A Discretization Method for Computing Chain Length Distributions

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Summary: The method of Kumar and Ramkrishna is a numerical technique to solve population balance equations (PBEs) by discretization while preserving two moments of the distribution. When the method is used to calculate chain length distributions in polymerization reactions, the polydispersity, which depends on the first three moments of the distribution, cannot be estimated correctly. This work presents a modification of the method that allows to preserve three moments and thus calculate the polydispersity correctly, independently of the number of grid points. The modified method is applied to a model of controlled radical polymerization via RAFT and compared with the original one.

Keywords: CLD; discretization methods; population balance equations

Introduction

Population balance equations (PBEs) have found many applications in diverse fields of chemical and reaction engineering[1, 2]. The successful use of PBEs depends on the ability to solve them numerically with reasonable computational effort. A great variety of numerical methods to solve PBEs have been presented through the years in the literature, such as the method of moments[3], the method of weighted residuals[4, 5] and its variations (such as orthogonal collocation[6], collocation on finite elements[7], specialized methods based on adaptive Galerkin h-p algorithm[8]), other particular discretization methods[9, 10] and the Monte Carlo method[11, 12]. The discretization method developed by Kumar and Ramkrishna[10] has emerged as an attractive alternative in terms of computational effort, in particular when selected properties of the unknown distribution are of primary interest. It can be regarded as a general formulation comprehensive of all previous methods of the same type while better presenting the corresponding theoretical framework. In the original papers, this method was developed aimed to preserve two integral properties of the unknown distribution and its extension to the preservation of more properties was only shortly

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mentioned with reference to four integral properties.

In this work a modification of the Kumar and Ramkrishna (KR) method allowing the preservation of three properties is presented. Even though these methods are designed for certain selected integral properties rather than for an accurate estimate of the entire unknown distribution[2], the comparative evaluation of the different methods will be carried out in terms of the estimated distributions.

The classical KR method preserving two integral properties

In the original work of Kumar and Ramkrishna[10], an approach for the solution of PBEs in the context of particle size distribution was presented. Butté et al[13, 14] adopted this approach to evaluate chain length distributions in controlled radical polymerization. In this section, the application of the KR method to the PBEs of polymer chains is shortly reviewed.

According to the KR method, the range of possible chain lengths is divided into discrete, contiguous intervals. Each interval i, ranging from the chain lengths n_i to $(n_{i+1}-1)$, is represented by a so-called pivot chain length $\overline{n}_i$. In the approximate distribution, all the chains belonging to interval i are considered to be concentrated at the corresponding pivot chain length $\overline{n}_i$ and the number of chains at each pivot value is denoted by N_i. In the frame of the KR method, the original PBEs of polymer chains P_n are transformed into a set of differential equations for N_i. This is done in a way such that two integral properties of the chain length distribution are preserved. The definition of those integral properties F is as follows:

$$F_1 = \sum_{n=0}^{\infty} f_1(n) P_n$$
$$F_2 = \sum_{n=0}^{\infty} f_2(n) P_n \qquad (1)$$

where f_1 and f_2 are functions of the chain length n. Preserving an integral property means that its value remains the same for the original distribution of P_n and its approximation, the set of N_i:

$$F = \sum_{n=0}^{\infty} f(n) P_n = \sum_{i=1}^{M} f(\overline{n}_i) N_i \qquad (2)$$

where M is the number of discretization intervals. When the PBEs are transformed into

differential equations for N_i, in general, some birth terms will arise that contribute to chain lengths other than the pivot chain lengths $\overline{n}_i$. When a chain of length n in the interval $\overline{n}_i \le n < \overline{n}_{i+1}$ is produced, it is split in fractions $a(n,\overline{n}_i)$ and $b(n,\overline{n}_{i+1})$ to the pivot chains lengths $\overline{n}_i$ and $\overline{n}_{i+1}$, respectively. The values of a and b are then determined so as to force the preservation of two integral properties of the distribution:

$$\begin{aligned} a(n,\overline{n}_i) f_1(\overline{n}_i) + b(n,\overline{n}_{i+1}) f_1(\overline{n}_{i+1}) &= f_1(n) \\ a(n,\overline{n}_i) f_2(\overline{n}_i) + b(n,\overline{n}_{i+1}) f_2(\overline{n}_{i+1}) &= f_2(n) \end{aligned} \tag{3}$$

