Particle State Dependent Radical Desorption and its Effect on the Kinetics of Emulsion Polymerization

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Abstract

Radical desorption from polymer particles is a kinetic event peculiar of the emulsion polymerization process. A careful modeling of this phenomenon is highly valuable in order to achieve accurate predictions of polymerization rate and average properties of molecular weight. In this work, radical desorption is described accounting for an aspect fully neglected in previous modeling literature. Specifically, particle state dependent desorption coefficients are used instead of a single average coefficient and the corresponding rate expressions are developed and applied to the solution of the well-known Smith-Ewart equations. Parametric model simulations show that the higher level of detail introduced in the description of radical desorption improves the accuracy of the predicted values of the average number of radicals per particle, especially in the cases of high desorption rate and slow reactions in the aqueous phase.

Keywords: emulsion polymerization, radical desorption, modeling, compartmentalization.

1. Introduction

Due to the major role which radical desorption from polymer particles may play in determining the reaction rate in emulsion polymerization, several models have been developed for the description of this process step.[1] Two main types of modeling approaches have been proposed so far: fully deterministic and based on Brownian dynamics.[2] Even though the latter models have proven to be more general, we focus here on the former type of models. As a matter of fact, such models have been widely applied to emulsion polymerization, are well assessed and involve parameters with readily understandable physical meaning. Most of the deterministic models assume that the desorbing species is a one-unit radical originated by chain transfer reaction to a monomer molecule or to some other small molecule (e.g., chain transfer agent). In order to overcome the limitations of the model proposed by Nomura,[3] which neglects aqueous phase reactions and assumes the system to be strictly zero-one, a more general model has been developed by Asua *et al.*[4]. This probabilistic model is able to explain experimental results which Nomura's model could not. Claiming that Asua's model did not properly distinguish between entry given by reabsorption of previously desorbed monomeric radicals (re-entry) and that of initiator-derived or thermally-generated radicals, Casey *et al.*[5] developed a kinetic model which leads to equations for the average number of radicals per particle $\bar{n}$ and for the rate of re-entry ρ_{re} in terms of rate coefficients of the elementary processes of the reaction and of measurable concentrations. With respect to Asua's results, however, the equations derived suffer stronger limitations: the system is considered to be zero-one and propagation of desorbed monomeric radicals in the aqueous phase is neglected. Later on, Barandiaran and Asua[6] devoted a full paper to demonstrate the complete equivalence of a kinetic approach such as that by Casey *et al.*[5] and the probabilistic approach by Asua *et al.*[4].

All of the works mentioned above deal with radical desorption from polymer particles by considering a single, average value of the desorption coefficient, which is independent of the particle state (i.e., of the number of contained radicals). A more recent paper by Asua[7] describes desorption as dependent from particle state; however the overall rate of radical exit is then obtained by summing over all particle states and only a single coefficient for net desorption is then calculated from this rate, not providing in this sense a real distinction from previous models. By "net desorption", as referred to in this publication, it is meant desorption minus reabsorption of monomeric radicals. An even more recent work by the same author and coworkers[8] develops a model where desorption and reabsorption are considered separately and modeled as functions of particle state. However, the implications of such an approach in comparison to previous ones are not discussed. Interestingly, this paper recognizes that for the calculation of the distribution of particles with n radicals by population balance equations it is more convenient to consider desorption and reabsorption separately, rather than combined into net desorption.

In the present work, the relevancy of correctly describing desorption by particle state dependent parameters is discussed, and important considerations are made on the desorption terms which appear in the classical Smith-Ewart equations. This is done starting from the definition given by Asua *et al.*[4] of the rate of desorption R_{dn} from particles containing a given number of radicals. Namely, two equivalent models aimed to express particle state dependent desorption coefficients are proposed. Such expressions are then used in the Smith-Ewart equations: it is shown that the use of a single, average value of the desorption coefficient may lead to significant errors in the prediction of the average number of radicals per particle, especially when the probability of reaction of desorbed monomeric radicals in the aqueous phase is negligible with respect to that of their re-entry into polymer particles. In this case, the use of particle state dependent desorption coefficients is required, and an

effective, simplified expression for the evaluation of these parameters is derived in this work. Finally, the full equivalence between the kinetic model by Casey *et al.*[5] and the probabilistic approach by Asua *et al.*[4] is further confirmed in a simple as well as general way.

2. Desorption from Particles in a Given State

In the probabilistic approach developed by Asua *et al.*[4], the rate of desorption from particles in a given state n, R_{dn}, is calculated as the rate of production of monomeric radicals in particles *already* containing n radicals times the probability that the resulting radicals desorb from such particles. The rate of production of monomeric radicals in particles containing n radicals is in turn given by the concentration of the same particles, N_n, times the frequency of any reaction causing a monomeric radical to appear in these particles, namely, chain transfer to a small molecule or re-entry of a previously desorbed radical. Accordingly, the following equation can be written:[4]

$$R_{dn} = k_{fm}C_m n N_n P_n + \rho_{re}N_n P_{n+1} \tag{1}$$

where k_{fm} is the rate constant of the chain transfer to monomer reaction, C_m is the monomer concentration in the particles, ρ_{re} is the frequency of reabsorption of exited monomeric radicals into the particles, and P_n is the probability of desorption (instead of propagation or termination) of a monomeric radical from a particle containing n radicals. The latter two parameters are defined as in Equations 2 and 3, respectively:

$$\rho_{re} = k\bar{n}(1 - \beta) \tag{2}$$

$$P_n = \frac{k_{dm}}{k_{dm} + k_p^1 C_m + 2c^1(n-1)} \tag{3}$$

In Equation 2, k is the average desorption frequency, $\bar{n}$ is the average number of radicals per particle, the product $k\bar{n}$ gives the average frequency of desorption and β is the probability for a desorbed monomeric radical of undergoing a reaction in the aqueous phase. Such probability is given by:

$$\beta = \frac{k_{t,aq}[T\cdot] + k_{p,aq}^1[M]_{aq}}{k_{re}\dfrac{N_T}{N_A} + k_{t,aq}[T\cdot] + k_{p,aq}^1[M]_{aq}} \tag{4}$$

where $k_{t,aq}$ and $k_{p,aq}^1$ are the bimolecular termination and propagation rate constants for a monomeric radical in the aqueous phase, $[T\cdot]$ and $[M]_{aq}$ are the concentrations of radicals and of monomer in the same phase, k_{re} is the rate constant for re-entry of monomeric radicals into polymer particles, and N_A is Avogadro's constant. Constant k_{re} is related to the frequency of re-entry by:

$$\rho_{re} = k_{re}[M\cdot]_{aq} \tag{5}$$

where $[M\cdot]_{aq}$ is the concentration of the monomeric free radicals in the aqueous phase. In Equation 3, k_{dm} and k_p^1 are the rate of diffusion out of a particle and the propagation rate coefficient for a monomeric radical, respectively, and c^1 is the pseudo-first order rate coefficient for bimolecular termination of the monomeric radical in the polymer particle:

$$c^1 = \frac{k_t^1}{2N_A V_P} \tag{6}$$

where V_P is the volume of the swollen polymer particle, and k_t^1 is the bimolecular termination rate constant for the low molecular weight, rapidly-diffusing monomeric radical (usually greater than that calculated as an average from the overall termination rate in a bulk, $k_t[R \cdot]^2$, where $R \cdot$ is the total radical concentration).

