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Emulsion Polymerization: Radical Segregation and Its Role in Controlled Polymerization

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Summary: A numerical approach based on a recently proposed discretization technique and suitable for molecular weight calculation in emulsion polymerization is presented. The main features of this approach are (i) the direct evaluation of the complete chain length distribution without the need of predefined model distributions (as in the case of moment based methods), (ii) the large flexibility when defining the computational grid, (iii) the capability of evaluating with accuracy two integral properties of the distribution no matter how coarse the grid is and (iv) the limited computational effort required. Selected applicative examples are reported with emphasis on cases where other computational approaches give unreliable or less detailed results.

Introduction

The major difference between emulsion and bulk polymerization is the so-called *radical compartmentalization* or *segregation*. In particular, radical segregation affects the kinetics of the process as well as the chain length distribution (CLD) of the final polymer. These effects become very evident in the so-called zero-one and zero-one-two systems,[1] where terminations are so much faster than radical entry that the maximum number of active chains per particle is one and two, respectively. In contrast to bulk systems (that in this context include also solution and dispersion polymerizations), the average number of radicals per particle, $\bar{n}$, is constant during the reaction and statistically equal to 0.5 for largely different operating conditions, provided that radical desorption is not taking place. The overall rate of polymerization per unit volume of aqueous phase is then given by $R_p = k_p M\,(\bar{n}/N_{Av})N_p$, where N_p indicates the concentration of polymer particles and N_{Av} the Avogadro number. On the other hand, the instantaneous number average degree of polymerization, DP_n, is given by the ratio between the frequencies of propagation and radical entry into the particles, $DP_n \approx k_p M/\rho$. Therefore, the strong coupling between polymerization rate and average chain length typical of bulk systems (where these quantities are given by $R_p = k_p M\,R^\bullet$ and $DP_n \approx k_p M/k_t R^\bullet$, respectively, being $R^\bullet$ the concentration of active chains) is no

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longer operative. This is a major plus for the emulsion process where productivity and molecular weight can be adjusted quite independently without the usual constraint typical of bulk polymerization, where increasing polymerization rate implies shorter chains and vice versa.

The segregation effects on the process kinetics are fully accounted for in the classical Smith-Ewart equations[2]. Under the quasi-steady-state assumption, the analytical solution of these equations is the active chain distribution, N_i, defined as the fraction of particles having i radicals. On the other hand, the problem of computing the polymer CLD is more difficult. With reference to a particle with two active chains, the last entered radical has growth time smaller than the first one, being termination much faster than entry. Therefore, the chain lengths of two radicals in the same particle are not independent from each other, as shown by Ghielmi *et al.*[3]. To properly evaluate the CLD in segregated systems, in 1980 Lichti *et al.*[4] proposed a new modeling approach. Accordingly, two *distinguished* distributions, $N_i'(t')$ and $N_i''(t',t'')$, are evaluated: the first one is defined as the fraction of particles having i radicals, one of which (the *distinguishing* one) growing for time t'. The second distribution is defined as the fraction of particles with i radicals, two of which with growth times equal to $t'+t''$ and t'', respectively. Using the first distribution, N_i', the CLD of the chains terminated by monomolecular events (*e.g.*, chain transfer to monomer, disproportionation) can be evaluated. On the other hand, the second distribution, N_i'', gives the probability of finding a couple of radicals with defined lengths in the same particle, which is necessary to compute the CLD of chains terminated by combination.

According to the approach proposed by Lichti *et al.*[4], the chain length is directly evaluated as the product between the frequency of propagation, k_pM, and the lifetime of the chain. This corresponds to model the discrete degree of polymerization as a continuous variable. It can be easily shown that this approach is correct only when the number of monomer units added by the chain is larger than few tenths[5], *i.e.* when the propagation event is by far the most probable during the chain life. This is obviously the case in most situations, but there are indeed a few but important exceptions where the chain lifetimes are so short that this assumption leads to large errors. This is the case of chains growing intermittently, like in living polymerization processes[6], where a different modeling approach is therefore needed.