For example, if these integral properties are chosen to be the 0^{th} and 1^{st} moment of the distribution, F_1 and F_2 are defined as follows:

$$\begin{aligned} F_1 &= \sum_{n=0}^{\infty} P_n \Rightarrow f_1(n) = 1 \\ F_2 &= \sum_{n=0}^{\infty} nP_n \Rightarrow f_2(n) = n \end{aligned} \tag{4}$$

and the partitioning coefficients a and b are given by:

$$\begin{aligned} a(n,\overline{n}_i) &= \frac{n - \overline{n}_{i+1}}{\overline{n}_i - \overline{n}_{i+1}} \\ b(n,\overline{n}_{i+1}) &= \frac{\overline{n}_{i+1} - n}{\overline{n}_i - \overline{n}_{i+1}} \end{aligned} \tag{5}$$

The modified KR method preserving the first three moments of the distribution

According to the formalism shown above, the KR method can easily be extended to calculate not two, but three integral properties of the distribution correctly. The partitioning of chains that are produced by any birth term must be carried out as described in eq. (3), but involving three pivot chain lengths instead of two. When a chain of length n in the interval $\overline{n}_i \le n < \overline{n}_{i+1}$ is produced, it can be represented by assigning the fractions $a(n,\overline{n}_i)$, $b(n,\overline{n}_{i+1})$ and $c(n,\overline{n}_{i+2})$ to the pivot chains lengths $\overline{n}_i$, $\overline{n}_{i+1}$ and $\overline{n}_{i+2}$ respectively. On the other hand, one can also choose to assign the fractions $a(n,\overline{n}_{i-1})$, $b(n,\overline{n}_i)$ and $c(n,\overline{n}_{i+1})$ to the pivot chains lengths $\overline{n}_{i-1}$, $\overline{n}_i$ and $\overline{n}_{i+1}$. This choice is a priori arbitrary and for further discussion we refer to these two possibilities as

forward partitioning and *backward partitioning*, respectively. For forward partitioning, the following set of equations hold for the partitioning coefficients:

$$\begin{aligned} a(n,\overline{n}_i)f_1(\overline{n}_i) + b(n,\overline{n}_{i+1})f_1(\overline{n}_{i+1}) + c(n,\overline{n}_{i+2})f_1(\overline{n}_{i+2}) &= f_1(n) \\ a(n,\overline{n}_i)f_2(\overline{n}_i) + b(n,\overline{n}_{i+1})f_2(\overline{n}_{i+1}) + c(n,\overline{n}_{i+2})f_2(\overline{n}_{i+2}) &= f_2(n) \\ a(n,\overline{n}_i)f_3(\overline{n}_i) + b(n,\overline{n}_{i+1})f_3(\overline{n}_{i+1}) + c(n,\overline{n}_{i+2})f_3(\overline{n}_{i+2}) &= f_3(n) \end{aligned} \tag{6}$$

If the three integral properties that shall be preserved are the first three moments of the CLD, in addition to eqs. (4), we define F_3 as follows:

$$F_3 = \sum_{n=0}^{\infty} n^2 P_n \Rightarrow f_3(n) = n^2 \tag{7}$$

and the partitioning coefficients are given by:

$$\begin{aligned} a(n,\overline{n}_i) &= \frac{\left(\overline{n}_{i+1}\overline{n}_{i+2} - \overline{n}_{i+1}n + n^2 - \overline{n}_{i+2}n\right)}{(\overline{n}_i - \overline{n}_{i+2})(\overline{n}_i - \overline{n}_{i+1})} \\ b(n,\overline{n}_{i+1}) &= \frac{\left(\overline{n}_i\overline{n}_{i+2} - \overline{n}_i n + n^2 - \overline{n}_{i+2}n\right)}{(\overline{n}_i - \overline{n}_{i+1})(\overline{n}_{i+2} - \overline{n}_{i+1})} \\ c(n,\overline{n}_{i+2}) &= \frac{\left(\overline{n}_i\overline{n}_{i+1} - \overline{n}_i n + n^2 - \overline{n}_{i+1}n\right)}{(\overline{n}_i - \overline{n}_{i+2})(\overline{n}_i - \overline{n}_{i+1})} \end{aligned} \tag{8}$$

