

Recent progresses in the development of more reliable predictions of average molecular weights and chain-length distributions for complex irreversible non-linear polymerizations

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Abstract

Prediction of the structure of branched polymers is a challenging problem, for which only more or less clumsy mathematical solutions have been made available for a long time in the case of kinetically controlled polymerizations. The matter has, nevertheless, considerable economic significance. For instance, a controlled amount of long branching is known to have many benefits on the rheologic properties of the widely used polyolefins (Nele et al., 2003). Development of processes and their optimization could benefit a lot with models with better predictive capacities.

Progresses in applied mathematics could at last bring about a considerable improvement in this situation. This paper reviews recent methods (Costa and Dias, 2003; Dias and Costa, 2003, 2005) allowing the direct computation of moments (i. e. avoiding Hulburt-Katz closures) of polymer chain length distributions, even in the presence of gel, overcoming past difficulties in their computational implementation. Description of non-linear free radical polymerizations is now possible, thanks to the development of methods for solving highly *stiff* two point boundary value problems (Cash et. al., 2001). Chain length distributions are obtained by adapting algorithms better known with Laplace transform inversion (Pappoulis, 1956; Weeks, 1966; Durbin, 1974). Numerous past inconsistencies leading to unwanted errors are now avoided through the use of well-founded chemical and mathematical principles.

1 Introduction

The use of discrete transforms or generating functions in the modeling of random processes such as polymer formation is known in Polymer Science and Engineering since its very beginnings. Obtaining the required discrete transforms of polymer chain length distribution, possibly in complex domain, is the most serious difficulty, and it can even be impossible. Irreversible polymerizations are always tractable, though. Most practical problems involve a tedious and error-prone mathematical formulation, which fortunately can be avoided through a general procedure for the solution of the resulting partial differential equations by the method of characteristics in an automated way (Costa and Dias, 1994, 2005). However, only recently could the severe numerical difficulties present with free-radical systems be overcome (Costa and Dias, 2003; Dias and Costa, 2003, 2005).

Inversion of numerically computed discrete transforms of polymer CLD was successfully carried out for polycondensations (Mills, 1986; Costa and Villermaux, 1988) but that method requires about half as many values of the discrete transform as the upper limit of the chain length where the distribution is sought. This is inadequate for most chain polymerizations, or systems close to gel point, where chain lengths of many millions are observed.

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An adaptation of methods used for inversion of Laplace transforms alleviates that problem (Miller et al., 1996). More recent works by Sarmoria's group (Asteasuain et al., 2002a,b) have been using it.

These latter studies have only dealt with very simple kinetic schemes, mostly linear polymerizations, as well as a free-radical polymerization showing transfer to polymer, but overly simplified, neglecting the presence of more than one free-radical site per molecule, and therefore introducing severe inconsistencies. The method of lines was used to solve the partial differential equations yielding the discrete transforms, disregarding previous works based on the method of characteristics. This ruins any attempt of dealing with complex multidimensional problems.

There are no such limitation on the approach we have been using since the early nineties. Predictions of average molecular weights have been compared with those using the pseudo-kinetic method, Monte Carlo method, different versions of the method of moments and with numerical fractionation (Costa and Dias, 2003, 2005; Dias and Costa, 2005) and shown to be more exact. A brief analysis of the possibility of predicting the CLD by this method has already been presented using a non-linear free radical polymerization as a case study (Dias and Costa, 2005). Legacy methods can only deal with distributions of a single kind of chain length, and try to take into account branching by considering multiple unidimensional distributions. The presence of many propagating sites per molecule destroys their predictive capabilities, which is specially serious in the neighborhood of gel point.

There is no numerical method for inverting Laplace transforms which can be universally trusted. Two or more different methods have to be used and their results compared. We have therefore studied a set of polymerization systems, allowing the analytical evaluation of the chain length distribution, to test the inversion method but now with CLDs showing much higher average chain lengths and including a distribution typical of a hyperbranched polymer.

The calculation of the CLD is here shown for a case study with industrial relevance: the metallocene catalyzed copolymerization of an olefin with a non-conjugated diene.

