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(Mini)emulsion Polymerization Kinetics Using Oil-Soluble Initiators

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ABSTRACT: The mechanisms involved in the initiation of (mini)emulsion polymerization using oil-soluble initiators were investigated by means of a first principles model. The model was assessed by comparing its predictions with experimental data. The model shows that desorption of initiator radicals from droplets and particles is the key mechanism controlling the kinetics of miniemulsion polymerization and particle growth in emulsion polymerization. For these systems, the contribution of the fraction of the initiator dissolved in the aqueous phase is minor. In ab initio emulsion polymerization, the fraction of the initiator dissolved in the aqueous phase was the main contributor to micellar nucleation.

Introduction

Both oil-soluble and water-soluble initiators are employed in emulsion polymerization, the water-soluble being the most frequently used. Oil-soluble initiators have a niche in conventional emulsion polymerization in applications that require minimization of polymerization in the aqueous phase.[1−3] In addition, they are increasingly used in the rapidly expanding field of miniemulsion polymerization.[4,5] Oil-soluble initiators provided a better control over polymerization than water-soluble initiators in the atom transfer radical polymerization with simultaneous reverse and normal initiation process conducted in miniemulsion.[6] They are advantageous producing narrow particle size distributions in miniemulsion polymerization stabilized by a well-defined amphiphilic gradient copolymer.[7] Silanol-functionalized[8] and hybrid acrylic−polyurethane[9] latexes have been synthesized by miniemulsion polymerization using oil-soluble initiators. Highly water-insoluble initiators can also be used to limit diffusional degradation of the monomer droplets in miniemulsion polymerization.[10] The choice of the initiator type (oil-soluble vs water-soluble) affects particle morphology in miniemulsion polymerization.[11]

The polymerization in dispersed media using oil-soluble initiators has been recently reviewed.[12] Although oil-soluble initiators are mainly located in the polymer particles, they show some water-solubility. Thus, the partition coefficient of AIBN at 50 °C is 115,[13] namely for a 50 wt % solids content system, more than 99% of the initiator is in the polymer particles. Therefore, most of the radicals are formed in the polymer particles. However, the efficiency of these radicals to start polymerization is low because they are restricted to a very small volume, and hence the probability of termination is high. A consequence of this low efficiency is that for equivalent concentrations of initiator, the kinetics of emulsion polymerization using oil-soluble initiators is slower than that using water-soluble ones. This has been the origin of a long lasting debate in literature about the predominant source of effective radicals in emulsion polymerization initiated with oil-soluble initiators. Some authors[13−15] considered that the probability of bimolecular termination of the pair of radicals newly formed in a polymer particle is that high that most of them terminate just after being formed, and consequently, they do not contribute to the kinetics of the process. Therefore, according to these authors the initiator dissolved in the aqueous phase is the main source of effective radicals. Other authors[16−19] consider that the rate of desorption of the initiator radicals is significant, and hence a substantial fraction of the newly formed radicals are separated before suffering bimolecular termination.

Much effort has been devoted to elucidate which is the main source of effective radicals in these systems. Simulations carried out by Asua et al.[18] suggested that radicals formed in the polymer particles are the main source of effective radicals. Opposite results were obtained also by simulation by Nomura and Fujita.[20] The opposite conclusions reached by Asua et al.[18] and Nomura and Fujita[20] were due to the different mechanisms included in their models. While Asua et al.[18] considered that the initiator radicals produced in the polymer particles may undergo desorption in competition with propagation and termination, Nomura and Fujita[20] wrongly considered that once the initiator radicals were formed they were indistinguishable form the existing ones, and hence desorption should occur through a chain transfer reaction followed by diffusion out of the particle. Because chain transfer is much slower than diffusion, the mechanism proposed by Nomura and Fujita[20] underestimated the rate of desorption of the initiator radicals. In addition, both models considered the desorption process in a rather simplistic way.

Experimental evidence is also conflicting. Seeded emulsion polymerizations carried out at varying organic phase/aqueous phase volume ratios showed that for the rest of conditions constant, the polymerization rate per polymer particle increased when the organic/aqueous volume ratio increased, namely when the amount of initiator dissolved in the aqueous phase per polymer particle decreased.[21] This is evidence against a dominant formation of radicals in the aqueous phase. On the other hand, these results are consistent with a mechanism in which the radicals are mainly produced in the oil-phase. Lou and Schork[22] reported that miniemulsion polymerization of butyl acrylate initiated with an oil-soluble initiator (2,2′-azobisisobutyronitrile, AIBN) proceeded slower in the presence of a water-soluble radical scavenger ($NaNO_2$) than in the absence of the scavenger. The effect being stronger for smaller polymer particles. This was considered as an indication that the radicals