Another situation where the approach of Lichti *et al.* cannot be applied, which also in some sense corresponds to chains growing intermittently, arises when dead chains can be reactivated, like in the case of branching systems. Even if it can be assumed that the frequency of propagation is constant during the lifetime of each reactivated radical, this frequency is generally very different from one growth period to the other. A chain reactivation can in fact occur after a significant time interval, where monomer and radical concentrations and all the other conditions in the reacting system may be substantially different. Accordingly, the total length of the chain cannot be simply evaluated as summation of all the chain lifetimes, since the corresponding growth frequencies are no longer available. This difficulty has been overcome by introducing the so-called chain *pre-life*, as proposed by Ghielmi *et al.*[7] In this approach, the two distinguished distributions defined above become two- and four-dimensional: $N_i'(t',n')$ and $N_i''(t',n',t'',n'')$, where n' and n'' represent the number of monomer units added by the two distinguishing chains before the last reactivation. In spite of the increased problem dimension, Ghielmi *et al.* solved the resulting population balances in terms of leading moments of the CLD with a limited computational effort. While average molecular weight properties are readily calculated through this approach, a suitable model distribution is needed when the complete CLD has to be evaluated. The choice of this distribution is not an easy task when no information on the final distribution is available a priori or in the case of complex (multimodal) distributions.

The aim of this paper is to develop a modeling approach designed to overcome both the difficulties mentioned above. The distinguished particle distribution concept is still used but based on discrete independent variables. Two distinguishing particle distributions, $N_{i,n}$ and $N_{i,n,m}$, are introduced and the resulting population balances are directly solved using the numerical approach recently proposed by Kumar and Ramkrishna[8]. The final result is a flexible modeling tool, kinetic scheme independent and able to provide an accurate solution not only in terms of integral properties but also of complete CLD. The approach is validated by selected parametric calculations, focused on frequently reactivated chains, i.e. branching and living polymerization systems.

Model development and numerical solution

The model is based on the evaluation of two distinguished particle distributions: $N_{i,n}$, defined as the fraction of particles with i radicals one of which of length n, and $N_{i,n,m}$, fraction of particles with i radicals, a couple of which with lengths n and m, respectively. In this section, the corresponding population balances are presented along with the approach adopted for their numerical solution.

Kumar and Ramkrishna[8] have recently presented a discretization approach to the numerical solution of population balance equations (PBEs). By this method (indicated by K-R method in the following), the entire population of polymer chains is divided into a finite number of macroscopic classes. Each class is representative of a well-defined range of chain lengths or, in other words, all chains whose chain length is in a defined range of values are lumped into a single class. All chains belonging to the same class are assumed characterized by one single chain length, or *pivot value*. Balance equations very similar to the original PBEs can be written for each class. Note that this method is something more than a simple discretization of the CLD aimed to reduce the computational effort. The distinguishing idea is in fact to write the discretized equations so as to conserve at least two selected macroscopic properties. Typical macroscopic properties of concern are low-order moments of the distribution, but any polymer property of the distribution can be used, depending upon the specific applicative interest. In particular, indicating by $f(n)$ the value of the generic property at chain length n, the corresponding overall property can be calculated as:

$$F = \sum_{i=0}^{\infty} f(n) P_n \tag{1}$$

where P_n represents the unknown CLD. So for example if $f(n) = n^j$, F is the j-th order moment of the distribution. The K-R method directly addresses the conservation of the property F through an appropriate discretization of the population balance equations, as shown in the following with reference to emulsion polymerization.

