almost only coagulum (cf. Figure 4C). Interestingly, the external look of the final reaction mixture of repeated batch copolymerizations as shown in Figure 4C differs quite greatly pointing already to scattering reaction conditions.

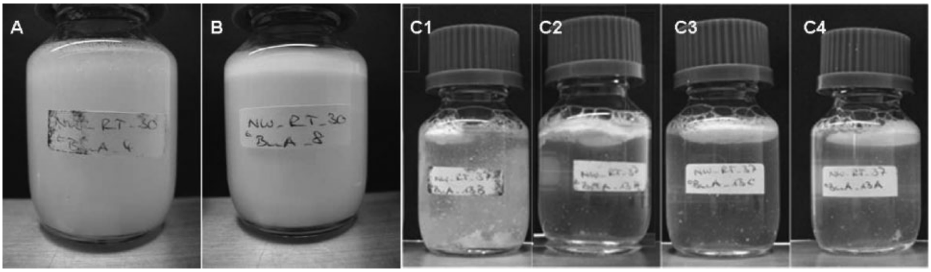

Figure 4.
Appearance of the final reaction mixtures of polymerizations in the rotation thermostat; A – thermal tBuA homopolymerization, B – thermal tBuA polymerization with three subsequent styrene additions after every 4 hours started after 41 hours, C – batch copolymerization of tBuA and styrene.

The TEM images depicted in Figure 5 reveal for tBuA homopolymerization (image A) particles with varying density (core – shell type morphology). Contrary, the particles after subsequent styrene additions in the course of the polymerization appear solid like (image B). On the other side, the TEM images of the particles of the runs C1 – C4 (repeated batch copolymerization) reveal rather erratic particle structures than a single uniform morphology.

The results for the batch thermally-initiated copolymerization of tBuA and styrene in the rotation thermostat exhibit quite a strong stochastic nature of this particular process. Again, despite all efforts maintaining as good as possible identical experimental conditions, the results of repeated polymerizations scatter considerably.

Swelling of Latex Particles

Within the molecular reflection of a colloidal polymer particle its surface is not homogeneous but patchy as it is attractive for functional groups with quite different properties. Interfaces are places

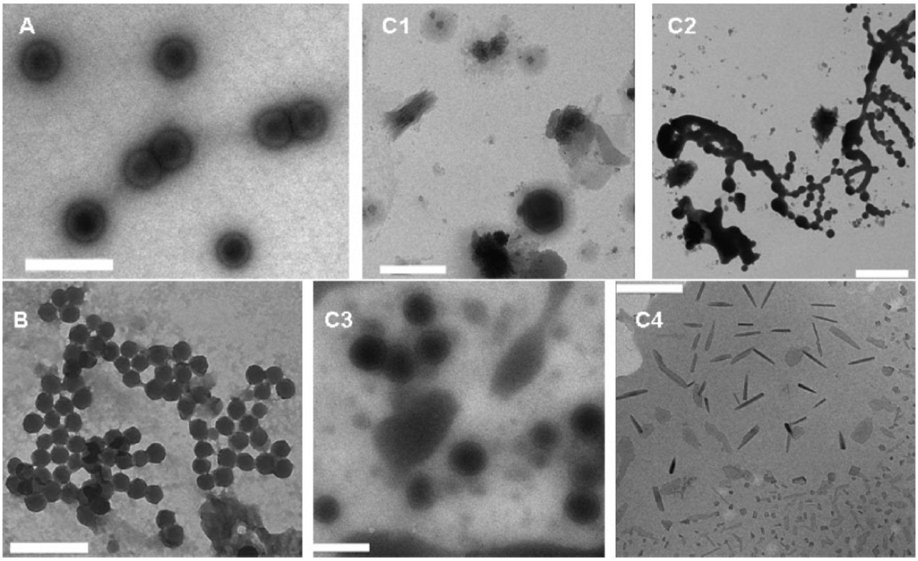

Figure 5.
TEM images of the particles observed in the dialyzed dispersions shown in Figure 4.

where, compared with homogeneous sites, additional forces act.[18] Interfacial effects are crucial for heterophase polymerizations as mass transfer of monomer and radicals are essential for the kinetics. The chemical composition of the contact area at the interface may canalize, induce, or support particular reaction pathways.