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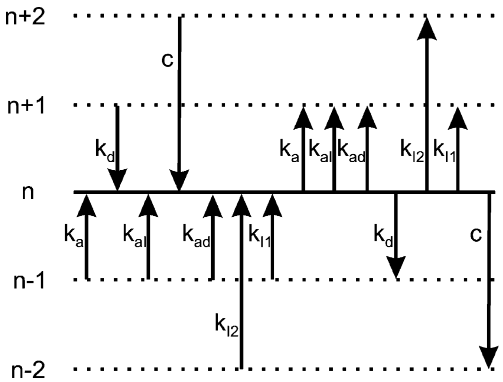

Figure 1. Processes leading to a change in the number of radicals of a particle.

formed in the aqueous phase contributed to the polymerization. Blythe et al.[23] found that the addition of a small amount of a water-soluble inhibitor (dipotassium 2,5-dihydroxy-1,4-benzenedisulfonate) produced large enhancements in both the rate of polymerization and the number of particles created in the miniemulsion polymerization of styrene initiated with an oil-soluble initiator (2,2′-azobis(2-methylbutyronitrile, AMBN). It was speculated that a possible reason for this result is that the driving force for desorption of initiator radicals may be enhanced by the creation of a radical sink in the aqueous phase, due to the presence of the inhibitor. Blythe et al.[19] reported that the polymerization rate of miniemulsion polymerization was greater than that of the conventional emulsion polymerization when an oil-soluble initiator (AMBN) was used. The reverse trend was found when a water-soluble initiator was used. This was interpreted as evidence that the most likely source of radicals when using oil-soluble initiators in miniemulsion polymerization is the oil phase. More recently, Suzuki and Nomura[24] failed to explain their experimental results using a model in which the initiator dissolved in the aqueous phase was the main source of effective radicals and they attributed the failure to the preferential formation of radicals in the polymer particles.

This article is an attempt to clarify this issue by analyzing the experimental findings by means of a new mathematical model based on rigorous polymer particle population balances in which the exit rate coefficients for radicals formed from the initiator and by chain transfer to monomer were calculated with a first principles model.

Mathematical Model

Let us consider a population of N_p polymer particles with a distribution of radicals per particle, such as N_0, N_1, N_2, ..., which are the number of particles with zero, one, two, ..., radicals. The number of radicals in a particular particle varies during the process due to radical entry and exit, bimolecular termination and formation of radicals by decomposition of the initiator within the polymer particle. Figure 1illustrates the processes leading to a change in the number of radicals of a particle containing n radicals. The population balance of particles with n radicals is

$$\begin{aligned}\frac{dN_n}{dt} = {} & k_a[P_{tot}]_w N_{n-1} + k_{aI(n-1)}[I^*]_w N_{n-1} + \\ & k_{ad(n-1)}N_{n-1}[M^*]_w + k_{I2(n-2)}N_{n-2} + k_{I1(n-1)}N_{n-1} + \\ & k_{d(n+1)}(n+1)N_{n+1} + c(n+2)(n+1)N_{n+2} - (k_a[P_{tot}]_w + \\ & k_{aI(n)}[I^*]_w + k_{ad(n)}[M^*]_w + k_{I2(n)} + k_{I1(n)} + k_{d(n)}n + \\ & cn(n-1))N_n \quad (1)\end{aligned}$$

for $n = 0, 1, 2, ...$, where k_a is the rate coefficient for entry of radicals (different from initiator and monomeric radicals) from the aqueous phase, $[P_{tot}]_w$ is the concentration of these radicals in the aqueous phase, $k_{aI(n)}$ is the rate coefficient for entry of initiator radicals from the aqueous phase, $[I^*]_w$ is the concentration of the initiator radicals in the aqueous phase, $k_{ad(n)}$ is the rate coefficient for entry of monomeric radicals from the aqueous phase, $[M^*]_w$ is the concentration of monomeric radicals in the aqueous phase, $k_{I2(n)}$ is the pseudo-first-order rate coefficient for the formation of a pair of radicals in polymer particles containing n radicals, and $k_{I1(n)}$ is the pseudo-first-order rate coefficient for the formation of single radicals in polymer particles containing n radicals. $k_{d(n)}$ is the desorption rate coefficient of monomeric radicals, and c is the pseudo-first-order rate coefficient for bimolecular termination ($c = k_t/\nu_p N_A$, where ν_p is the volume of the polymer particle and N_A is Avogadro's number). It was considered that single radicals were formed by desorption of one of the two radicals formed by decomposition of an initiator molecule. This desorption was considered to occur immediately after the initiator decomposition.

Let $R_{dI(n)}$ be the rate of desorption of initiator radicals from particles with n radicals and $R_{I(n)}$ the rate of radical generation of initiator radicals in these particles. Then, the probability of desorption of initiator radicals from these particles is

$$P_{I(n)} = \frac{R_{dI(n)}}{R_{I(n)}} \quad (2)$$

where the rate of radical generation in particles with n radicals is

$$R_{I(n)} = 2fk_I[I_2]_p \nu_p N_A N_n \quad (3)$$

where f is the efficiency factor for initiator decomposition, k_I is the rate coefficient for initiator decomposition, and $[I_2]_p$ is the concentration of initiator in the polymer particles.