2 Overview of the method of CLD prediction through discrete transforms

According to our general kinetic analysis of non-linear irreversible polymerizations (Costa and Dias, 1994, 2005), the chemical system should be first described through the mole concentrations of distinguishable chemical groups in polymer as well as the individual species, such as monomers, initiators, transfer agents collected in a vector $\mathbf{A} = [A_j]$ of size N_A . For easeness of presentation, the sub-set of the N_P groups with lower indices will be considered to contain the chemical groups in polymer. Polymer molecules are lumped into classes with same counts of chemical groups, or chain lengths. The m -th such class is defined by vector \mathbf{a}_m of size N_P and named $P(\mathbf{a}_m)$. Its mole concentration is $P(\mathbf{a}_m)$. In the usual situation where a sample of polymer with infinite size is considered, the probability function of the CLD in number of molecules $P_n(\mathbf{a})$ is obtained normalizing by the overall mole concentration of polymer $P = \sum_{a_1=0}^{\infty} \dots \sum_{a_{N_P}=0}^{\infty} P(a_1, \dots, a_{N_P})$:

$$P_n(\mathbf{a}) = \frac{P(\mathbf{a})}{P} \quad (1)$$

$G_n(\mathbf{s})$, the probability generating function (PGF) of the CLD is the discrete transform (also known as the vectorial moment generating function MGF) of $P_n(\mathbf{a})$ with respect to the group counts, related to the MGF of the mole concentrations $G(\mathbf{s})$:

$$G(\mathbf{s}) = \sum_{a_1=0}^{\infty} \dots \sum_{a_{N_P}=0}^{\infty} s_1^{a_1} \dots s_{N_P}^{a_{N_P}} P(a_1, \dots, a_{N_P})$$

$$G_n(\mathbf{s}) = \frac{G(\mathbf{s})}{P} \quad (2)$$

The reactions among the groups in polymer and/or individual chemical compounds are described using suitable sets of stoichiometric coefficients (Costa and Dias, 1994, 2005). In the case of irreversible polymerizations, taking advantage of Flory's Principle of the Equal Reactivity, it is possible to write

a general master equation describing the time change of $G(\mathbf{s})$ in ideal reactors, such as in a CSTR of constant space-time τ (but in a transient state), which is a hyperbolic first-order partial differential equation taking the aspect below shown when volume changes are negligible:

$$\frac{\partial G}{\partial t} = G_{R_P}(\mathbf{A}, \mathbf{s}, \mathbf{G}') + \frac{G_F(t) - G}{\tau} \quad (3)$$

G_{R_P} is the MGF of the rate equation of formation of polymer species by chemical reaction. It may be found in Costa and Dias (2005), as well as the functions $R_{A_j}, R_{G'_j}, s'_j$ and R_G below used. The vector \mathbf{G}' contains the partial derivatives of G with respect to $\log s_j$, $G'_j = \frac{\partial G}{\partial \log s_j}$, but involving only the groups, again preferably ranged in the lower indices $j = 1, \dots, N_{A_P}$, present in the polymer which are consumed by chemical reaction. Eq. (3) is solved by the method of characteristics, leading to the ordinary differential equations Eqs. (4-7) to be solved between $t = 0$ and $t = t_f$ with initial and boundary conditions Eqs. (8-11):

$$\frac{dA_j}{dt} = R_{A_j}(\mathbf{A}) + \frac{A_{jF} - A_j}{\tau} \quad j = 1, \dots, N_A \quad (4)$$

$$\frac{dG'_j}{dt} = R_{G'_j}(\mathbf{A}, \mathbf{s}, \mathbf{G}') + \frac{G'_{jF} - G'_j}{\tau} \quad j = 1, \dots, N_{A_P} \quad (5)$$

$$\frac{ds_j}{dt} = s'_j(\mathbf{A}, \mathbf{s}, \mathbf{G}') \quad j = 1, \dots, N_{A_P} \quad (6)$$

$$\frac{dG}{dt} = R_G(\mathbf{A}, \mathbf{s}, \mathbf{G}') + \frac{G_F - G}{\tau} \quad (7)$$

$$A_{j|t=0} = A_{j_0} \quad j = 1, \dots, N_A \quad (8)$$

$$G'_{j|t=0} = \frac{\partial G_0}{\partial \log s_j}(\mathbf{s}_0) \quad j = 1, \dots, N_{A_P} \quad (9)$$

$$s_{j|t=0} = s_{j_0} \quad s_{j|t=t_f} = s_j(t_f) \quad j = 1, \dots, N_{A_P} \quad (10)$$

$$G|_{t=0} = G_0(\mathbf{s}_0) \quad (11)$$

The inversion of $G(\mathbf{s})$ needs the repeated solution of the above two-point boundary value problem for a set of values of $\mathbf{s}(t_f)$, which may be real or complex according to the method chosen. For the moment, only unidimensional distributions have been computed, and so all dummy Laplace variables are set equal to one, except the one with respect to the chain length (or group count) to investigate. Thus, Papoulis' method uses only real values of s_j , while Weeks' and Durbin's methods need complex values. The increased computational effort is counteracted by the much higher accuracy of these latter two methods. Our numerical experiments with many kinds of CLDs have shown that Durbin's method requires much more evaluations of the MGF, and should be used mostly for checking the accuracy, as it is a lot more exact. An exception occurs with narrow CLDs (such as the Poisson distribution of ideal living polymerizations), for which Durbin's method is the only which does not break down.