Equations 2 to 5 above refer to radicals of monomeric length. Looking in particular at Equation 4, it must be pointed out that propagation of such a radical leads of course to its disappearance but to the appearance of a longer active species, which will be easily absorbed by polymer particles and further propagate in the particle phase. Such irreversible re-entry $\rho_{re,irr}$ has rigorously to be taken into account in the calculation of the global entry coefficient.

Note that the probability P_{n+1} appears in the last term of Equation 1, since re-entry of a monomeric radical into a particle in state *n* causes the particle to pass on to state *n*+1. Re-desorption of such a radical would get the particle back to state *n*. It is therefore clear that, given this definition of R_{dn}, the rate of desorption from particles in state *n* does not coincide with the rate of disappearance of particles in state *n* due to the same process.

If the rate of desorption from particles in state *n* is instead calculated as the rate of production of monomeric radicals in particles in the same state *(after* the appearance of the desorbing species) times the probability for the monomeric radical to actually desorb, Equation 1 has to be slightly modified:

$$R'_{dn} = k_{fm}C_m n N_n P_n + \rho_{re}N_{n-1}P_n \tag{7}$$

With this new definition, the rate of desorption from state n particles is actually equal to the rate of disappearance of particles in state n as a consequence of desorption. This is of course also equal to the rate of production of particles in state n-1 from particles in state n.

The two definitions of R_{dn} and R'_{dn} lead to the same overall rate of desorption as summation upon all particle states:

$$k\bar{n}N_T = \sum_{n=0}^{\infty} R_{dn} = \sum_{n=1}^{\infty} R'_{dn} \tag{8}$$

where k is the average desorption frequency mentioned above (Equation 2). However, the definition of R'_{dn} is more convenient because its expression can be compared to the desorption terms knN_n and $k(n+1)N_{n+1}$ in the Smith-Ewart equations as ordinarily written:

$$\frac{dN_n}{dt} = \rho N_{n-1} - [\rho + kn + cn(n-1)]N_n + k(n+1)N_{n+1}$$
$$+ c(n+2)(n+1)N_{n+2} \tag{9}$$

with:

$$c = \frac{k_t}{2N_A V_P} \tag{10}$$

In Equation 9, k is the average desorption frequency, and ρ is the overall frequency of entry of initiator-derived, thermally-generated and previously desorbed monomeric radicals:

$$\rho = \rho_I + \rho_{th} + \rho_{re} \tag{11}$$

As discussed above, a term $\rho_{re,irr}$ (stemming from radicals desorbed and propagated in the aqueous phase) should be added in the calculation of the overall frequency of entry. However in this paper the contribution of all terms of ρ except for ρ_{re} is parameterized and such rigor would not change the conclusions of the work.

2.1 Particle State Dependent Desorption Coefficients: Model 1. The term $-knN_n$ in the Smith-Ewart equations (Equation 9) represents the rate of consumption of particles in state n due to desorption, which corresponds to a production rate of particles in state n-1. As already mentioned, this term can be expressed through the rate of desorption from particles in state n, R'_{dn}, defined by Equation 7. While it is generally assumed in the term $-knN_n$ that the desorption coefficient is independent of particle state and it is assigned an average value, this is not true *a priori*. Accordingly, a particle state dependent desorption frequency parameter k_n has to be considered and its expression is obtained by imposing the following equality:

$$k_n n N_n = R'_{dn} = k_{fm}C_m n N_n P_n + \rho_{re}N_{n-1}P_n \tag{12}$$

Combining Equations 12 and 2 one obtains:

$$k_n = \frac{k_{fm}C_m n N_n P_n + k\bar{n}(1-\beta)N_{n-1}P_n}{nN_n} \tag{13}$$

An expression of the average value k in terms of particle distributions N_n and desorption probabilities P_n can be obtained from Equation 8 taking advantage of R'_{dn} as given by Equation 7 and expressing ρ_{re} through Equation 2:

$$k = k_{fm} C_m \frac{\sum_{n=1}^{\infty} \frac{n P_n N_n}{N_T}}{\bar{n}\left[1 - (1-\beta)\sum_{n=1}^{\infty} \frac{P_n N_{n-1}}{N_T}\right]} \quad (14)$$

This is exactly the expression previously derived by Asua *et al.*[4]. Now, if one substitutes Equation 14 for k in Equation 13, the following expression for k_n is finally obtained:

$$k_n = k_{fm} C_m P_n \left[1 + (1-\beta)\frac{N_{n-1}}{n N_n} \cdot \frac{\sum_{n=1}^{\infty} \frac{n P_n N_n}{N_T}}{1 - (1-\beta)\sum_{n=1}^{\infty} \frac{P_n N_{n-1}}{N_T}}\right] \quad (15)$$

which, in general, is a function of the particle state *n*. Notably, the relationship between the average desorption coefficient k and the corresponding particle state dependent k_n is readily worked out through Equations 8 and 12 as follows:

$$k = \frac{\sum_{n=1}^{\infty} k_n n N_n}{\bar{n} N_T} \quad (16)$$

The Smith-Ewart equations are rigorously written introducing the particle state dependent desorption frequencies given by Equation 15:

$$\frac{dN_n}{dt} = \rho N_{n-1} - [\rho + k_n n + cn(n-1)]N_n + k_{n+1}(n+1)N_{n+1}$$
$$+ c(n+2)(n+1)N_{n+2} \quad (17)$$

Equations 15 and 17, along with Equations 2, 3, 11 and 16, constitute a system of $3n+3$ equations, which can be readily solved iteratively.

For the sake of clarity, it has to be pointed out that the desorption coefficients k and k_n above are by no means elemental rate coefficients but lumped parameters resulting from the combination of a number of processes. These parameters allow to express the desorption process in terms of frequencies of radical exit from polymer particles. k and k_n are in fact frequencies (per radical and per particle, dimension s^{-1}) at which a monomeric radical appears to exit the particle phase, such that the products $k_n n N_n$ and $k \bar{n} N_T$ express a total rate of desorption (from state-n particles and from all particles, respectively) to the water phase.