The fraction of particles already containing n radicals that lose the two radicals formed by initiator decomposition is $P_{I(n)}^2$ and that that lose one radical is $2P_{I(n)}(1 - P_{I(n)})$. The fraction that does not lose any of the initiator radicals produced is $(1 - P_{I(n)})^2$. Therefore

$$k_{I1(n)}N_n = fk_I[I_2]_p \nu_p N_A N_n \times 2P_{I(n)}(1 - P_{I(n)}) \quad (4)$$

$$k_{I2(n)}N_n = fk_I[I_2]_p \nu_p N_A N_n (1 - P_{I(n)})^2 \quad (5)$$

Equations 2−5 define $k_{I1(n)}$ and $k_{I2(n)}$ in terms of the initiator decomposition rate and the rate of desorption of initiator radicals.

The rate of desorption of initiator radicals and the rate coefficient for entry of initiator radicals from the aqueous phase are (see Appendix I for their deduction):

$$R_{dI(n)} = \lambda_{I(n)} \frac{\gamma_I N_A N_n}{\eta_{I(n)} m_I} \quad (6)$$

$$k_{aI(n)} = \lambda_{I(n)} \quad (7)$$

where $\lambda_{I(n)}$, γ_I, $\eta_{I(n)}$, and m_I are defined in Appendix I.

Desorption of monomeric radicals has been recently discussed in terms of the net rate of desorption, namely, desorption minus reabsorption.[25] This is useful for the calculation of the average number of radicals per particle, however for the calculation of the distribution of particles with n radicals (eq 1) it is more convenient to consider desorption and reabsorption separately. The rate coefficient for desorption of monomeric radicals is

$$k_{\mathrm{d}(n)} = \lambda_{\mathrm{M}(n)} \frac{\gamma_{\mathrm{M}} N_{\mathrm{A}}}{\eta_{\mathrm{M}(n)} m_{\mathrm{M}}} \tag{8}$$

and the rate coefficient for reabsorption of monomeric radicals is

$$k_{\mathrm{ad}(n)} = \lambda_{\mathrm{M}(n)} N_{\mathrm{A}} \tag{9}$$

where $\eta_{\mathrm{M}(n)}$ and $\lambda_{\mathrm{M}(n)}$ can be calculated with eqs I-4 and I-11 (Appendix I) using the parameters of the monomeric radicals (m_{M}, D_{MP}, D_{Mh}, $D_{M\mathrm{w}}$). On the other hand γ_{M} is given by

$$\gamma_{\mathrm{M}} = \left(k_{\mathrm{tr}}^{\mathrm{mon}} [\mathrm{M}]_{\mathrm{p}} \frac{1}{\nu_{\mathrm{p}} N_{\mathrm{A}}} \right) / D_{\mathrm{MP}} \tag{10}$$

where $k_{\mathrm{tr}}^{\mathrm{mon}}$ is the rate coefficient for chain transfer to monomer.

Equation 1 involves the concentration in the aqueous phase of radicals different from initiator and monomeric radicals ($[\mathrm{P_{tot}}]_{\mathrm{w}}$) and those of the initiator, $[\mathrm{I}^*]_{\mathrm{w}}$, and monomeric radicals $[\mathrm{M}^*]_{\mathrm{w}}$. The mass balances for these radicals in the aqueous phase are

$$\frac{\mathrm{d}[\mathrm{P_{tot}}]_{\mathrm{w}}}{\mathrm{d}t} = k_{\mathrm{pI}}[\mathrm{I}^*]_{\mathrm{w}}[\mathrm{M}]_{\mathrm{w}} + k_{\mathrm{p}}^{1}[\mathrm{M}^*]_{\mathrm{w}}[\mathrm{M}]_{\mathrm{w}} - 2k_{\mathrm{tw}}[\mathrm{P_{tot}}]_{\mathrm{w}}^{2} - 2k_{\mathrm{tIw}}[\mathrm{P_{tot}}]_{\mathrm{w}}[\mathrm{I}^*]_{\mathrm{w}} - 2k_{\mathrm{tw}}^{1}[\mathrm{M}^*]_{\mathrm{w}}[\mathrm{P_{tot}}]_{\mathrm{w}} - k_{\mathrm{a}}[\mathrm{P_{tot}}]_{\mathrm{w}} \frac{N_{\mathrm{p}}}{N_{\mathrm{A}} V_{\mathrm{w}}} \tag{11}$$