Choice of the pivot lengths for partitioning

Figure 1 shows the numerical values of the partitioning coefficients a, b and c for forward and backward partitioning. It is seen that in both cases one of the partitioning coefficients is negative for all n values in the interval $\overline{n}_i \le n < \overline{n}_{i+1}$. This fact deserves some attention: it means that the number of chains at one of the pivot lengths is *decreased* when chains are *produced* at a certain length. Although this behavior of the model is mathematically correct, it might disturb the resulting distribution considerably, as shown by the results presented below. By choosing between forward partitioning and backward partitioning, one can decide whether a negative partitioning coefficient is assigned to the pivot length $\overline{n}_{i+2}$ (using forward partitioning), or to the pivot length $\overline{n}_{i-1}$ (using backward partitioning). This choice might influence the resulting CLD considerably and there is no justification to prefer one choice over the other. The point is then to develop a partitioning method that, on the one hand, avoids as much as possible negative partitioning

coefficients and, on the other hand, smoothes disturbing influences on the distribution.

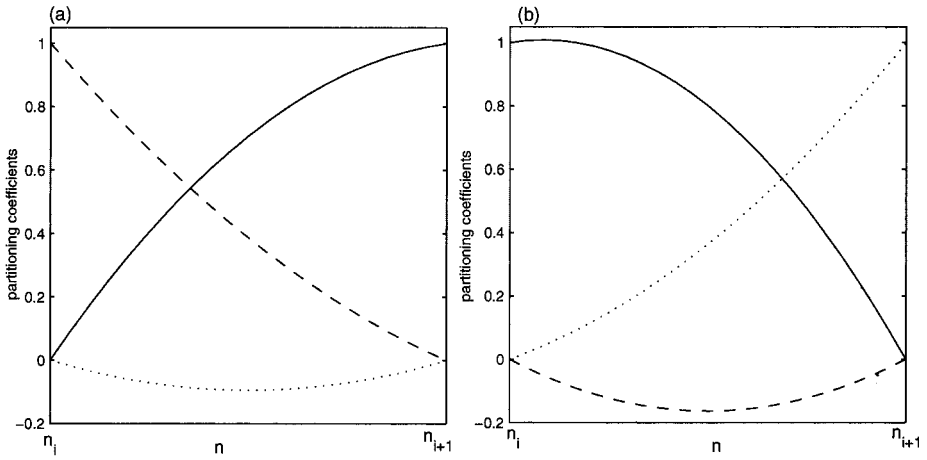

Figure 1. Partitioning coefficients for forward partitioning (a) and backward partitioning (b). $a(n,\overline{n}_i)$ (dashed), $b(n,\overline{n}_{i+1})$ (solid) and $c(n,\overline{n}_{i+2})$ (dotted) in the interval $\overline{n}_i \le n < \overline{n}_{i+1}$ for the case where $\overline{n}_{i+1} = 1.2\overline{n}_i$.

For this, we consider that in all previous instances each partitioning coefficient refers to a single pivot length. Accordingly, in the three constraints of eqs. (6), the three partitioning coefficients refer to three pivot lengths. On the other hand, one single partitioning coefficient can be used with more than one pivot length.

In the method presented here, for chains produced in the interval $\overline{n}_i \le n < \overline{n}_{i+1}$, the partitioning coefficients a and b are used with the neighboring pivot lengths $\overline{n}_i$ and $\overline{n}_{i+1}$, as in the original KR method. The novelty is the use of the third partitioning coefficient c for *all* pivot lengths, weighed with the corresponding number of chains already present at these lengths, N_i. The resulting set of equations is the following:

$$
\begin{aligned}
a(n,\overline{n}_i)f_1(\overline{n}_i) + b(n,\overline{n}_{i+1})f_1(\overline{n}_{i+1}) + c(n)\sum_{k=1}^{M} N_k f_1(\overline{n}_k) &= f_1(n) \\
a(n,\overline{n}_i)f_2(\overline{n}_i) + b(n,\overline{n}_{i+1})f_2(\overline{n}_{i+1}) + c(n)\sum_{k=1}^{M} N_k f_2(\overline{n}_k) &= f_2(n) \\
a(n,\overline{n}_i)f_3(\overline{n}_i) + b(n,\overline{n}_{i+1})f_3(\overline{n}_{i+1}) + c(n)\sum_{k=1}^{M} N_k f_3(\overline{n}_k) &= f_3(n)
\end{aligned}
\tag{9}
$$