2.2 Particle State Dependent Desorption Coefficients: Model 2. The Smith-Ewart equations worked out considering particle state dependent desorption coefficients (Equation 17) in combination with the definition of entry and desorption given by Equations 11 and 7, respectively, imply the following assumptions:

- an entry event takes place whenever a radical of any type enters a particle, independent of its fate within the particle;

- a desorption event occurs whenever a (monomeric) radical exits a particle, independent of its origin (chain transfer in the same particle or re-entry from the aqueous phase). This feature is consistent with the definitions of entry and exit (or desorption) variously adopted in previous literature including Asua *et al.*[4] and Casey *et al.*[5].

Now, considering Equation 12 and substituting it in Equation 17, the latter can be re-written as follows:

$$\frac{dN_n}{dt} = (\rho - \rho_{re}P_n)N_{n-1} - \left[\rho - \rho_{re}P_{n+1} + k_{fm}C_m n P_n + cn(n-1)\right]N_n$$
$$+ k_{fm}C_m(n+1)P_{n+1}N_{n+1} + c(n+2)(n+1)N_{n+2}$$

(18)

Defining the two new quantities:

$$\rho_n' = \rho - \rho_{re}P_{n+1} = \rho_I + \rho_{th} + \rho_{re}(1 - P_{n+1}) \tag{19}$$

$$k_n' = k_{fm}C_m P_n \tag{20}$$

the Smith-Ewart equations can be written in the following form, which is alternative to Equation 17:

$$\frac{dN_n}{dt} = \rho_{n-1}'N_{n-1} - [\rho_n' + k_n'n + cn(n-1)]N_n + k_{n+1}'(n+1)N_{n+1}$$
$$+ c(n+2)(n+1)N_{n+2} \tag{21}$$

Once more, particle state dependent coefficients are involved. The particle state dependent entry coefficient defined by Equation 19 states that a radical has "effectively" entered a particle only when its fate is different from re-desorption. If a previously desorbed radical re-enters a state-n particle (which is turned into a state-$n+1$ particle) and then desorbs again (therefore with probability P_{n+1}), this event is considered as "neutral" (i.e., the particle state is not considered to be changed). This conceptual model for entry is reasonable, since a radical entering from the aqueous phase (homogeneous phase) and exiting again to the same phase without undergoing any other reactions leaves the particle and the whole polymerization system unchanged. Accordingly, since this entry-exit event of a monomeric radical is neglected as a whole, it does not have to be accounted for when calculating the desorption rate. Consistently, the newly defined particle state dependent desorption coefficients (Equation 20) account uniquely for exit of radicals originated by chain transfer to

monomer, thus at their first desorption event (desorption of "newborn" monomeric radicals). Subsequent re-entry and re-desorption is then computed as "ineffective re-entry".

In general, coefficients ρ'_n and k'_n are a function of n through P_n (i.e., the probability of a radical of re-exiting a particle after re-entry or of desorbing after chain transfer depends on how many radicals are in the same particle). Particularly, ρ'_n are functions of ρ_{re}, whose evaluation requires the knowledge of k, as shown in Equation 2, and therefore of k_n, according to Equation 16.

In order to estimate the parameters of Model 2, the following correlation between ρ_{re} and the "effective" average desorption coefficient k' has been determined:

$$\rho_{re} = \frac{k'\bar{n}\,(1-\beta)}{1-(1-\beta)\sum_{n=1}^{\infty}\frac{P_n N_{n-1}}{N_T}} \tag{22}$$

with:

$$k' = \frac{\sum_{n=1}^{\infty} k'_n n N_n}{\bar{n}N_T} \tag{23}$$

The product $k'\bar{n}N_T$ represents the overall rate of desorption of "newborn" monomeric radicals (radicals generated by chain transfer to monomer at their first desorption event) from the particle phase to the water phase.

Details about the mathematical derivation of Equation 22 are given in the Appendix. Equations 19, 20 and 21, along with Equations 22, 3, 11 and 23, constitute a system of $4n+3$ equations, which, again, can be solved iteratively.

2.3 Equivalence of the two Models. Although desorption and entry parameters are defined and evaluated in different ways, the same predictions of particle state distribution N_n have to be provided by the two models presented above: this equivalence is numerically checked in this subsection. Namely, both the models have been run using the parameter values reported in Table 1 while assuming constant input values of β $(= 0.1)$ and $c = c^1$ $(= 20 \ s^{-1})$ as well as of the overall entry contributions from initiator-derived and thermally-generated radicals $(\rho_A = \rho_I + \rho_{th} = 0.01 \ s^{-1})$. The model results are compared in Table 2.

TABLE 1

TABLE 2

The equivalence between the two models is apparent. In the same table, the difference between k_n and k_n' values at corresponding n is also reported: not only the portion of re-desorbing radicals $(k_n - k_n')$ is notable with respect to that of the "newborn" desorbing ones, but this fraction increases with n (i.e., the k_n values increase while the k_n' values change very slightly as n increases). The mathematical relationship between desorption coefficients k_n and k_n' and their averages k and k' is reported in the Appendix. As expected, the two models predict also an identical value of the overall re-entry frequency $(\rho_{re} = 3.86 \ 10^{-2} \ \text{s}^{-1})$.

The complete equivalence of the two models is thus fully confirmed. Therefore, the selection of one specific model can be made based on convenience of use. Although Model 2 involves a larger number of equations ($4n+3$, versus $3n+3$ for Model 1), only $2n+3$ equations need to be solved inside the iterative loop for both models. Therefore, Model 1 and Model 2 are fully equivalent also from the point of view of computational complexity. On the other hand, Model 1 provides an average desorption coefficient (Equation 16) directly comparable

to that of the particle state independent parameter conventionally considered in the Smith-Ewart equations. Accordingly, this model has been selected to develop a model comparison aimed at clarifying the role of particle state dependent desorption coefficients. This comparison is reported in the section 3.

2.4 Meaning of the desorption parameters. Considering the behavior of the desorption coefficients k_n and k'_n in Table 2, the fact that the dependency of k'_n on particle state is weak while that of k_n is strong can be explained by their definition. k'_n expresses a desorption frequency (per radical) as a result of a chain transfer to monomer event followed by exit (with a certain probability P_n), see Equation 20. It has been previously shown[4] that probability P_n is most often weakly dependent upon particle state: therefore, k'_n is also a weak function of the particle state. k_n, instead, includes the contribution of redesorption. This contribution becomes increasingly important, compared to the desorption of "newborn" radicals, at increasing particle states. This is because particles in state n containing a monomeric radical which can re-desorb originate, via reabsorption, from particles in state n-1. These are normally much more numerous than particles in state n in systems with a low average number of radicals per particle. This is increasingly true at increasing n and is represented by the ratio N_{n-1}/nN_n increasing strongly with n, which implies the coefficient k_n to correspondingly increase at constant (or quasi-constant) k'_n (cf. the relationship between these two parameters, equation B of the Appendix).