$$\frac{\mathrm{d}[\mathrm{I}^*]_{\mathrm{w}}}{\mathrm{d}t} = 2fk_{\mathrm{I}}[\mathrm{I}_2]_{\mathrm{w}} + \sum_{n=0}^{\infty} \frac{R_{\mathrm{dI}(n)}}{N_{\mathrm{A}} V_{\mathrm{w}}} - \sum_{n=0}^{\infty} k_{\mathrm{aI}(n)} \frac{N_n [\mathrm{I}^*]_{\mathrm{w}}}{N_{\mathrm{A}} V_{\mathrm{w}}} - k_{\mathrm{pI}}[\mathrm{I}^*]_{\mathrm{w}}[\mathrm{M}]_{\mathrm{w}} - 2k_{\mathrm{tIw}}[\mathrm{P_{tot}}]_{\mathrm{w}}[\mathrm{I}^*]_{\mathrm{w}} - 2k_{\mathrm{tIw}}^{1}[\mathrm{I}^*]_{\mathrm{w}}^{2} - 2k_{\mathrm{tw}}^{11}[\mathrm{I}^*]_{\mathrm{w}}[\mathrm{M}^*]_{\mathrm{w}} \tag{12}$$

$$\frac{\mathrm{d}[\mathrm{M}^*]_{\mathrm{w}}}{\mathrm{d}t} = \sum_{n=1}^{\infty} k_{\mathrm{d}(n)} \frac{nN_n}{N_{\mathrm{A}} V_{\mathrm{w}}} - \sum_{n=0}^{\infty} k_{\mathrm{ad}(n)} \frac{N_n}{N_{\mathrm{A}} V_{\mathrm{w}}} [\mathrm{M}^*]_{\mathrm{w}} - k_{\mathrm{p}}^{1}[\mathrm{M}^*]_{\mathrm{w}}[\mathrm{M}]_{\mathrm{w}} - 2k_{\mathrm{tw}}^{1}[\mathrm{M}^*]_{\mathrm{w}}[\mathrm{P_{tot}}]_{\mathrm{w}} - 2k_{\mathrm{tw}}^{11}[\mathrm{M}^*]_{\mathrm{w}}^{2} - 2k_{\mathrm{tw}}^{11}[\mathrm{I}^*]_{\mathrm{w}}[\mathrm{M}^*]_{\mathrm{w}} \tag{13}$$

where $[\mathrm{M}]_{\mathrm{w}}$ and $[\mathrm{I}_2]_{\mathrm{w}}$ are the concentrations in the aqueous phase of monomer and initiator, respectively, V_{w} is the volume of the aqueous phase, k_{pI} and k_{p}^{1} are the propagation rate coefficients of the initiator and monomeric radicals, respectively, k_{tIw} and k_{tw}^{1} are the termination rate coefficients of initiator and monomeric radicals, with long radicals in the aqueous phase, and k_{tw}^{11} is the termination rate coefficients of two small radicals (initiator and monomeric radicals) in the aqueous phase.

Equations 1, 11, 12, and 13 were solved under quasi steady-state conditions ($\mathrm{d}x/\mathrm{d}t = 0$) by means of an iterative approach, which included (i) assuming a distribution of particles with n radicals; (ii) calculating the rate parameters in Figure 1; (iii) calculating $[\mathrm{P_{tot}}]_{\mathrm{w}}$, $[\mathrm{I}^*]_{\mathrm{w}}$ and $[\mathrm{M}^*]_{\mathrm{w}}$ from eqs 11−13; (iv) calculating N_n from eq 1 for a maximum number of radicals per particle m. Step iv involved an iteraction to find the value of m. Steps ii−iv were repeated until convergence.

Assessment of the Model. In order to assess the model, the kinetic data reported by Luo and Schork[22] on the miniemulsion polymerization of butyl acrylate initiated with AIBN were considered. In those experiments, two levels of emulsifier were used, with and without a water-soluble free radical scavenger ($\mathrm{NaNO_2}$). The results are summarized in Table 1, together with the predictions of the model. The values of the parameters of the model were taken from literature. In some cases, the reported range is ample, and hence it was a relatively easy task to fit one of the experiments. However, the consideration of the experiments with and without water-soluble free radical scavenger was a demanding test for the model because no parameter was specifically related to this aspect. The parameters used in the simulations are given in Table 2. They were chosen from the range of values reported in literature to exactly fit the experiment carried out with a high surfactant concentration and without scavenger. These parameters were used to predict the values of the average number of radicals per particle under the other conditions. The effect of the particle size was specifically accounted for in the model and the effect of the water-soluble free radical scavenger was simulated by making zero the concentrations of radicals ($[P_{\mathrm{tot}}]_{\mathrm{w}}$; $[\mathrm{I}^*]_{\mathrm{w}}$ and $[\mathrm{M}^*]_{\mathrm{w}}$) in the aqueous phase. Table 1 shows that model predicted remarkably well the effects of both the particle size and the presence of a water-soluble scavenger. This is a strong indication that the model included the most important mechanisms.

According to the model the main effect of the water-soluble scavenger was to avoid reentry of the desorbed initiator radicals.