In textbooks and many articles on emulsion polymerization the swelling of latex particles is considered as being perfectly understood on the basis of equilibrium thermodynamics as developed during the 1950ies.[19] This equilibrium monomer volume fraction in polystyrene latex particles of an unswollen size of 100 nm is about 0.5 depending at given temperature and molecular weight on the monomer – polymer interaction and the interfacial tension.[20]

It is practically impossible to get direct experimental proof how the decoration of the particles surface influences mass transfer. Yet it is possible to demonstrate the basics of the idea by the TEM images put together in Figure 6. These images were obtained from polystyrene gel particles with different chemical composition dispersed in either water or ethyl benzene. The particles differ regarding the concentration of sulfonate groups. The original polystyrene gel particles (PS-gel) have a sulfur content of 0.24% stemming from the styrene sulfonate comonomer and initiator end groups. These particles (image A) contain no further stabilizer and the quite hydrophobic solid can be redispersed easily in ethyl benzene and with some more efforts also in water (TEM images C and B). After sulfonation (sulfur content of 10.3%, image B) the redispersion is now very easily possible in water but practically impossible in ethyl benzene (TEM images E and F of Figure 6).

For both samples, the TEM images of the particles redispersed in water (B, E) reveal nothing special as they look like ordinary latex particles except some deviation from sphericity due to crosslinking. In contrast, in ethyl benzene (image C, F) both

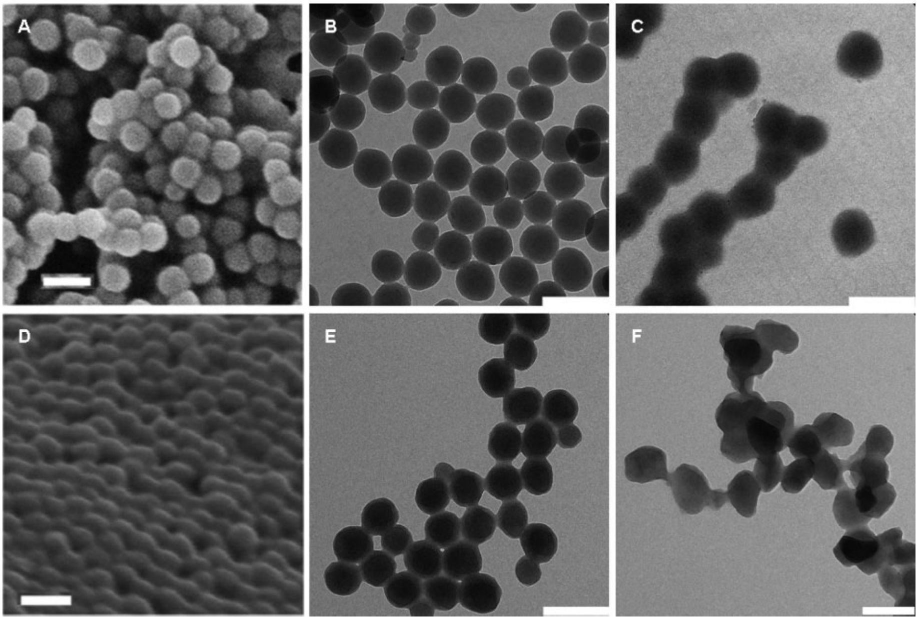

Figure 6.
SEM and TEM images illustrating the redispersion behavior of original and sulfonated polystyrene gel particles; A – dry original particles, B – original particles in water, C – original particles in ethyl benzene, D – dry sulfonated particles, E – sulfonated particles in water, F – sulfonated particles in ethyl benzene; the bars indicate 200 nm.

sorts of particles look differently. The swollen state of the original, more hydrophobic particles can be imagined as they appear in the TEM quite fluffy with less dense edges. Moreover, during drying the particles do aggregate and, compared with the aqueous system, their contact areas are larger. This is due to fact that the electrostatic repulsion is less effective and that in the interstitial volume the concentration of dangling chains is quite high so that an additional attractive force is operating.[21] The sulfonated, more hydrophilic particles show only weak interaction with ethyl benzene. Quite large lumps of aggregated particles are detectable by visual inspection, yet after sonication. The degree of swelling of the particles is so low that they are even unable to relax to the spherical shape. The high concentration of hydrophilic sulfonate groups prevents effectively the penetration of ethyl benzene.