For the sake of clarity, it has to be pointed out that all the desorption coefficients in this work (k, k_n, k' and k'_n) are associated to desorption of radicals from the particle phase to the water phase, i.e. to a flow of radicals out of the particles R_{out}. In this sense, their meaning is analogous to e.g. the parameter k_d employed by Asua *et al.*[4]. Reabsorption represents a flow of radicals R_{in} in the opposite direction (from the water phase to the particles). Net

desorption, as e.g. employed by Asua,[7] is obtained by subtracting reabsorption from desorption: $R_{net} = R_{out} - R_{in}$. By expressing desorption and reabsorption through the desorption and re-entry coefficients, one obtains:

$$R_{net} = k\bar{n}N_T - \rho_{re}N_T = k\bar{n}N_T - k\bar{n}(1-\beta)N_T = \beta k\bar{n}N_T \qquad (24)$$

If net desorption is expressed through a desorption coefficient k_{net} such that:

$$R_{net} = k_{net}\bar{n}N_T \qquad (25)$$

it is then apparent that:

$$k_{net} = \beta k \qquad (26)$$

Note that k_{net} has an equivalent meaning as e.g. the parameter k_d employed by Asua[7]. The physical limits of k_{net} are correct: for $\beta = 1$ (no re-entry), $k_{net} = k$, i.e. net desorption corresponds to desorption; for $\beta = 0$ (all desorbed radicals re-enter), $k_{net} = 0$, i.e. net desorption is zero.

This clarification about desorption and net desorption has been felt necessary due to some confusion existing in the previous literature related to the two parameters here referred to as k and k_{net}. For example, Asua[7] criticizes the equation for the calculation of k_d employed by Asua *et al.*[4] (equation 16 of that paper) as erroneous and with inconsistent limits in the cases of $\beta = 0$ and $\beta = 1$. The new (approximate) expression derived by the same Author is identical except for a coefficient β (cf. equation I-7 of this paper[7]). Actually, both equations are correct, once the correct physical meaning is assigned to the two coefficients, the first one

associated to an overall desorption and the second one to a net desorption flow. Also, in the extensive review on desorption by Hernandez and Tauer[1], Table I reports all desorption coefficients previously derived in the relevant literature, without however appropriately distinguishing between desorption and net desorption.

3. Assessment of the Proposed Model

In order to study the impact on model predictions of particle state dependent desorption coefficients, the relative error between the average number of radicals per particle calculated considering ($\bar{n}_C$) or neglecting ($\bar{n}_N$) this dependence can be defined as follows:

$$\varepsilon = 100 \cdot \frac{\bar{n}_C - \bar{n}_N}{\bar{n}_C} \tag{27}$$

where $\bar{n}_C$ is calculated through Equations 15 and 17, thus considering particle state dependent desorption frequencies k_n, and $\bar{n}_N$ is calculated through Equations 9 and 14, thus assuming a single, average value of k for all of the particle states (prior-art approach).

In Figure 1, the relative error ε is reported as a function of $\bar{n}_C$ (varied by modifying the entry parameter ρ_A previously defined) at different values of the parameter β.

FIGURE 1

Once more the parameter values in Table 1 have been used, while the bimolecular termination frequency c has been set again equal to 20 s^{-1}. Frequency ρ_{re} has been calculated through Equation 2 and the bimolecular termination frequency c^1 has been assumed equal to c. Note that $\beta = 0$ and $\beta = 1$ correspond to the two limits of complete re-entry and no re-entry,

respectively. Even though β is a function of $\bar{n}$ through the radical concentration in the aqueous phase, $[T \cdot]$, constant β values have been used for simplicity. With respect to this assumption, it is worth noting that smaller values of ρ_A, corresponding to smaller values of $\bar{n}_C$ in Figure 1, imply a lower concentration of radicals $[T \cdot]$ in water phase, thus lower β values. This means that, at decreasing $\bar{n}_C$ values in the figure, the trajectory describing the evolution of a real polymerization would actually cross the curves at constant β moving from higher to lower β values.

Figure 1 shows that the error in the prediction of $\bar{n}$ increases at decreasing β values, achieving maximum values in the limit of complete re-entry. Approaching this limit, significant values of the error are obtained (up to 180%) in a wide region of $\bar{n}$ values lower than 0.5. Accordingly, in these conditions a model accounting for particle state dependent desorption coefficients is necessary for an accurate kinetic description of the system. In the opposite limit of $\beta = 1$, the predicted relative error ε is virtually zero at all $\bar{n}$ values. This feature can be readily understood by considering the expression of k_n (Equation 15) for $\beta = 1$:

$$k_n^{(\beta=1)} = k_{fm} C_m P_n \tag{28}$$

Equation 28 states that, in absence of re-entry, the frequency (per active chain) of desorption from a state n particle is simply given by the frequency of chain transfer (per active chain) times the desorption probability of the resulting monomeric radical. Since, as shown by Asua et al.[4], probability P_n decreases slowly at increasing n values (at least when the particle volume V_P is not too small), if the maximum particle state n_{max} is low enough (i.e., $\bar{n}$ is not too high), P_n can be considered independent of particle state and equal to P_1. Thus:

$$k_n^{(\beta=1)} \cong k_{fm} C_m P_1 \qquad \forall n \geq 1 \qquad\qquad (29)$$

Namely, desorption coefficients k_n become approximately particle state independent and equal to the average desorption coefficient k in the limit $\beta = 1$, thus resulting in a negligible error.

At high $\bar{n}$ values the error tends to disappear for all β values. This is also expected because in this limit $\bar{n}$ becomes independent of desorption[9] (at least for values of the ratio $m = k/c \leq 1$) and dependent only upon the ratio between the entry frequency ρ_A and the bimolecular termination frequency c. Accordingly, $\bar{n}$ values are not sensitive to inaccuracies in the evaluation of the desorption frequency.