The effect of the water-soluble scavenger showed the importance of the reactions occurring in the aqueous phase, but it was not conclusive about the role played by the radicals formed in the polymer particles and in the aqueous phase. In order to shed light on the role of the fraction of the initiator in the aqueous phase, simulations were carried out by making zero (i) the concentration of initiator in the aqueous phase and (ii) the concentration of initiator in the polymer particles. Table 3 compares these results with that obtained for the real system (high surfactant without scavenger in Table 1), in which the initiator partitions between both phases.

Table 3 shows that $\bar{n}$ was only marginally affected by making zero the concentration of initiator in the aqueous phase. On the other hand, a substantially smaller $\bar{n}$ was obtained when only the initiator contained in the aqueous phase was considered. This shows that the main source of radicals was the initiator dissolved in the polymer particles. Combination of these results with those obtained in the presence of inhibitor support the idea that desorption of initiator radicals from the polymer particles play a key role in the (mini)emulsion polymerization using oil-soluble initiators. In order to check this idea, the desorption of initiator radicals was made negligible, maintaining the rate of production of radicals in both the polymer particles and in the aqueous phase. The average number of radicals per particle was $\bar{n} = 0.133$, substantially smaller than that calculated considering radical desorption ($\bar{n} = 0.235$). This demonstrates that the desorption of initiator radicals is the key mechanism in (mini)emulsion polymerization initiated by oil-soluble initiators.

The discussion above regards polymerization in droplets and particles. This represents miniemulsion polymerization and particle growth in conventional emulsion polymerization. However, micellar nucleation which strongly affects kinetics in ab initio conventional emulsion polymerization was not discussed. Luo and Schork[22] reported that in the emulsion polymerization of butyl acrylate initiated with AIBN typical latex particles were formed. However, when a water-soluble free radical scavenger was used, latex particles were not nucleated and polymerization proceed in bulk in the big monomer droplets. Radical generation in a monomer swollen micellar system with and without water-soluble scavenger was simulated by means of the model, assuming that the radius of the micelles was 5 nm. The number

Table 1. Summary of the Results of Luo and Schork[22]

	without scavenger					with scavenger ($NaNO_2$)				
surfactant level	conversion	$N_p \times 10^{-16}$ (particles)	$d_p{}^a$ (nm)	$\bar{n}_{exp}$	$\bar{n}_{model}$	conversion	$N_p \times 10^{-16}$ (particles)	$d_p{}^a$ (nm)	$\bar{n}_{exp}$	$\bar{n}_{model}$
high	0.13	2.26	191.2	0.235	0.235	0.20	3.23	169.5	0.0169	0.0495
low	0.17	1.0	250.2	0.334	0.316	0.19	1.23	234.0	0.103	0.115

[a] Monomer swollen particle diameter estimated from N_p and the formulation

Table 2. Parameter Values Used in the Simulations

parameter	value	ref
k_p (L/mol s)	2.25×10^4	26
k_{pI} (L/mol s)	2.25×10^4	
k_p^1 (L/mol s)	9.0×10^4	27
$k_t = k_{tw}$ (L/mol s)[a]	1.1×10^8	26
$k_{tI}^1 = k_{tIw}^1$ (L/mol s)	2×10^9	28
$k_t^{11} = k_{tw}^{11}$ (L/mol s)	3.3×10^8	29, 30
$k_{tI} = k_{tIw}$ (L/mol s)	$\sqrt{k_{tI}^1 k_t}$	
$k_t^1 = k_{tw}^1$ (L/mol s)	$\sqrt{k_t^{11} k_t}$	
k_I (s^{-1})	4.8×10^{-7}	31
k_a (L/mol s)	1.0×10^6	32
k_{tr}^{mon} (L/mol s)	7.42×10^{-1}	33
m_I	115	13
m_M	480	34
$[M]_p$ (mol/L)	4.52	34
$[M]_w$ (mol/L)	9.38×10^{-3}	34
$[I_2]_p$ (mol/L)	1.337×10^{-2}	22
$D_{Ip} = D_{Mp}$ (m^2/s)	5×10^{-11}	
$D_{Iw} = D_{Mw}$ (m^2/s)	1.2×10^{-9}	
$D_{Ih} = D_{Mh}$ (m^2/s)	1×10^{-10}	
δ_1 (nm)	5	
f	0.6	

[a] Gel effect was taken into account according to ref 35.