Let us consider a simplified kinetic scheme, including only propagation ($p = k_p M$), radical entry (ρ) and bimolecular termination by combination ($c = k_t / 2N_A v_p$). Following the classic approach by Lichti et al.[4], the PBEs for the distinguishing distributions of active chains, $N_{i,n}$ and $N_{i,n,m}$, as well as those for the dead chains are as follows:

$$\frac{dN_{i,n}}{dt} = -\left(p + \rho + ci(i-1)\right)N_{i,n} + pN_{i,n-1} + \rho N_{i-1,n} + ci(i+1)N_{i+2,n} + \delta_{n,0}\rho N_{i-1} \tag{2}$$

$$\begin{aligned} \frac{dN_{i,n,m}}{dt} = &-\left(2p + \rho + ci(i-1)\right)N_{i,n,m} + p\left(N_{i,n-1,m} + N_{i,n,m-1}\right) + \rho N_{i-1,n,m} + \\ &+ ci(i-1)N_{i+2,n,m} + \delta_{n,0}\rho N_{i-1,m} \end{aligned} \tag{3}$$

$$\frac{dP_n}{dt} = \frac{2c}{N_A v_p} \sum_{i=2}^{\infty} \sum_{m=0}^{n/2} N_{i,m,n-m} \tag{4}$$

where $\delta_{n,0}$ indicates the Kronecker delta. To apply the K-R method to this set of PBEs, let us partition the populations into a finite number of classes. With reference to the distribution of the singly distinguished particles, $N_{i,n}$, this is carried out by introducing the following set of new variables:

$$S_{i,j} = \sum_{n=n_j}^{n_{j+1}-1} N_{i,n} \tag{5}$$

where $S_{i,j}$ represents the class of particles having i radicals, one of which with chain length in between n_j and $n_{j+1}-1$. The same summation operator is applied to the remaining two distributions, twice to $N_{i,n,m}$ and once to P_n, thus obtaining the new distributions in terms of $S_{i,j,k}$ and Q_j, defined similarly as in Eq 5. Finally, within each class we represent the population as a discrete set of particle number values corresponding to each pivot value x_j, with $n_j \le x_j \le n_{j+1}-1$. Accordingly, the population is now "concentrated" at the representative chain length values, x_j.

In this new frame, let us consider the formation of terminated chains by bimolecular combination. By combination of two chains from classes i and j, a new chain whose length does not necessarily match any of the pivotal chain lengths is produced. Therefore, indicating as x_k and x_{k+1} two adjacent pivot values, the typical situation is as follows: $x_k < x_i + x_j < x_{k+1}$. A new problem arises: how to attribute the resulting individual to the previously defined pivotal classes? The solution to this problem is to partition the new chains between the neighboring classes so as to preserve the two selected properties of the distribution. This is done by suitable saturation of two degrees of freedom, $a(x_l, x_k)$ and $b(x_l, x_{k+1})$, defined as the fractions of chains with length x_l assigned to classes x_k and x_{k+1}, respectively, according to the following system of equations:

$$\begin{cases} a(x_i + x_j, x_k) f_1(x_k) + b(x_i + x_j, x_{k+1}) f_1(x_{k+1}) = f_1(x_i + x_j) \\ a(x_i + x_j, x_k) f_2(x_k) + b(x_i + x_j, x_{k+1}) f_2(x_{k+1}) = f_2(x_i + x_j) \end{cases} \tag{6}$$

where f_1 and f_2 are the two selected properties. A typical choice is to preserve zero-th and first order moments (i.e., number of chains and linked monomer unit, respectively). With respect to Eqs 6, this corresponds to have $f_1 = 1$ and $f_2 = n$. Note that this same approach has been applied to the polymer chain growth. Each propagation step of a chain in class j is regarded as a combination with an individual of chain length one.

Accordingly, the factors $a(x_j+1,x_j)=a_j$ and $b(x_j+1,x_{j+1})=b_j$ are introduced and evaluated using two equations fully equivalent to Eqs 6.