There are other experimental facts and theoretical arguments supporting the necessity of changing the view on swelling.[22] It turned out that the knowledge of the physical state of the monomer in the reaction system is extremely helpful, not only for swelling but for better understanding of emulsion polymerization in general.[22–24] The images of Figure 7 give a glimpse about the real situation and illustrate essential features.

In comparison to image A, image B shows that upon contact with the swelling agent the overall turbidity of the latex increases. As result of swelling, the size of the particles and their scattering intensity is expected to grow by a factor of about 1.26 and 4, respectively. However, the light microscopy images C and D reveal that beside the swollen latex particles with a size of 50 nm, which are only visible as background haze under oblique transmission (image D), much larger objects of up to 25 μm in diameter with a broad size distribution freely move in the dispersion. This means, the monomer is during any stage of the emulsion polymerization not only present either molecularly dissolved or in micrometer sized droplets, formed by mechanical comminution, but molecules coexist with aggregates and drops of various sizes. The smaller monomer droplets are generated via spontaneous emulsification,[24] which is facilitated by the presence of surfactant in the dispersion. From a molecular perspective all these monomer species can interact with particles and contribute to swelling.

Molecular Versus Deterministic Modeling

The experiments presented above elucidated some of the challenges in predicting emulsion polymerization kinetics. Many different chemical and physical processes take place simultaneously and sometimes

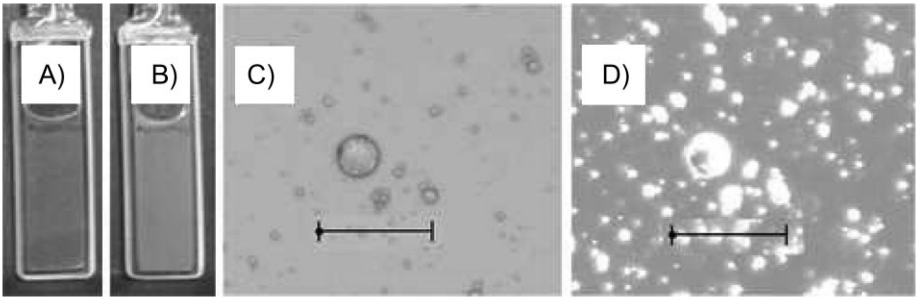

Figure 7.
Light microscopy images of a polystyrene latex with an unswollen size of 40 nm exposed quiescently for about 60 hours time (in the absence of any external shear forces) to ethyl benzene as swelling agent; A – pure latex, B – swollen latex with ethyl benzene on top, C – image of swollen latex with perpendicularly transmitted light, D – image of swollen latex with oblique transmission; the bars indicates 50 μm.

competitively in the different phases. Because some of these processes cannot be investigated independently, the conventional approach to determine the kinetics of emulsion polymerization relies on many kinetic model assumptions followed by the identification of the model parameters from experimental data.[25] One the other hand, the development of powerful and reliable techniques for the simulation of the behavior of atoms and molecules has allowed the determination of the kinetics of individual, completely independent processes in emulsion polymerization.[22,26,27] The main advantage of this new approach is the precise control of the ‘‘experimental’’ conditions, which allows the identification of the true effect of individual phenomena on the reaction kinetics. One step forward in the development of a complete as possible model of emulsion polymerization consists in the consideration of various phenomena at different time and/or space scales by means of multiscale integration techniques.[28]