Table 3. Simulations Carried out Making Zero the Initiator Concentration in the Aqueous Phase and in the Polymer Particles

$[I_2]_p$	$[I_2]_w$	$\bar{n}$
1.337×10^{-5}	1.163×10^{-7}	0.235
1.337×10^{-5}	0	0.214
0	1.163×10^{-7}	0.132

of micelles was calculated from the amount of emulsifier used in the formulation and the aggregation number of 30.[36] The values of the average number of radicals in micelles, $\bar{n}_m$, were calculated as an indication of the probability of nucleation. It was found that $\bar{n}_m = 1.17 \times 10^{-3}$ and $\bar{n}_{scavenger} = 3.8 \times 10^{-7}$, namely micellar nucleation was slow with oil-soluble initiators and very unlikely in the presence of a water-soluble scavenger. According to the model most the radicals formed in the micelles terminated. The ratio between the desorbed initiator radicals and the initiator radicals generated in the aqueous phase (which is an indication of the relative importance of the fraction of the initiator dissolved in the aqueous phase) was 0.19; therefore, most of the radicals were formed in the aqueous phase. Therefore, the fraction of the initiator dissolved in the aqueous phase was the main contributor to micellar nucleation in conventional emulsion polymerization. These predictions explained the experimental results reported by Blythe et al.[19] When using oil-soluble initiators, the polymerization rate of miniemulsion polymerization was faster than that of the emulsion polymerization because the probability of droplet nucleation is much higher than that of micellar nucleation. On the other hand, water-soluble initiator are very efficient nucleating micelles, and hence, the polymerization rate was higher in conventional emulsion polymerization.

Conclusions

The mechanisms involved in the initiation of (mini)emulsion polymerization using oil-soluble initiators were investigated by means of a mathematical model based on rigorous polymer particle population balances in which the exit rate coefficients for radicals formed from the initiator and by chain transfer to monomer were calculated with a first principles model. The model predicted remarkably well the effects of both the particle size and the presence of a water-soluble scavenger on the average number of radicals per particle for the miniemulsion polymerization of butyl acrylate initiated with AIBN. The model shows that desorption of initiator radicals was the key mechanism in controlling the kinetics of the process. Desorption (and reentry) is an efficient way of generating single radicals in the polymer particles. The model was also used to analyze micellar nucleation in conventional emulsion polymerization using oil-soluble initiators. It was found that most of the radicals formed in the micelles terminated. The fraction of the initiator dissolved in the aqueous phase was the main contributor to micellar nucleation.

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Appendix I

Desorption of Initiator Radicals. Let us consider a particle with n radicals in which two initiator radicals are formed by thermal decomposition of an initiator molecule. The initiator radicals will perform a diffusive random walk through the amorphous structure of the monomer swollen polymer particle until they either react in the polymer particle (by either propagation or bimolecular termination) or desorb from the polymer particle. Similar processes occur in all particles containing n radicals. In practice, one cannot handle the information associated with each of the individual trajectories of the initiator radicals in every polymer particle, and some kind of average is needed. This average is given by the behavior of a single polymer particle representative of the population of polymer particles with n radicals.

In order to develop the equations describing the behavior of the representative particle, it is useful considering the similarity between the present case and the Monte Carlo simulations carried out to model the diffusion of small molecules in polymers. In these simulations, the diffusion paths of a series of small molecules are computed and then averaged to estimate a diffusion rate coefficient. In the present case, the trajectory of each initiator radical is the equivalent to one of the Monte Carlo paths. Therefore, the average of all the trajectories results in a concentration profile of initiator radicals (such as that illustrated in Figure 2), which can be modeled using a Fickian equation. This concentration profile depends on the relative rates of generation, diffusion, propagation, and termination of initiator

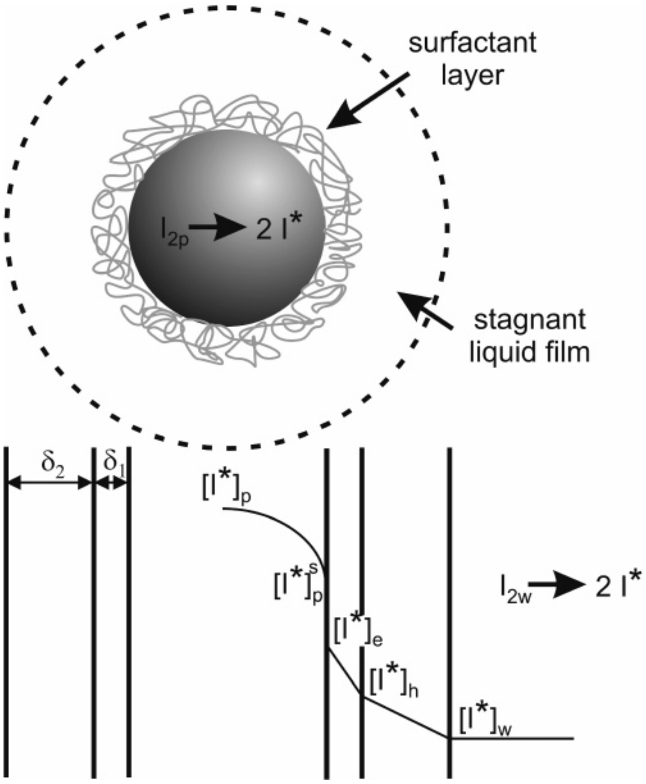

Figure 2. Schematic representation of the resistances to initiator radical diffusion in a polymer particle.

radicals in the polymer particles, and on the resistances offered by the hairy layer formed by the steric surfactant (if present) and by the stagnant liquid film around the polymer particle.