The partitioning coefficient c assigns to each pivot length $\overline{n}_i$ a value that is proportional to N_i. That means, the whole set of N_i is multiplied with one value, or in other words, the CLD is rescaled. Summarizing, when a new chain is produced, it is partitioned between the two neighboring pivot lengths, and the entire distribution is rescaled, in order to preserve three integral properties. This method is referred to as *spread partitioning* in the following. Assuming that the three integral properties to be preserved are the first three moments of the distribution, the three partitioning coefficients are expressed as follows:

$$
\begin{aligned}
a(n,\overline{n}_i) &= \frac{\left(-\mu_1 n^2 + n\mu_2 + \mu_0 n^2 \overline{n}_{i+1} - \mu_0 \overline{n}_{i+1}{}^2 n + \overline{n}_{i+1}{}^2 \mu_1 - \mu_2 \overline{n}_{i+1}\right)}{\left(-\overline{n}_i\mu_1 + \overline{n}_i\mu_0\overline{n}_{i+1} + \mu_2 - \overline{n}_{i+1}\mu_1\right)\left(\overline{n}_i - \overline{n}_{i+1}\right)} \\
b(n,\overline{n}_{i+1}) &= \frac{\left(\mu_1 n^2 - n\mu_2 - \mu_0 n^2 \overline{n}_i + \mu_0 \overline{n}_i{}^2 n - \overline{n}_i{}^2 \mu_1 + \mu_2 \overline{n}_i\right)}{\left(-\overline{n}_i\mu_1 + \overline{n}_i\mu_0\overline{n}_{i+1} + \mu_2 - \overline{n}_{i+1}\mu_1\right)\left(\overline{n}_i - \overline{n}_{i+1}\right)} \\
c(n,\overline{n}_{i+2}) &= \frac{\left(-\overline{n}_i n + \overline{n}_i\overline{n}_{i+1} + n^2 - \overline{n}_{i+1} n\right)}{\left(-\overline{n}_i\mu_1 + \overline{n}_i\mu_0\overline{n}_{i+1} + \mu_2 - \overline{n}_{i+1}\mu_1\right)}
\end{aligned}
\tag{10}
$$

By analyzing the above equations, two important facts can be stated: first, the partitioning coefficients are a function of the distribution, or, more precisely, of its first three moments. Second, by direct computation it can be seen that the partitioning coefficient $c(n)$ is negative. This means that partitioning with a negative value never affects one single pivot value, but it is spread over the entire distribution. The four plots in Figure 2 show the partitioning coefficient $c(n)$ for different values of the moments of the CLD in terms of the number average molecular weight M_n and the polydispersity. In particular, we have considered situations where n is similar, or quite different from M_n with low and high polydispersity. Only for the case where n is similar to M_n and the polydispersity is very low, the negative values of c are comparable to the negative values that occur when the forward or backward partitioning is used, as seen in Figure 1.

In all other cases (n far from M_n, higher polydispersity), the negative values of c are much closer to zero. Accordingly, this method seems to meet the conditions indicated above fairly well.