By applying this "particle sharing" concept to the Eqs 2-4, it is possible to obtain the following new set of equations in $S_{i,j}$, $S_{i,j,k}$ and Q_j, respectively:

$$\frac{dS_{i,j}}{dt}=-\left(pb_j+\rho+ci(i-1)\right)S_{i,j}+pb_{j-1}S_{i,j-1}+\rho S_{i-1,j}+ci(i+1)S_{i+2,j}+\delta_{n,0}\rho N_{i-1} \tag{7}$$

$$\begin{aligned}\frac{dS_{i,j,k}}{dt}= & -\left(\left(b_j+b_k\right)p+\rho+ci(i-1)\right)S_{i,j,k}+p\left(b_{j-1}S_{i,j-1,k}+b_{k-1}S_{i,j,k-1}\right)+ \\ & +\rho S_{i-1,j,k}+ci(i-1)S_{i+2,j,k}+\delta_{n,0}\rho S_{i-1,k}\end{aligned} \tag{8}$$

$$\frac{dQ_j}{dt}=\frac{c}{N_A v_p}\sum_{i=2}^{\infty}\left(\sum_{\substack{k,l \\ x_{j-1}\le x_k+x_l<x_j}} b(x_k+x_l,x_j)S_{i,k,l}+\sum_{\substack{k,l \\ x_j\le x_k+x_l<x_{j+1}}} a(x_k+x_l,x_j)S_{i,k,l}\right) \tag{9}$$

This is a set of ordinary differential equations with initial conditions only and it can be solved by any among the many available numerical integrators. The size of the system is related to the adopted numerical grid but, notably, all factors *a* and *b* can be evaluated at once before starting the time integration. Further details about the grid selection and the CLD reconstruction according to the K-R method can be found elsewhere [9(a)].

Simulation results

In this section, the potential of the discretization technique proposed by Kumar and Ramkrishna when applied to CLD calculations in segregated systems is shown through a series of parametric calculations. Some advantages in using a discrete approach instead of the previously adopted continuous ones are also discussed.

Role of segregation. In Figure 1, the instantaneous polydispersity of the CLD, $P_d = M_w/M_n$, is reported versus the average number of radicals per particle, $\bar{n}$, for a system where, in addition to propagation, bimolecular termination by combination, radical entry from the water phase, chain transfer to monomer and radical desorption are present. Note that $\bar{n}$ has been varied by properly tuning the frequency of entry. The results of two different approaches are reported. In the first approach (detailed model, continuous line) the segregation effect is correctly accounted for. Accordingly, a chain can react only with another chain contained in the same particle in the frame of the detailed model, Eqs (7)-(9). On the other hand, the second model (dashed line) is based on the so-called "mini-bulk" approach, where the probability of having two chains with

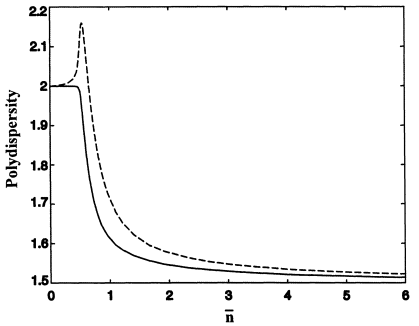

Figure 1 – Polydispersity value versus average number of radicals per particle. Detailed model (solid curve) and mini-bulk model (dashed curve). For more details see Ref. 3.

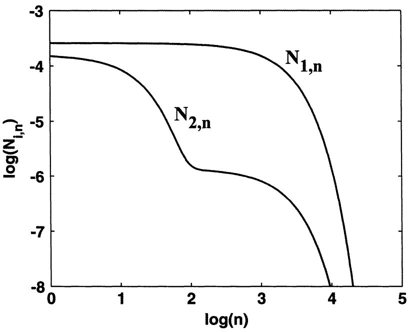

Figure 2 – Singly distinguished distributions of the particles with one and two active chains, $N_{1,n}$ and $N_{2,n}$, at 60% conversion. For more details see Ref. 9(b).