The fact that the probabilities P_n are approximately constant at low enough n_{max} values (low $\bar{n}$) and that $\bar{n}$ is not sensitive at high values to inaccuracies in the desorption frequency evaluation, can suggest a simplified general expression for the desorption coefficients. This is obtained from Equation 15 by assuming $P_n \cong const = P_1, \forall n \geq 1$:

$$k_n = k_{fm} C_m P_1 \left[1 + \frac{(1-\beta)P_1}{1 - (1-\beta)P_1} \cdot \frac{\bar{n} N_{n-1}}{n N_n} \cdot \right] \qquad\qquad (30)$$

It is readily verified that Equation 30 satisfies the condition imposed by Equation 16. In fact, averaging the k_n coefficients given by Equation 30 in agreement with Equation 16, one obtains:

$$k = \frac{k_{fm} C_m P_1}{1 - (1-\beta)P_1} \qquad\qquad (31)$$

which is the average desorption frequency given by Equation 14 when $P_n = P_1, \forall n \geq 1$ is assumed.

The accuracy of the approximation implied in Equation 30 can be verified by studying the error introduced in the calculation of the average number of radicals per particle, $\bar{n}$. To this purpose, the relative error ε_A is defined:

$$\varepsilon_A = 100 \cdot \frac{|\bar{n}_C - \bar{n}_A|}{\bar{n}_A} \tag{32}$$

where $\bar{n}_A$ and $\bar{n}_C$ are calculated through the approximated (Equation 30) and complete (Equation 15) expressions, respectively, as before coupled to the Smith-Ewart equations (Equation 17). In Figure 2, error ε_A is plotted versus $\bar{n}_C$ for several β values; all model parameter values are the same adopted for Figure 1 and reported in Table 1.

FIGURE 2

The error is seen to be negligible at all $\bar{n}_C$ values, and the effectiveness of the approximate expression (Equation 30) is confirmed.

Turning back to the analysis of Figure 1, it can be seen that the error ε approaches zero at $\bar{n}_C \to 0$ for all values of β. Actually, for $\rho_A \to 0$ any model must predict $\bar{n} \to 0$, no matter how desorption is accounted for, and this has to result in an absolute error $|\bar{n}_C - \bar{n}_N| \to 0$. Moreover, in the same limit, only desorption from state one particles is important and, accordingly, a single desorption frequency k_1 has to be calculated, which must coincide with the average desorption frequency. This implies that the two approaches (i.e., accounting for and neglecting the dependency of desorption coefficients upon particle state) necessarily

converge one to the other at $\rho_A \to 0$. However, since at $\rho_A \to 0$ the quantity $\bar{n}_C \to 0$, the relative error ε going to zero requires the difference $|\bar{n}_C - \bar{n}_N|$ to approach zero faster than $\bar{n}_C$. This actually happens at all values of β.

In Figure 3a and 3b, the relative error ε is plotted as a function of $\bar{n}_C$ for $\beta = 0$ and $\beta = 0.5$, respectively, and several values of the bimolecular termination frequency c.

FIGURE 3

The values of all the other model parameters are again those reported in Table 1. These figures show that, moving from low ($c = 0.1$ s^{-1}) to high ($c = 20$ s^{-1}) c values, the maximum error increases; however, the error decays more rapidly at increasing $\bar{n}$ values. Moving further to higher c values, ($c = 100$ s^{-1}), the maximum error starts decreasing again, and the decay at increasing $\bar{n}$ values is even faster (i.e., ε becomes smaller at all $\bar{n}$ values). It is noteworthy that the error on $\bar{n}$ introduced neglecting particle state dependency of desorption coefficients is significant for low β values in a wide range of values of the bimolecular termination frequency, c, and of $\bar{n}$ itself. For greater β values, the uncertainties affecting some of the model parameters (such as the entry rate ρ_A or the transport coefficient for exit k_{dm}) can lead to errors of comparable, if not greater, magnitude. Accordingly, the use of the detailed model for desorption developed in this work is not relevant in gaining accuracy on the calculated average number of radicals per particle in this case.

Real Case Study: Methyl Methacrylate at 50°C. Due to the rather high water solubility of methyl methacrylate, radical desorption plays a major role in determining the kinetics of its emulsion polymerization. Although the average number of radicals per particle in this system is often smaller than 0.5, especially at low conversion, the zero-one system

assumption is not valid (with the exception of the extreme case of particles less than 10 nm in swollen radius), since desorption is more probable than bimolecular combination when a monomeric radical re-enters a particle already containing a growing chain[5]. Accordingly, the "instantaneous termination" assumption does not hold, and a model allowing for the existence of particles of state higher than one is required. Considering the water phase kinetics, it has been shown[5] that re-entry is the most probable fate of exited monomeric radicals ($\beta \rightarrow 0$) at all possible initiator concentrations and typical concentrations of polymer particles ($N_T \geq 10^{12}$ cm^{-3}).

The results shown above suggest that high desorption frequencies and low β values make this system a good candidate for testing the usefulness of the detailed desorption model here developed on a real system of significant importance. The relative error ε between the average number of radicals calculated neglecting and considering particle state dependent desorption coefficients (cf. Equation 27) is shown in Figure 4 at different values of the swollen particle radius r_P.

FIGURE 4

As in the previous figures, the average number of radicals per particle is varied in a wide interval by modifying the entry frequency ρ_A. Values of $\bar{n}$ reported in the literature for this system extend across a very wide range, from magnitudes in the order of 10^{-2} to several hundred (at high conversion).[10-12] The parameter values selected for methyl methacrylate have been calculated from the parameters (cf. Table I in Casey *et al.*[5]) and relations reported by Casey *et al.*[5], and are reported in Table 3 (r_P independent quantities) and Table 4 (r_P dependent quantities).

TABLE 3

TABLE 4

The only exception is represented by the bimolecular termination frequency c, calculated from the average bulk value of the bimolecular termination rate constant $k_t = 6.9 \cdot 10^{10}$ cm^3 mol^{-1} s^{-1} through Equation 10.[13] The β values have been calculated through Equation 4 assuming a particle concentration of 10^{13} cm^{-3}, an initiator concentration $[I] = 5 \cdot 10^{-6}$ mol cm^{-3} and low initiator efficiency:[10] $[T \cdot] = (2k_I[I] / k_{t,aq})^{1/2}$. Although, as already discussed, β is actually dependent upon $\bar{n}$, considering a single value of β for each particle radius introduces small errors since the aqueous phase reaction of monomeric radicals is negligible at all initiator concentrations (i.e., β values are always very close to zero). This also justifies the rough calculation of β mentioned above.