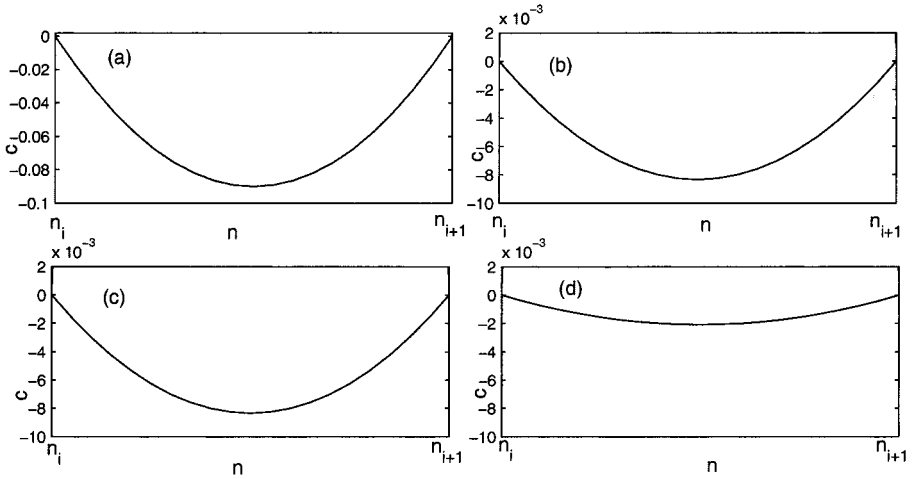

Figure 2. The negative partitioning coefficient $c(n)$ for spread partitioning in the interval $\overline{n}_i \le n < \overline{n}_{i+1}$, for the case that $\overline{n}_{i+1} = 1.2\overline{n}_i$ and $\mu_0 = 1$. (a) $M_n = 1.1\overline{n}_i$, $Pd = 1.1$, (b) $M_n = 1.1\overline{n}_i$, $Pd = 2.0$, (c) $M_n = 2.0\overline{n}_i$, $Pd = 1.1$, (d) $M_n = 2.0\overline{n}_i$, $Pd = 2.0$.

Results and Discussion

In this section we will illustrate the results of the different partitioning methods described above in simulating the chain length distribution resulting from a controlled free radical polymerization via RAFT. This polymerization has been described extensively in the literature[15] and the application of the KR method to such polymerization systems has been described in detail by Butté et al[13, 14]. Tables 2 to 4 report the kinetic scheme of the system, as well as the values of the model parameters and the initial conditions. The model calculations provide sets of N_i, from which the entire distributions can be reconstructed with the method described in the Appendix.

In Figures 3 to 5 the dormant chain distribution D_n, computed by each of the different methods presented above, that is the classical KR method preserving two moments, as well as forward and

spread partitioning, both preserving three moments, is compared with a reference solution that has been calculated by solving individually the entire set of the PBEs numerically up to a chain length of $n = 500$. In each Figure the results corresponding to four different grids of $\overline{n}_i$ are shown. The used grids are described in Table 1: grid one is the coarsest, while grid four is the finest.

The results of the original KR method preserving two moments of the distribution are shown in Figure 3. The polydispersity is generally overestimated so that the distribution is always broader than the reference distribution. Figure 6 shows the relative error of the polydispersity for the four different grids of $\overline{n}_i$. The error appears to be proportional to $s-1$, where $s = \overline{n}_{i+1} / \overline{n}_i$ for a geometrical grid.

The results of the modified KR method preserving three moments with forward partitioning are shown in Figure 4. When the grid is too coarse, this method fails to predict the distribution and introduces oscillations that sometimes even lead to negative values. This is a direct consequence of the arbitrary choice of partitioning that leads to negative partitioning coefficients at single pivot lengths. Apparently, there is a certain critical grid density that has to be overcome to prevent the occurrence of oscillations. In the case presented here, only grid 4 is fine enough to avoid this behavior.

Finally, Figure 5 shows the result of the modified KR method preserving three moments using spread partitioning. With the exception of the coarsest grid, the results that are obtained here appear to be in good agreement with the reference solution. We can also observe a certain critical grid density (between grid one and grid two in the case under examination) that has to be overcome to prevent the occurrence of oscillations that, although to a much smaller extent, can occur also in this case. The critical grid density is in fact much lower than in the case shown in Figure 4.

It is to be noted that by increasing the grid densities, the results of all presented methods converge to the reference solution.