specific length in the same particle is not accounted for.[3] In this frame, the probability of having a second chain with length *m* is independent on the presence of a chain with length *n* in the same particle. This simplified approach reduces the computational effort, since the doubly-distinguished distribution $N_{i,n,m}$ is not needed, but it can be used only when a large number of radicals is contained into the particle. By inspection of the calculated results, the largest difference between the two models is found at an average number of radicals between 0.3 and 2, which is the usual range of values for an emulsion polymerization. On the other hand, the two approaches give again the same results at very small $\bar{n}$ values, where no particle contains two radicals simultaneously and, therefore, terminations are only monomolecular. At $\bar{n} = 0.5$, the mini-bulk model overpredicts the instantaneous polydispersity of about 10%. This result can be explained by considering that, while only combinations between short and long chains are possible due to radical segregation, as correctly predicted by the detailed model, the simplified model allows also combinations between short-short and long-long pair of chains, thus overestimating the polydispersity of the resulting CLD [3].

The presence of two well-distinct families of chains is shown in Figure 2, where the $N_{1,n}$ and $N_{2,n}$ distributions are reported. While all the chain lengths are equally probable in the particles with one radical up to a chain length that roughly corresponds to the frequency of entry, in the particles with 2 radicals, the two families of chains become evident. The first one, generated by the second entry and therefore with small chain length, and the second one originated by the first entry and with longer chain length. This chain length difference is the reason for the specific behavior of bimolecular

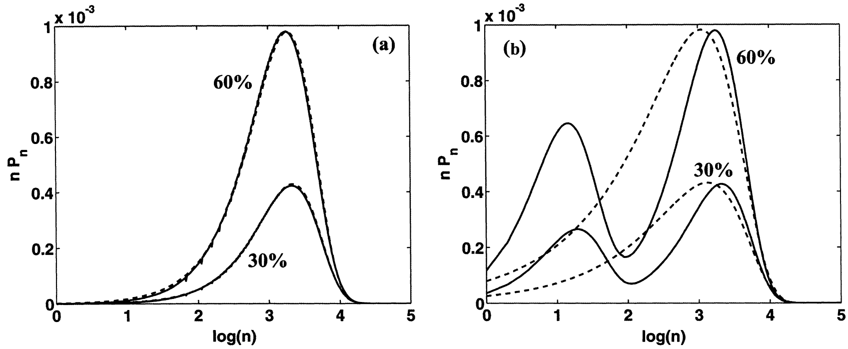

Figure 3 – Weight distribution of chain length in the presence of bimolecular termination by (a) combination and (b) disproportionation. K-R method (solid curve) and method of moments (dashed curve). For more details see Ref. 9(b).

termination by combination mentioned above. It is worth noting that, when termination by disproportionation is present, the same CLD polydispersity is evaluated by the two methods. Chain lengths are in fact preserved by this termination mechanism and, thus, the CLD of the dead chains is calculated using only the singly distinguished distribution, $N_{i,n}$.

The capabilities of the K-R method applied to a discrete approach become especially evident when considering the calculated CLD shown in Figures 3a and 3b for systems dominated by bimolecular termination through combination and disproportionation, respectively. The dashed lines correspond to the CLD calculated by applying the method of moments to the equations proposed by Lichti *et al.*[4], and reconstructing the distribution as a perturbation of a Gamma distribution in terms of those moments. Such an assumption is not necessary for the K-R method. Note that a grid of 400 pivot values was used in the K-R method, corresponding to a computational time of few seconds on a HP workstation C180. In the case of termination by combination, the final distribution is monomodal and is predicted with good accuracy in both cases (Figure 3a). On the other hand, when termination by disproportionation is present, the CLD is bimodal and it is correctly calculated only using the K-R numerical approach. By the method of moments it is possible to correctly evaluate the integral properties of the distribution (i.e., its moments), but it is difficult to identify *a priori* a model distribution suitable to predict the unknown (in this case bimodal) CLD.