In Figure 4, significant values of ε have been obtained in a wide range of $\bar{n}_C$ values smaller than 0.5, justifying the need for the more detailed model in this region. Note that Figure 4 has been obtained assuming a value of c corresponding to the average bulk value of the rate coefficient k_t in the solution of the Smith-Ewart equations (Equations 9 and 17). However, bimolecular terminations between short and long chain radicals can be very significant in emulsion polymerization and higher values of the coefficient c are required for a correct evaluation of $\bar{n}$. For our purposes, it is sufficient to repeat the calculations at the highest limit of bimolecular termination values (i.e., assuming $c = c^l$): the true values will stand somewhere in the middle and will be in general a function of $\bar{n}$. The results obtained assuming $c = c^l$ are shown in Figure 5.

FIGURE 5

It can be seen that relevant differences with respect to Figure 4 arise only in the range $0.45 < \bar{n} < 0.7$. This is expected, since at low $\bar{n}$ values bimolecular termination doesn't play any significant role due to high radical compartmentalization, while at high $\bar{n}$ values ε must go to zero, as already discussed. Since the results are practically unchanged within the region $\bar{n} < 0.45$, where the error is the largest, the need of a model accounting for particle state dependent desorption coefficients is confirmed for this case of practical interest.

4. Comparison between Kinetic and Probabilistic Model

As already mentioned in the Introduction, the complete equivalence of Casey's kinetic approach[5] and Asua's probabilistic one[4] has been demonstrated by Barandiaran and Asua.[6] However, this has been done by writing a rather complicated balance for monomeric radicals in particles containing i active chains (particles in "state i") and by introducing some simplifications which do not appear through the probabilistic treatment. In this last section of the work, the equivalence of the two approaches in the limiting case considered by Casey *et al.*[5] (zero-one system where propagation of monomeric radicals in the aqueous phase is negligible) is confirmed in a more simple way by deriving the general form of Casey's equation for $\bar{n}$ using the cited probabilistic approach. Moreover, it is shown that the same expression for the frequency of re-entry ρ_{re} is obtained through the two approaches.

4.1. Average Number of Radicals per Particle. For a zero-one system where particle nucleation does not occur, the balance equation for the concentration of particles containing one radical N_1 can be written as:

$$\frac{dN_1}{dt} = \rho N_0 - (\rho + k)N_1 \tag{33}$$

where N_0 is the concentration of particles containing no radicals. Following Asua's approach, the rate of desorption from particles containing one radical is given by:

$$R_{d1} = k_{fm} C_m N_1 P_1 \qquad (34)$$

which represents the rate of production of monomeric radicals through chain transfer $k_{fm} C_m N_1$ times the probability P_1 for a monomeric radical to desorb rather than to propagate. The probability P_1 is given by:

$$P_1 = \frac{k_{dm}}{k_{dm} + k_p^1 C_m} \qquad (35)$$

The rate of desorption from particles containing no radicals is given by:

$$R_{d0} = \rho_{re} N_0 P_1 \qquad (36)$$

where $\rho_{re} N_0$ is the rate of re-entry into particles containing no radicals. The overall rate of desorption is therefore given by:

$$R_d = R_{d0} + R_{d1} = k_{fm} C_m N_1 P_1 + \rho_{re} N_0 P_1 \qquad (37)$$

which corresponds to Equation 7 written for $n = 1$. Since $R_d = kN_1$ for a zero-one system, one can substitute Equation 37 in Equation 33 obtaining:

$$\frac{dN_1}{dt} = (\rho - \rho_{re}P_1)N_0 - (\rho + k_{fm}C_mP_1)N_1 \tag{38}$$

Considering that $N_0 = N_T - N_1$ and dividing by N_T, Equation 38 can be rewritten in the form:

$$\frac{d\bar{n}}{dt} = \rho(1 - 2\bar{n}) - \rho_{re}P_1(1 - \bar{n}) - k_{fm}C_mP_1\bar{n} \tag{39}$$

Finally, introducing the definition of P_1 in Equation 39, one obtains:

$$\frac{d\bar{n}}{dt} = \rho(1 - 2\bar{n}) - \frac{\rho_{re}k_{dm}}{k_{dm} + k_p^1C_m}(1 - \bar{n}) - \frac{k_{fm}C_mk_{dm}\bar{n}}{k_{dm} + k_p^1C_m} \tag{40}$$

which is identical to the equation derived by Casey *et al.*[5] through a kinetic approach.

4.2. Frequency of Re-Entry. Following the probabilistic approach, if one takes Equation 4 for β and neglects the propagation of monomeric radicals in the aqueous phase, as done by Casey *et al.*, β reduces to:

$$\beta = \frac{k_{t,aq}[T\cdot]}{k_{re}\dfrac{N_T}{N_A} + k_{t,aq}[T\cdot]} \tag{41}$$

Dividing Equation 37 by N_T, where $R_d/N_T = k\bar{n}$, one obtains:

$$k\bar{n} = k_{fm}C_m\bar{n}P_1 + \rho_{re}(1 - \bar{n})P_1 \tag{42}$$

By introducing this new expression for $k\bar{n}$ in Equation 2, the latter can be rewritten as:

$$\rho_{re} = \left[k_{fm}C_m\bar{n}P_1 + \rho_{re}(1-\bar{n})P_1\right](1-\beta) \tag{43}$$

Solving for ρ_{re} leads to:

$$\rho_{re} = \frac{k_{fm}C_m\bar{n}P_1(1-\beta)}{1-(1-\bar{n})P_1(1-\beta)} = \frac{k_{fm}C_m\bar{n}}{\dfrac{1}{P_1(1-\beta)} - (1-\bar{n})} \tag{44}$$

which, upon substitution of the definitions of probabilities P_1 (Equation 35) and β (Equation 41), leads to:

$$\rho_{re} = \frac{k_{fm}C_m\bar{n}}{\left(1 + \dfrac{k_p^1 C_m}{k_{dm}}\right)\left(1 + \dfrac{k_{t,aq}[T\cdot]}{k_{re}\dfrac{N_T}{N_A}}\right) - (1-\bar{n})} \tag{45}$$

This equation is identical to that obtained by Casey *et al.* through the kinetic approach.

It is therefore proven that the equations derived by Casey *et al.*[5] for the description of the radical desorption process are easily re-obtained through the probabilistic approach proposed by Asua *et al.*[4]. The latter approach is however more general since it is not limited to the case of zero-one system. Moreover, differently from what stated by Casey *et al.*, distinction is made between re-entry of previously desorbed free radicals and absorption of other kinds of radicals (i.e., initiator-derived and thermally-generated): the re-entry after desorption process,

which involves specifically the monomeric radicals created by chain transfer, is described independently of any other absorption process.