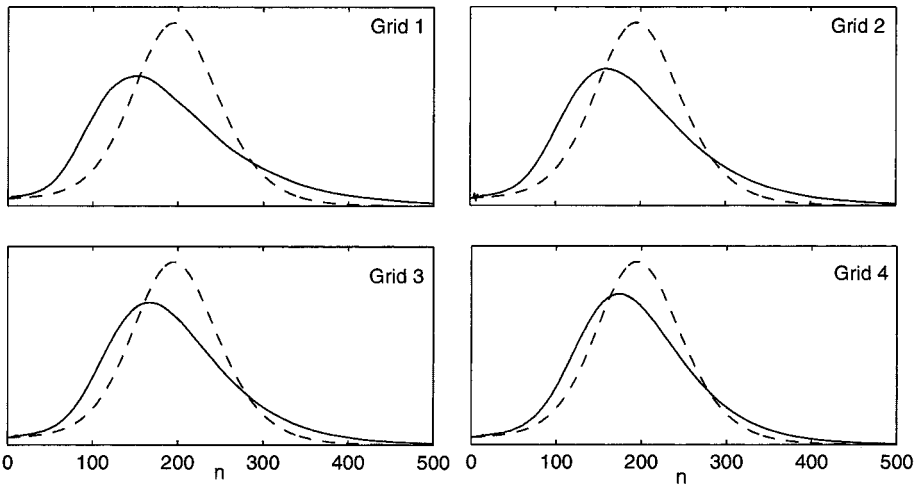

Figure 3. Number distribution of dormant chains D_n at conversion = 40% calculated using the classical KR method preserving the first two moments (solid); reference solution (dashed).

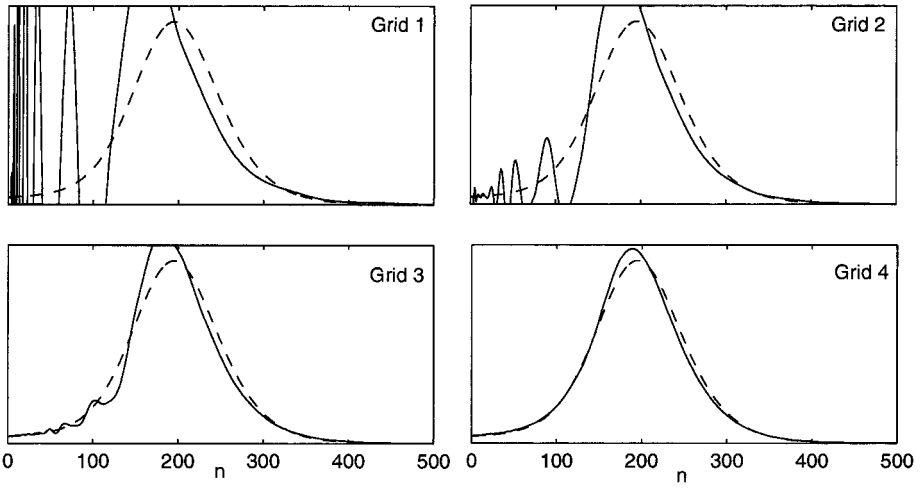

Figure 4. Number distribution of dormant chains D_n at conversion = 40% calculated using the modified KR method preserving the first three moments with forward partitioning (solid); reference solution (dashed).

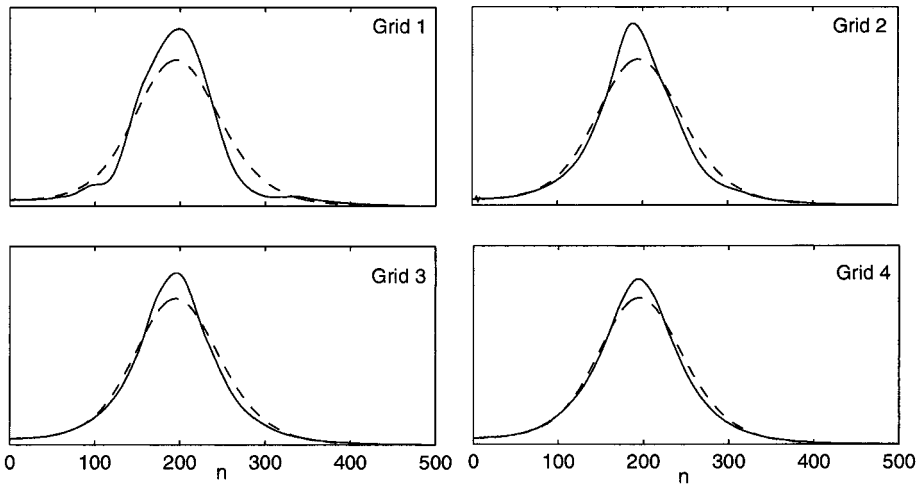

Figure 5. Number distribution of dormant chains D_n at conversion = 40% calculated using the modified KR method preserving the first three moments with spread partitioning (solid); reference solution (dashed).