Using the K-R method, the entire CLD is predicted with accuracy also when a chain branching mechanism is present. This is shown in Figure 4, where the calculated

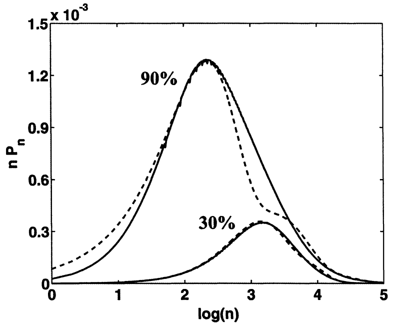

Figure 4 – Weight distribution of chain length in the presence of bimolecular combination and chain transfer to polymer. K-R method (solid curve) and method of moments (dashed curve). For more details see Ref. 9(b).

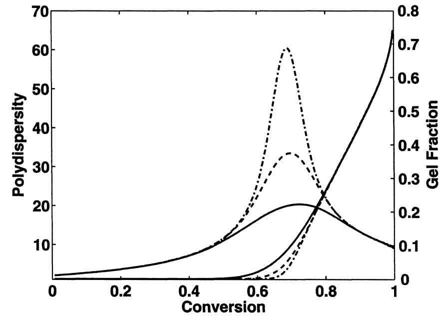

Figure 5 – Polydispersity and gel fraction as a function of conversion in the presence of chain transfer to polymer and bimolecular combination at increasing values of the maximum chain length: $2 \cdot 10^6$ (solid curve), $7 \cdot 10^6$ (dashed curve) and $1 \cdot 10^7$ (dash-dotted curve). For more details see Ref. 9(a).

distribution is shown for a system where chain transfer to polymer and bimolecular combination are the dominating kinetic events. The resulting CLD is compared with the one obtained solving the population balances based on the lifetime concept, including pre-life, by the so-called numerical fractionation technique[10] (NF). In this case, the polymer is fractionated into "generations" and the overall CLD is obtained by summing up the distributions of each generation after reconstructing them from the corresponding moments. Note that, differently from the discretization approach developed here, the polymer classes are partly superimposed and not contiguous. Looking at the calculated results, it is readily verified that, while an artificial shoulder in the distribution is predicted by the model solved with the NF method (dashed line), this is not the case for the K-R method (solid line). It can be concluded that this is a numerical artifact induced by the distribution reconstruction applied in the NF case. The same problem was reported when applying this approach to bulk systems and it was ascribed to the insufficient fractionation of the polymer population[11].

Again with reference to systems involving nonlinear chains, another key feature when evaluating different modeling approaches is given by the model capabilities in terms of prediction of gel formation. This is easily included in the frame of the K-R method, where the CLD is discretized up to a maximum chain length, which is defined as the limiting chain length of the polymer sol-fraction. All longer polymer chains are considered as "gel", i.e. high molecular weight, insoluble material. While this maximum chain length cannot be defined *a priori*, it can be identified for each specific system by

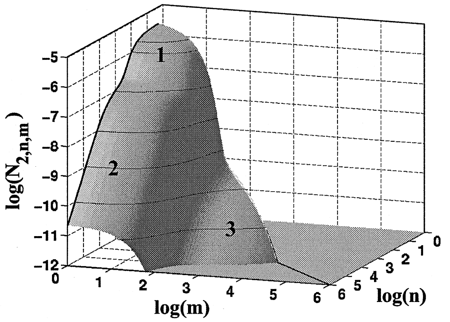

Figure 6 – Doubly distinguished distribution, $N_{2,n,m}$, in the presence of bimolecular termination by combination and chain transfer to polymer calculated with the K-R method. For more details see Ref. 8(a).