Under steady-state conditions, the material balance of initiator radicals in polymer particles containing n radicals is

$$D_{\mathrm{Ip}}\frac{1}{r^2}\frac{\mathrm{d}\left(r^2\frac{\mathrm{d}[\mathrm{I}^*]_{\mathrm{p}}}{\mathrm{d}r}\right)}{\mathrm{d}r}+2fk_{\mathrm{I}}[\mathrm{I}_2]_{\mathrm{p}}=\left(k_{\mathrm{pI}}[\mathrm{M}]_{\mathrm{p}}+2\left(\frac{k_{\mathrm{tI}}n+k_{\mathrm{tI}}^{1}}{\nu_{\mathrm{p}}N_{\mathrm{A}}}\right)\right)[\mathrm{I}^*]_{\mathrm{p}}\ (\mathrm{mol/L\ s})\quad(\text{I-1})$$

where D_{Ip} is the diffusion rate coefficient of the initiator radicals in the polymer particles, $[\mathrm{I}^*]_{\mathrm{p}}$ is the concentration of initiator radicals in the polymer particles, k_{pI} is the propagation rate constant of the initiator radicals, $[\mathrm{M}]_{\mathrm{p}}$ is the concentration of monomer in the polymer particles, and k_{tI} is the termination rate constant of the initiator radicals in the polymer particles.

Equation I-1 can be integrated analytically giving the following concentration profile of monomeric radicals

$$\frac{[\mathrm{I}^*]_{\mathrm{p}}}{[\mathrm{I}^*]_{\mathrm{p}}^{\mathrm{s}}}=\frac{R}{r}\left(1-\frac{\gamma_{\mathrm{I}}}{\eta_{\mathrm{I}(n)}[\mathrm{I}^*]_{\mathrm{p}}^{\mathrm{s}}}\right)\frac{\sinh(\mathrm{r}\sqrt{\eta_{\mathrm{I}(n)}})}{\sinh(R\sqrt{\eta_{\mathrm{I}(n)}})}+\frac{\gamma_{\mathrm{I}}}{\eta_{\mathrm{I}(n)}[\mathrm{I}^*]_{\mathrm{p}}^{\mathrm{s}}}\quad(\text{I-2})$$

where $[\mathrm{I}^*]_{\mathrm{p}}^{\mathrm{s}}$ is the concentration of initiator radicals at the surface of the polymer particles (see Figure 2), and

$$\gamma_{\mathrm{I}}=(2fk_{\mathrm{I}}[\mathrm{I}_2]_{\mathrm{p}})/D_{\mathrm{Ip}}\quad(\text{I-3})$$

$$\eta_{\mathrm{I}(n)}=\left(k_{\mathrm{pI}}[\mathrm{M}]_{\mathrm{p}}+2\left(\frac{k_{\mathrm{tI}}n+k_{\mathrm{tI}}^{1}}{\nu_{\mathrm{p}}N_{\mathrm{A}}}\right)\right)/D_{\mathrm{Ip}}\quad(\text{I-4})$$

where the term $(k_{\mathrm{tI}}n+k_{\mathrm{tI}}^{1})$ appears because the initiator radical may terminate with the n radicals already in the polymer particle and with the other initiator radical formed by initiator decomposition.

The net rate of exit of initiator radicals (i.e., that accounting for both desorption and reabsorption of radicals) from polymer particles containing n radicals is as follows:

$$R_{\mathrm{exit1}}(n)=4\pi R^2D_{\mathrm{Ip}}\left(-\frac{\mathrm{d}[\mathrm{I}^*]_{\mathrm{p}}}{\mathrm{d}r}\right)_{r=R}N_n=4\pi RD_{\mathrm{Ip}}(R\sqrt{\eta_{\mathrm{I}(n)}}\coth R\sqrt{\eta_{\mathrm{I}(n)}}-1)\left[\frac{\gamma_{\mathrm{I}}}{\eta_{\mathrm{I}(n)}}-[\mathrm{I}^*]_{\mathrm{p}}^{\mathrm{s}}\right]N_n\ (\mathrm{mol/s})\quad(\text{I-5})$$