The following example is thought just to illustrate the differences between both modeling strategies. Let us consider polymerization inside particles with CM being 5 mol/L and constant during the time of the simulation as a result of the replenishment of monomer from the continuous phase. The rate coefficient of propagation (kp) and the molecular weight (wM) of the monomer be 240 L/(mol s) and 100 g/mol, respectively. Thus, the propagation frequency is 1200 s-1 inside the particles. Exemplarily, let us now assume that the radicals are generated in the continuous phase and they enter the particles at a rate (ρa) of 1 s-1. Finally, instantaneous termination is assumed when 2 radicals are present in the same particle, that is, the particles obey zero-one kinetics. Following the ‘‘conventional’’ modeling approach, the chain length of the polymer formed inside the particles is given by Equation (3)

$$L = \int_{t}^{t+\tau_{\mathrm{entry}}} \frac{k_p C_M}{w_M} dt = \frac{k_p C_M \tau_{\mathrm{entry}}}{w_M} \qquad (3)$$

where L is the average chain length of the polymer formed inside the particles, and τ_{entry} is the time between two consecutive entry events ($\tau_{\mathrm{entry}} = 1/\rho_a$). Using the values of the example, it is found that the average chain length of the polymer formed is 12. With this simple deterministic approach it is not possible to determine the chain length distribution, so the result is a perfectly monodisperse distribution of chain lengths. It is possible to improve the deterministic model by considering a full set of population balance equations, that is, solving mass balance equations for the living and dead chains of all chain lengths.[29] Now it is possible to obtain polydisperse chain length distributions but the complexity of the model is enormously increased since the size of the system is of the order of magnitude of the largest chain length. This value is usually unknown a priori but typically quite large for emulsion polymerization. It is possible to reduce the computational load by using approximation functions for describing the chain length distribution, which is the basis of the Galerkin method[30] used by the commercial software PREDICI. Clearly, these methods do not consider random fluctuations at a molecular scale and therefore they always predict the same results for the same recipe and process conditions. Such behavior is, however, according to the experimental results presented in the previous sections, not always the case in emulsion polymerization.

On the other hand, a ‘molecular’ stochastic simulation considers that all entry and all propagation events follow a Poisson distribution with a mean value given by the reciprocal of the corresponding rate. Running these simulations leads for different particles typically to slightly different results scattering around an average (cf. Figure 8). This is due to the random nature of all the processes taking place at a molecular scale, including for example Brownian motion, temperature and velocity fluctuations, rotation of non-symmetrical molecules, etc. Stochastic simulation methods not only allow the prediction of

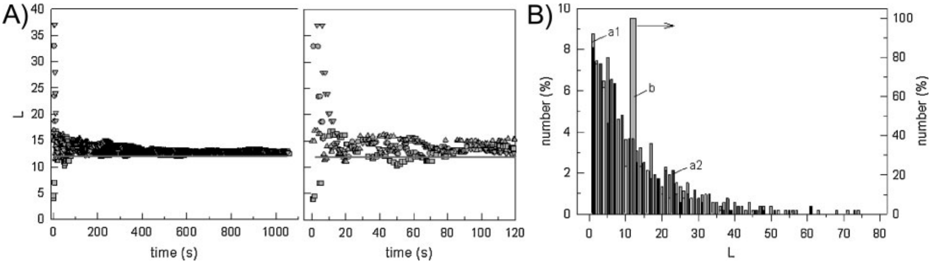

Figure 8.
Average chain length (A) and cumulative chain lengths distributions (B) after 1000 seconds obtained using the conventional and the molecular approach for the emulsion polymerization of a single particle; $k_p = 240$ L/(mol · s), $C_M = 5$ mol/L, $\rho_a = 1\ s^{-1}$, $w_M = 100$ g/mol; A – line is the result of conventional, deterministic modeling and the points are the results of four molecular modeling runs representing four different particles, the right graph is a zoom of the first 2 minutes; B – a1, a2 chain lengths distributions of two molecular modeling runs, b is a monodisperse distribution (L = 12) as the result of deterministic modeling (Equation 3).

the variability of a given process, but also result in a closer approximation to the real situation.

The second example is related to the rate of radical capture by or radical entry in the particles. In the previous example, an arbitrary rate of radical entry was assumed. However in practice, the determination of the kinetics of radical capture requires the use of a model of the process. In this case, we can also use a conventional or a molecular approach. The conventional approach consists in assuming a kinetic expression for the rate of radical capture, as a function of radical diffusion coefficient and particle size (linear, squared, etc.), and then testing the model against experimental data.[25] In the molecular approach, a technique called Brownian Dynamics simulation is used for simulating the behavior of the radical under the conditions of the process, and then, after a certain number of replicas, a distribution of capture times are obtained which can be used to determine the rate of radical capture.[26] The distribution of capture times obtained is a Poisson-type distribution, so the rate can be easily determined from the reciprocal of the average capture time. Using Brownian Dynamics simulation it was found that the rate of radical capture strongly depends on the concentration of polymer particles in the system. Thus, for highly diluted systems an almost linear dependence of the rate of capture on particle size is observed, but for more concentrated systems (>0.1% volume fraction), a second or higher order dependence on particle size is evidenced.