"numerical experiments". This means that the same simulation is iteratively carried out with increasing values of this maximum chain length until convergence of the predicted onset of gel formation and of the gel fraction evolution with conversion is obtained. Note that this chain length value does not correspond to the actual chain length of the gel polymer but it is only a kind of threshold value above which the polymer can be considered as a gel. A completely equivalent approach was previously adopted when using the NF method to identify the maximum number of generations required to have a reliable estimate of the polymer gel fraction[10]. The above mentioned convergence of the calculated gel fraction at increasing values of the maximum chain length is shown in Figure 5 for the corresponding bulk case. It can be verified that the results become fully superimposed at maximum chain lengths larger than ten millions.

Finally, once more with reference to branching systems, it is worth noting that the KR method allows to evaluate some additional characteristics of the CLD. In Figure 6, the doubly-distinguished distribution of the particles containing two active chains, $N_{2,n,m}$, is shown at 90% of conversion. Three well-distinct regions have been identified as indicated by the indexes 1, 2 and 3. They correspond to the particles where a termination between two short, a short and a long or two long chains is taking place, respectively. This picture explains why gelation occurs later in a segregated system with respect to the equivalent bulk process. In fact, in order to form gel, a mechanism connecting together the branched chains is essential, so as to have a geometric growth of their size[10]. In contrast, termination is very fast in a particle with two active chains and the first entered chain (which may have undergone a chain transfer to polymer) most likely terminates with a short radical. Of course, this effect cannot be taken into account using the mini-bulk approach, which in fact has been shown to largely underestimate the conversion value at which gelation takes place in segregated systems[3].

Fast reactivating systems. As mentioned above, the continuous approximation used by Lichti et al.[4] can be adopted only when the number of monomer units added by a radical during its actual lifetime is large enough, i.e. chain propagation is by far the most probable event taking place during the chain lifetime. Under these conditions, the difference involved in the growth term, $N_{i,n} - N_{i,n-1}$, can be expressed in terms of the following Taylor expansion:

$$N_{i,n} - N_{i,n-1} = N_i(n) - N_i(n-1) = -\left.\frac{\partial N_i}{\partial n}\right|_n + \frac{1}{2}\left.\frac{\partial^2 N_i}{\partial n^2}\right|_n - \ldots \cong -\left.\frac{\partial N_i}{\partial n}\right|_n \qquad (10)$$

which can be limited to the first order term without any significant loss of accuracy. This is precisely the approximation adopted in evaluating the chain growth term in the approach based on chain lifetime times propagation frequency introduced by Lichti et al.. However, this approach cannot be applied when additional reaction events competing with propagation are present. A significant example is given by living polymerization, say by RAFT[12], where each chain experiences a series of growth (active) and quiescent (dormant) periods during the entire process as a result of the living transfer reaction. In such systems, the larger the number of active periods every chain experience, the more homogeneous is the growth of the whole polymer. Therefore, a frequency of propagation comparable to that of the transfer reaction is desired so that the number of monomer units added during each active period can be as low as one. Under these conditions, it is clear that the continuous approach above is not valid. To show how large can be the error introduced by this approach with respect to the discrete one, let us consider a particle with only one active chain and a large number of dormant chains with constant chain length equal to *n*. Under such conditions, the population balance of the active chains is readily written down and solved analytically. The resulting expressions corresponding to the continuous and discrete approach, respectively, are as follows:

$$\frac{N_1'(n')}{N_1} = \alpha \exp(-\alpha n') \qquad (11)$$

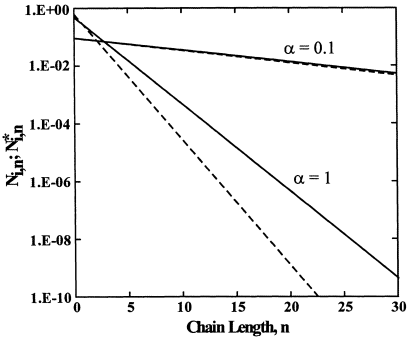

Figure 7 – CLD of the active chains in a living polymerization as calculated by the discrete (solid line) and the continuous (dashed line) approach.