Similarly, the material balance for initiator radicals in the hairy layer surrounding the polymer particles led to the following rate of exit of initiator radicals through the hairy layer:

$$R_{\mathrm{exit2}}(n)=4\pi R\frac{(R+\delta_1)}{\delta_1}D_{\mathrm{Ih}}([\mathrm{I}^*]_{\mathrm{e}}-[\mathrm{I}^*]_{\mathrm{h}})N_n\ (\mathrm{mol/\ s})\quad(\text{I-6})$$

where δ_1 is the thickness of the hairy layer, D_{Ih} is the diffusion rate coefficient of the initiator radicals in the hairy layer, $[\mathrm{I}^*]_{\mathrm{h}}$ is the concentration of monomeric radicals at the interface between the hairy layer and the aqueous phase, and $[\mathrm{I}^*]_{\mathrm{e}}$ is related to the concentration of initiator radicals at the surface of the polymer particles by means of a partition coefficient, m_{I}

$$[\mathrm{I}^*]_{\mathrm{p}}^{\mathrm{s}}=m_{\mathrm{I}}[\mathrm{I}^*]_{\mathrm{e}}\quad(\text{I-7})$$

The material balance in the stagnant layer surrounding the polymer particle led to the rate of exiting initiator radicals going through this layer:

$$R_{\mathrm{exit3}}(n)=4\pi(R+\delta_1)\frac{(R+\delta_1+\delta_2)}{\delta_2}D_{\mathrm{Iw}}([\mathrm{I}^*]_{\mathrm{h}}-[\mathrm{I}^*]_{\mathrm{w}})N_n\ (\mathrm{mol/\ s})\quad(\text{I-8})$$

where δ_2 is the thickness of the stagnant liquid film, D_{Iw} is the diffusion rate coefficient in the aqueous phase, and $[\mathrm{I}^*]_{\mathrm{w}}$ the concentration of monomeric radicals in the aqueous phase.

Under steady-state conditions, $R_{\mathrm{exit}}=R_{\mathrm{exit1}}=R_{\mathrm{exit2}}=R_{\mathrm{exit3}}$, and combination of eqs I-5 to I-8 yields the following equation for the net rate of exit of initiator radicals from particles with n radicals.

$$\begin{aligned}R_{\mathrm{exit}}(n)&=\left(\frac{a_1}{1+a_2+a_3}\right)\times\left(\frac{\gamma_1}{\eta_{\mathrm{I}(n)}m_{\mathrm{I}}}-[\mathrm{I}^*]_{\mathrm{w}}\right)N_n\qquad(\mathrm{mol/s})\\a_1&=\frac{4\pi D_{\mathrm{Iw}}(\mathrm{R}+\delta_1)(R+\delta_1+\delta_2)}{\delta_2}\\a_2&=\frac{D_{\mathrm{Iw}}}{D_{\mathrm{Ih}}}\frac{(R+\delta_1+\delta_2)\delta_1}{R\delta_2}\\a_3&=\frac{D_{\mathrm{Iw}}}{D_{\mathrm{Ip}}m_{\mathrm{I}}}\frac{(R+\delta_1)(R+\delta_1+\delta_2)}{R\delta_2(R\sqrt{\eta_{\mathrm{I}(n)}}\coth R\sqrt{\eta_{\mathrm{I}(n)}}-1)}\end{aligned}\quad(\text{I-9})$$

Assuming that $\delta_1 \ll R$ and $\delta_2 \gg R^{25}$

$$R_{\mathrm{exit}}(n) = \lambda_{\mathrm{I}(n)}\left(\frac{\gamma_{\mathrm{I}}}{\eta_{\mathrm{I}(n)} m_{\mathrm{I}}} - [\mathrm{I}^*]_{\mathrm{w}}\right) N_n \ (\mathrm{mol/s}) \qquad \text{(I-10)}$$

where

$$\lambda_{\mathrm{I}(n)} = \frac{4\pi D_{\mathrm{Iw}} R}{1 + \frac{D_{\mathrm{Iw}}}{D_{\mathrm{Ih}}}\frac{\delta_1}{R} + \frac{D_{\mathrm{Iw}}}{D_{\mathrm{Ip}} m_{\mathrm{I}}}\frac{1}{(R\sqrt{\eta_{\mathrm{I}(n)}}\,\mathrm{coth} R\sqrt{\eta_{\mathrm{I}(n)}} - 1)}} \qquad \text{(I-11)}$$

Equation I-10 gives the net rate of desorption of initiator radicals, namely considering both desorption and reabsorption of initiator radicals. However, for the population balance of particles with *n* radicals (eq 1), it is more convenient to separate desorption from reabsorption. Therefore, the rate of desorption of initiator radicals is

$$R_{\mathrm{dI}(n)} = \lambda_{\mathrm{I}(n)} \frac{\gamma_{\mathrm{I}}}{\eta_{\mathrm{I}(n)} m_{\mathrm{I}}} N_n \qquad \text{(I-12)}$$

and the rate of reabsorption is

$$R_{\mathrm{rabI}(n)} = \lambda_{\mathrm{I}(n)} [\mathrm{I}^*]_{\mathrm{w}} N_n \qquad \text{(I-13)}$$

Therefore, the rate coefficient for entry of initiator radicals from the aqueous phase (eq 1, Figure 1) is

$$k_{\mathrm{aI}(n)} = \lambda_{\mathrm{I}(n)} \qquad \text{(I-14)}$$

References and Notes

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