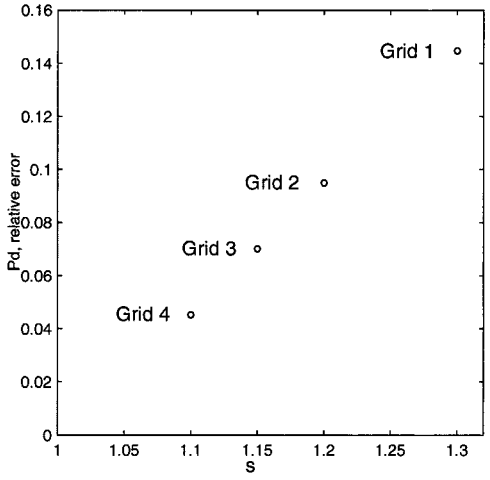

Figure 6. Relative error in estimating the polydispersity of the dormant chains D_n at conversion = 40% calculated with the classical KR method preserving the first two moments (cf. Figure 3). $s = \overline{n}_{i+1} / \overline{n}_i$

Table 1. Definition of the grids used for the model calculations in Figures 3 to 5

Grid 1	$\overline{n}_i = \begin{cases} i & i \le 10 \\ s\overline{n}_{i-1} & i > 10 \end{cases}$	$s = 1.10$
Grid 2	$\overline{n}_i = \begin{cases} i & i \le 7 \\ s\overline{n}_{i-1} & i > 7 \end{cases}$	$s = 1.15$
Grid 3	$\overline{n}_i = \begin{cases} i & i \le 6 \\ s\overline{n}_{i-1} & i > 6 \end{cases}$	$s = 1.20$
Grid 4	$\overline{n}_i = \begin{cases} i & i \le 4 \\ s\overline{n}_{i-1} & i > 4 \end{cases}$	$s = 1.30$

Conclusion

When modeling the evolution of chain length distributions during polymerization reactions, it is desirable to compute correctly the polydispersity of the distribution, which involves its first three moments. For this, in this work, the Kumar Ramkrishna method has been modified in order to preserve the first three moments of the distribution. It has been found that a proper choice of the partitioning method is essential to avoid oscillating solutions that give correct moments but do not reflect the real shape of the distribution. The so-called spread partitioning has been introduced to significantly reduce such oscillations, as demonstrated for an example of controlled free radical polymerization via RAFT.

Table 2. Kinetic scheme of the model calculations

Initiator decomposition	$I_2 \xrightarrow{k_d\eta} 2I$
Radical formation	$I + M \xrightarrow{k_p} R_1$
Propagation	$R_n + M \xrightarrow{k_p} R_{n+1}$
Termination by Combination	$R_n + R_m \xrightarrow{k_{tc}(x)} P_{n+m}$
Termination by Disproportionation	$R_n + R_m \xrightarrow{k_{td}(x)} P_n + P_m$
Chain transfer to monomer	$R_n + M \xrightarrow{k_{fm}} P_n + R_1$
RAFT exchange (dormant chains)	$R_n + D_m \xrightarrow{k_{ex}(x)} D_n + R_m$
RAFT exchange (RAFT agent)	$R_n + D_0 \xrightarrow{{}^0k_{ex}(x)} D_n + I$