5. Conclusions

The desorption terms in the Smith-Ewart equations have been critically examined in this work. Making use of a probabilistic approach, which has the advantage of a greater simplicity, detailed expressions for particle state dependent desorption coefficients have been derived. Specifically, two equivalent models accounting for this feature have been developed, differing in the way the re-entry and re-desorption terms are considered in the definitions of entry and exit of monomeric radicals from particles. A comparison with the results obtained by the use of a single, average desorption coefficient in the Smith-Ewart equations (as ordinarily written) reveals that neglecting the dependency of the desorption coefficients upon particle state may lead to significant errors in the calculation of the average number of radicals per particle $\bar{n}$ (i.e., of the reaction rate). This is especially true in the limit of complete re-entry of desorbed radicals and for values of $\bar{n}$ typical of systems characterized by high desorption rates. In these conditions a detailed model is required, accounting for particle state dependent desorption frequencies. The following, generally valid, simplified expression for these parameters has been derived:

$$k_n = k_{fm} C_m P_1 \left[1 + \frac{(1-\beta)P_1}{1-(1-\beta)P_1} \cdot \frac{\bar{n} N_{n-1}}{n N_n} \right]$$

An analysis of a real system of considerable importance, methyl methacrylate polymerized at 50°C, has been conducted revealing the usefulness of the detailed model here developed at $\bar{n}$

< 0.45. Finally, the complete equivalence between kinetic and probabilistic approaches (previously proved in the literature) is re-established in a more direct and simple way.

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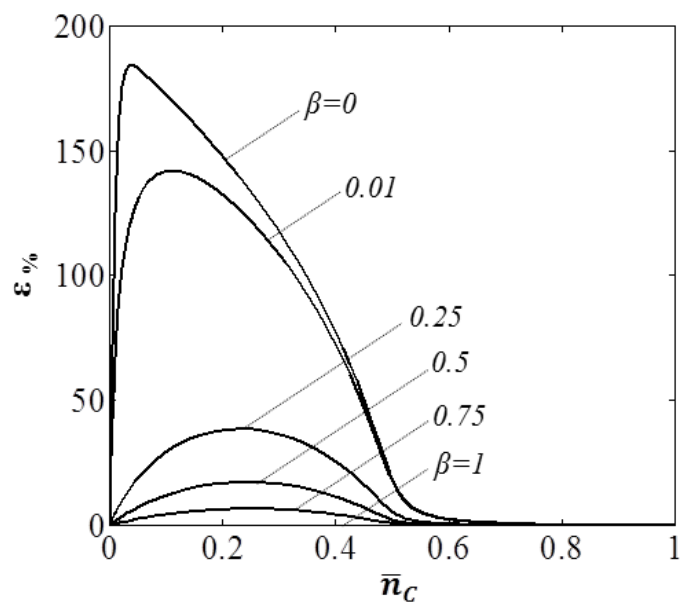
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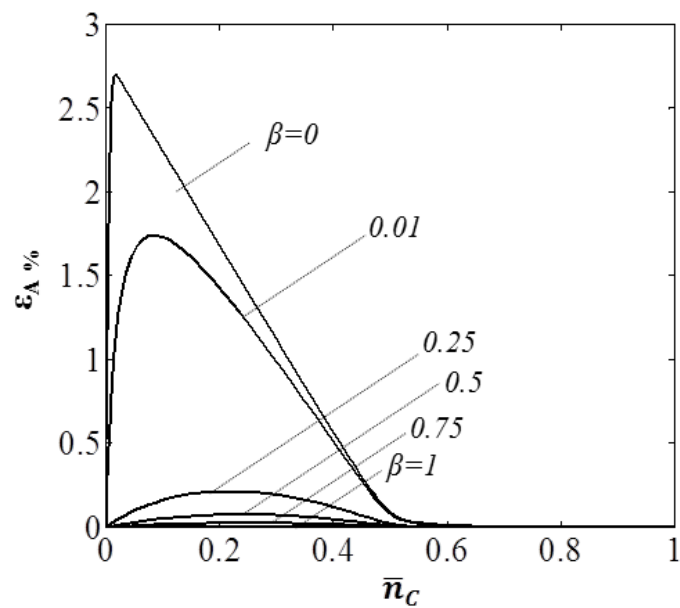
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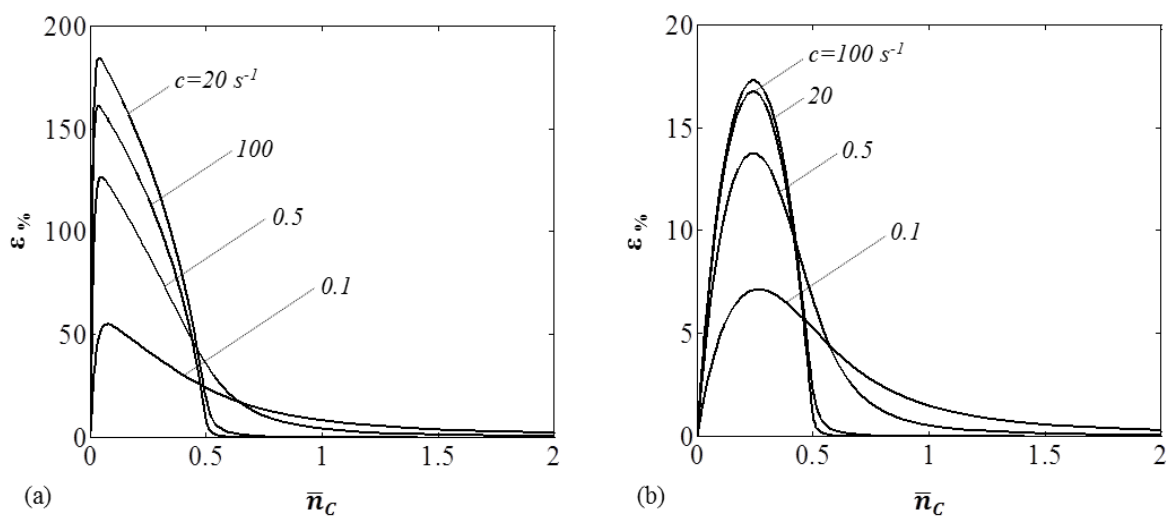
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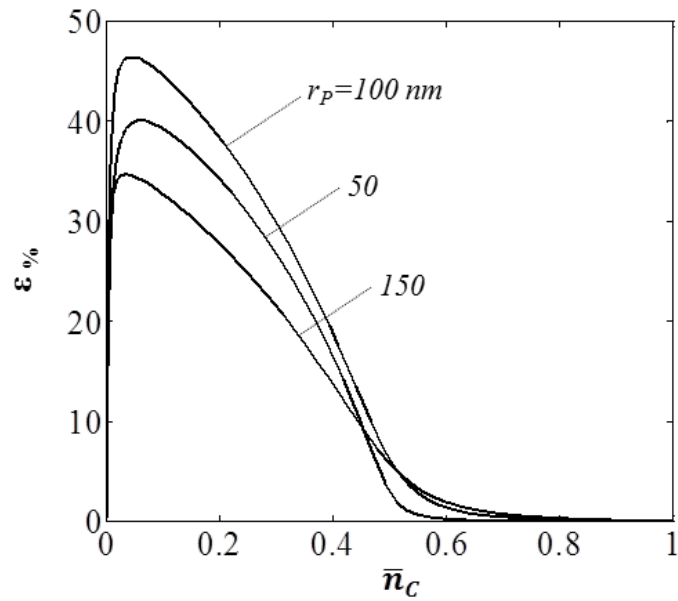
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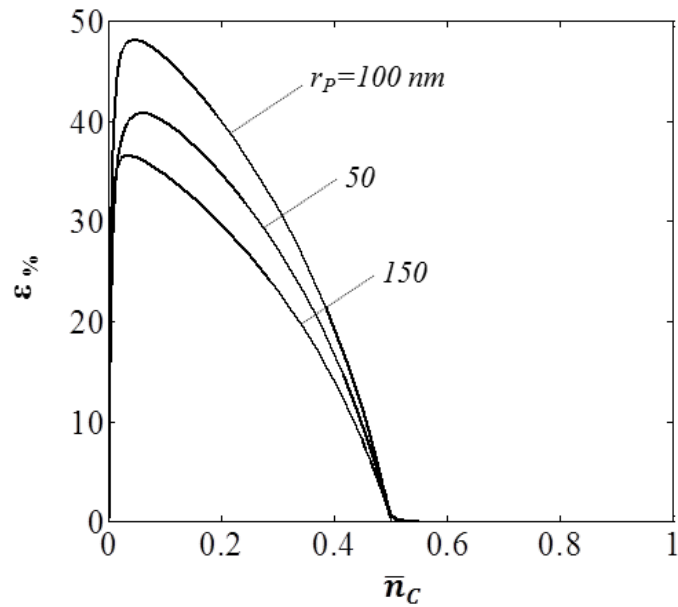
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Table 1. Numerical values of the model parameters.