Now, a big step forward is attained in the modeling of the first example if Brownian Dynamics simulation is used to determine the rate of radical capture and then, the process is simulated using the molecular approach. This is the basis of multiscale integration. Multiscale modeling has been used to study secondary nucleation during seeded emulsion polymerization, and it was particularly possible to investigate the effect of the locus of radical generation. This effect could hardly be evaluated using conventional modeling, but it turned out to be relatively simple to investigate using the molecular approach.[31] Another interesting example is the modeling of particle swelling during emulsion polymerization. Swelling is the net result of two opposite processes, absorption and desorption of monomer molecules by and from the polymer particles, from and to the continuous phase. A multiscale modeling approach may consist in the determination of monomer absorption and desorption rates by means of Brownian Dynamics simulation, followed by the simulation of the consumption of monomer by propagation either inside the particles or in the continuous phase. As a result of this

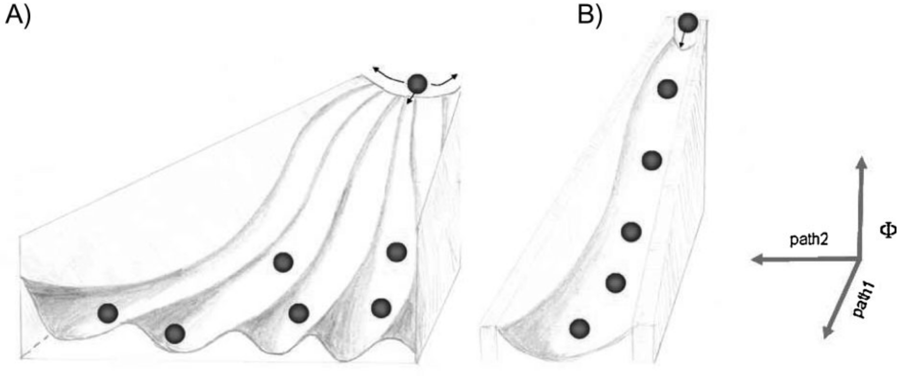

Figure 9.
Illustration of scatter in chemical reactions by means of multiple (A) or single (B) reaction pathways in dependence on the driving force for the conversion, in case A there are two paths whereas in B there is no path 2; the driving force Φ is defined as overall energy difference between initial and final state.

multiscale approach, it is possible to determine the change in polymer particle size during emulsion polymerization under any particular conditions.[22] The results obtained describe very precisely the behavior observed experimentally by different researchers, demonstrating the potential of multiscale molecular modeling for simulating in detail an emulsion polymerization process.

Conclusion

Emulsion polymerization kinetics appears to be an ideal example illustrating the interchange between determinism and indeterminism of physical and chemical processes as discussed by Schrödinger: "The relative margin of indeterminacy (the spread of the statistics) is large for small systems but for large systems the margin is usually, though not necessarily, small, which makes it possible to account for the apparent determinacy of inanimate Nature."[32] For emulsion polymerization the small system is the individual particle with a low number of monomer molecules and even a still lower number of growing radicals inside and the large system is the overall reaction volume consisting of about 10^{21} particles per m^3. This discussion is all about the relation between N, C_M, and $\bar{n}$ which are together with the propagation rate constant combined in Equation (1).

Due to the heterogeneous nature emulsion polymerization, especially the ab-initio, non-seeded version, is prone to statistical scatter which opens multiple reaction pathways as illustrated by image A of Figure 9.

In the sense of Schrödinger the base of any law of nature is chance or random cause.[33] The experimental data of Figures 1–3 seem to prove that the transition from the initial to the final state of an emulsion polymerization is predictable or affected by low scatter (cf. image B of Figure 9) only if the driving force (Φ) is high enough.

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