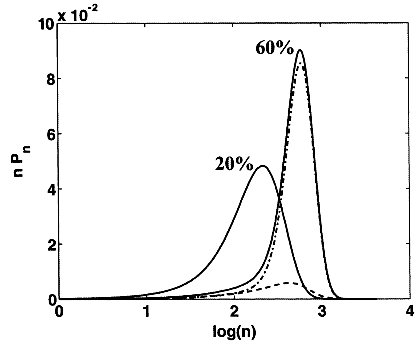

Figure 8 – Weight distribution of average chain length at two conversion values for a living polymerization calculated with the K-R method; overall (solid curve), dormant (dash-dotted curve) and dead (dashed curve) chain distributions. For more details see Ref. 9(b).

$$\frac{N_{1,n}}{N_1}=\frac{\alpha}{(1+\alpha)^{n+1}} \tag{12}$$

where $\alpha = k_{ex}D_n/k_pM$ is the ratio between the frequencies of the transfer and propagation reactions, i.e. $1/\alpha$ is the average number of monomer units added during each active period. The resulting CLDs are shown in Figure 7 for two different values of the parameter α. Note that, in order to make possible the comparison between the two distributions, the one obtained by the continuous approach has been rearranged in terms of the new quantity $N^*_{1,n}$, corresponding to the integral of $N_1'(n')$ from n' to $n'+1$. By inspection of the figure, it can be concluded that, while the two approaches give the same results for values of the parameter α smaller than one, at $\alpha = 1$ the number of short chains is underestimated by the continuous approach (e.g. a fraction of active chains with length 4 monomer units equal to 1.1% is predicted by the continuous model while the same fraction is equal to 3.1% according to the discrete one). This difference is particularly evident in terms of polydispersity of the resulting CLD, equal to 2 in the first case at all α values (like in a system dominated by monomolecular terminations) and equal to $2+\alpha$ in the second case, thus indicating a much broader distribution.

To validate the applicability of the modeling approach under examination, the results of the simulation of a living polymerization by RAFT in miniemulsion are shown in Figure 8. The shift of the CLD peak with conversion, typical of living processes and due to the continuous growth of the polymer chains, is readily verified. Moreover, the contribution to the overall CLD given by dormant and dead polymer chains is also reported at the larger conversion value. With this respect, the segregation appears to be particularly helpful to the process livingness. In fact, in bulk polymerization the need of keeping small the final amount of dead chains relative to dormant chains is a stringent requirement and poses a major limitation to the maximum admissible radical concentration and, thus, to the maximum polymerization rate. On the other hand, in emulsion polymerization radical concentration and termination rate are decoupled and larger reaction rates are achieved without loosing the CLD homogeneity. Namely, the same kinetics of a non-living process is obtained when using a living mechanism based on degenerative transfer and the final amount of terminated chains can be independently controlled by properly tuning the entry rate.

Concluding remarks

The discrete version of the population balance equations needed to evaluate the CLD in emulsion polymerization is effectively solved using the discretization approach proposed by Kumar and Ramkrishna.[8] Thanks to this approach, a detailed description of the process evolution is obtained with a reasonable computational effort. The pretreatment of the original PBEs is very limited and the resulting discretized equations are not affected by the specific numerical grid. The main features of the process kinetics, the so-called radical compartmentalization, is accounted for in a way not suffering the limitations typical of previous modeling approaches.[4,7]

The applicability of the model to different process conditions is proved by a series of parametric calculations. Namely, the case of reactivating polymerizations is analyzed, with reference to branching and living conditions. Using this numerical method, the direct solution of the equations involving the natural, discrete variable degree of polymerization is readily achieved. Previously reported difficulties in CLD reconstruction have been overcome also in the case of bimodal distributions.

Acknowledgments

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