Parameter	Value
C_m	$4.8 \cdot 10^{-3}$ mol cm^{-3}
k_{fm}	10 cm^3 mol^{-1} s^{-1}
k_p^1	$1.26 \cdot 10^5$ cm^3 mol^{-1} s^{-1}
k_{dm}	$5 \cdot 10^3$ s^{-1}

Table 2. Comparison between the performances of the two models accounting for particle state dependent desorption coefficients.

N	Model 1		Model 2		Comparison
	N_n	k_n	N_n	k'_n	$k_n - k'_n$
0	$8.01\ 10^{-1}$	-	$8.01\ 10^{-1}$	-	-
1	$1.99\ 10^{-1}$	$1.82\ 10^{-1}$	$1.99\ 10^{-1}$	$4.28\ 10^{-2}$	$1.39\ 10^{-1}$
2	$7.13\ 10^{-5}$	$4.76\ 10^{1}$	$7.13\ 10^{-5}$	$4.25\ 10^{-2}$	$4.76\ 10^{1}$
3	$8.70\ 10^{-9}$	$9.29\ 10^{1}$	$8.70\ 10^{-9}$	$4.22\ 10^{-2}$	$9.29\ 10^{1}$
4	$5.39\ 10^{-13}$	$1.36\ 10^{2}$	$5.39\ 10^{-13}$	$4.19\ 10^{-2}$	$1.36\ 10^{2}$
5	$< 10^{-15}$	$1.77\ 10^{2}$	$< 10^{-15}$	$4.16\ 10^{-2}$	$1.77\ 10^{2}$
Average	0.199	$2.16\ 10^{-1}$	0.199	$4.28\ 10^{-2}$	$1.73\ 10^{-1}$

Table 3. Numerical values of the model parameters for methyl methacrylate. Particle size independent coefficients.

Parameter	Value
C_m	$6.6 \cdot 10^{-3}$ mol cm^{-3}
k_{fm}	23 cm^3 mol^{-1} s^{-1}
k_p^1	$5.8 \cdot 10^5$ cm^3 mol^{-1} s^{-1}

Table 4. Numerical values of the model parameters for methyl methacrylate. Particle size dependent coefficients.

Parameter	r_P = 50 nm	r_P = 100 nm	r_P = 150 nm
c	109.4 s^{-1}	13.7 s^{-1}	4.0 s^{-1}
c^I	1.66$\cdot$10^4 s^{-1}	2.07$\cdot$10^3 s^{-1}	6.13$\cdot$10^2 s^{-1}
k_{dm}	4.31$\cdot$10^4 s^{-1}	1.08$\cdot$10^4 s^{-1}	4.78$\cdot$10^3 s^{-1}
β	8.7$\cdot$10^{-3}	4.4$\cdot$10^{-3}	2.9$\cdot$10^{-3}

Appendix

Relationship between the desorption coefficients of Model 1 and Model 2

Starting from Equation 12 and recalling the definition of k_n' (Equation 20) one can write:

$$k_n n N_n = k_n' n N_n + \rho_{re} N_{n-1} P_n \tag{A}$$

which immediately gives the relationship between the particle state dependent desorption coefficients according to the two models:

$$k_n = k_n' + \rho_{re} \frac{N_{n-1}}{n N_n} P_n \tag{B}$$

In order to obtain the relationship between their average values:

$$k = \frac{\sum_{n=1}^{\infty} k_n n N_n}{\bar{n} N_T}$$

and

$$k' = \frac{\sum_{n=1}^{\infty} k_n' n N_n}{\bar{n} N_T}$$

summation of Equation A upon all particle states (from 1 to infinity) can be carried out:

$$k \bar{n} N_T = k' \bar{n} N_T + \rho_{re} \sum_{n=1}^{\infty} N_{n-1} P_n$$

Substituting Equation 2 for ρ_{re} and solving for k yields:

$$k = \frac{k'}{1 - (1 - \beta) \sum_{n=1}^{\infty} \frac{P_n N_{n-1}}{N_T}} \tag{C}$$

which correlates the average desorption coefficients according to Model 1 and Model 2. By substituting Equation B for k in Equation 2, the following expression for ρ_{re} as a function of k' is obtained (cf. Equation 22 in the main text):

$$\rho_{re} = \frac{k' \bar{n} (1 - \beta)}{1 - (1 - \beta) \sum_{n=1}^{\infty} \frac{P_n N_{n-1}}{N_T}}$$