Table 3. Kinetic parameters

$k_I = 1.05 * 10^{15}\mathrm{s}^{-1} \exp\left(-128287\mathrm{Jmol}^{-1}/RT\right)$
$\eta = 0.5$
$k_p = 4.92 * 10^{5}\mathrm{Lmol}^{-1}\mathrm{s}^{-1} \exp\left(-18213\mathrm{Jmol}^{-1}/RT\right)$
$k_{t0} = 9.8 * 10^{7}\,\mathrm{Lmol}^{-1}\mathrm{s}^{-1} \exp\left(-2933\mathrm{Jmol}^{-1}/RT\right)$
$\frac{k_{td}}{k_{tc}} = 2.57 * 10^{3} \exp\left(-17113\mathrm{Jmol}^{-1}/RT\right)$
$k_{fm} = 4.66 * 10^{9}\mathrm{Lmol}^{-1}\mathrm{s}^{-1} \exp\left(-76290\mathrm{Jmol}^{-1}/RT\right)$
$k_{ex0} = 1.0 * 10^{6}\mathrm{Lmol}^{-1}\mathrm{s}^{-1}$
${}^0k_{ex0} = 1.3 * 10^{4}\mathrm{Lmol}^{-1}\mathrm{s}^{-1}$

Table 4 Initial conditions.

$I_{2,0} = 0.01\mathrm{mol/L}$	$D_{0,0} = 0.02\mathrm{mol/L}$
$M_0 = 10\mathrm{mol/L}$	$T = 70^{\circ}\mathrm{C}$

Appendix – Reconstruction of the distribution

All the numerical techniques discussed in this work provide an estimate of the distribution N_i, at the pivot lengths $\overline{n}_i$. In order to reconstruct the entire distribution P_n from that result, we need an appropriate procedure. In this work, we made the assumption that within each interval i, the distribution P_n is a third order polynomial of n.

$$\overline{n}_i \le n < \overline{n}_{i+1} \qquad P_n = c_{i,0} + c_{i,1}n + c_{i,2}n^2 + c_{i,3}n^3 \tag{11}$$

where $c_{i,0},\ldots,c_{i,3}$ are the coefficients of the polynomial that have to be evaluated for each interval i. Each polynomial expands between two neighboring pivot lengths. Since the distribution and its first derivative must be continuous, the following conditions apply:

$$\begin{aligned} c_{i-1,0} + c_{i-1,1}\overline{n}_i + c_{i-1,2}\overline{n}_i^2 + c_{i-1,3}\overline{n}_i^3 &= c_{i,0} + c_{i,1}\overline{n}_i + c_{i,2}\overline{n}_i^2 + c_{i,3}\overline{n}_i^3 \\ c_{i-1,1} + 2c_{i-1,2}\overline{n}_i + 3c_{i-1,3}\overline{n}_i^2 &= c_{i,1} + 2c_{i,2}\overline{n}_i + 3c_{i,3}\overline{n}_i^2 \end{aligned} \tag{12}$$

In addition, the slope of the distribution at a pivot chain length $\overline{n}_i$ shall be equivalent to the slope of the cord of the distribution between the two neighboring pivot chain lengths $\overline{n}_{i-1}$ and $\overline{n}_{i+1}$:

$$c_{i,1} + 2c_{i,2}\overline{n}_i + 3c_{i,3}\overline{n}_i^2 = \frac{P_{\overline{n}_{i+1}} - P_{\overline{n}_{i-1}}}{\overline{n}_{i+1} - \overline{n}_{i-1}} \tag{13}$$

For the very first and the very last considered chain length, the slope is set to 0. The last condition arises from the fact that the distribution P_n must give the set of N_i that was obtained from the model calculations, if the classical KR method is applied to the distribution. This implies that for each N_i the following equation must hold:

$$N_i = \sum_{n=\overline{n}_{i-1}}^{\overline{n}_i - 1} b(n,\overline{n}_i)\,P_n + \sum_{n=\overline{n}_i}^{\overline{n}_{i+1}-1} a(n,\overline{n}_i)\,P_n \tag{14}$$

For a reconstruction that corresponds to the classical KR method, a and b are defined in eq. (5). Reconstruction methods that correspond to the modified KR methods would be mathematically more complex and do not improve the results significantly. Therefore, eqs. (14) and (5) have been used for reconstruction for the modified KR methods as well.

From these conditions, a unique solution for P_n can be calculated for any given set of N_i.

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