3 The simulation of the metallocene catalyzed copolymerization of an olefin with a non-conjugated diene

In the metallocene catalyzed olefin polymerization, long chain branching is introduced through the polymerization of terminal double bonds generated by β -hydride elimination. It has also been suggested that the copolymerization of an olefin with a non-conjugated diene can be used for producing long chain branching polyolefins under mild conditions. In this case, the polymer will contain pendant double bonds from the diene monomer in addition to those resulting from β -hydride elimination. Gelation becomes

possible, and this must be avoided in industrial production.

An olefin/diene polymerization system was recently simulated in the pre-gel region by using a finite element procedure (Nele et al., 2003). The kinetic scheme considered initiations, propagations, chain transfers (to hydrogen), β -hydride elimination and deactivation of polymer chains. The chemical groups are:

- Olefin-terminated active chain (OTAC)
- Diene-terminated active chain (DTAC)
- Pendant double bond-terminated active chain (PTAC)
- Terminal double bond-terminated active chain (TTAC)
- Pendant double bond (PDB)
- Terminal double bond (TDB)
- Olefin monomer
- Diene monomer
- Initiator
- Chain transfer agent
- Polymerized olefin unit
- Polymerized diene unit
- Branching point

A total number of $N_A = 13$ chemical groups is considered, $N_P = 9$ of them being present in the polymer molecules, from which $N_{AP} = 6$ are active. Four different kinds of active chains with different reactivities are distinguished. Likewise, pendant double bonds (from diene) are distinguished from terminal double bonds (originated by β -hydride eliminations). Four initiation reactions are therefore considered and 16 propagation reactions are distinguished. With chain transfer, β -hydride elimination and deactivation reactions, a total number of 32 chemical reactions are obtained. Transfer to monomers, deactivation of the catalysts or ring formation have been neglected; they could be easily included if needed so, as shown with other polymerization systems (Costa and Dias, 2003, 2005; Dias and Costa, 2003, 2005). The numerical values of the 32 kinetic parameters of the present kinetic scheme used in simulations are similar to those used before in related works (Nele et al., 2003). Other values have been postulated taking into account the decreased reactivity of pendant and terminal double bonds.

Figure 1 shows the predict average chain lengths for batch and transient operation of a CSTR for the metallocene catalyzed copolymerization of an olefin with a non-conjugated diene. With the present method it is possible the calculation of average chain lengths before and after gelation as shown in Figure 1.

The calculation of the CLD for this polymerization system is also possible before and after gelation. Papoulis, Weeks (or its implementation by Garbow) and Durbin's methods were used.

The time evolution of the CLD for the present polymerization system is presented in Figure 2 in a batch reactor and in Figure 3 for batch and CSTR.

The reliability of these calculations was verified by comparing the results obtained with Papoulis, Weeks and Durbin's inversion methods, and a very good agreement between the results of the different techniques has been found. With Papoulis' method, 5 terms in the polynomial expansion were considered for each value of chain length. In these circumstances, around 10 min of CPU time are needed for the calculation of a single point of the CLD. Garbow's implementation of Weeks' method was applied with maximum order 128 and the minimum value of absolute uniform pseudo accuracy that allows convergence (a typical value was 10^{-13}) was considered. For these conditions, less than 40 min of CPU time were needed for each range of chain length considered. The calculations with Durbin's method were performed with common values for absolute and relative accuracies 10^{-14} . 3 h of CPU time can be needed for the computation of a single value of the CLD, requiring about 200 evaluations of transform.

4 Conclusions

A general method for the numerical calculation of chain length distributions in non linear polymerizations was presented. The major distinctive features of this approach are:

- Calculation of CLD both before and after gelation
- A kind of interpreter of irreversible polymerization systems makes possible the consideration of complex kinetic schemes in an automated way
- An improved accuracy in the evaluation of PGF is obtained by eliminating several simplifying assumptions (such as the absence of multiple propagating species and the need for moment closures)

Adaptations of methods originally applied in the inversion of Laplace transforms could lead to reliable results with moderate use of CPU time.

Predictions before and after gelation are possible, as shown for the copolymerization of an olefin with a non-conjugated diene, something which alternative methods (such as the so-called "numerical fractionation") are unable to do.

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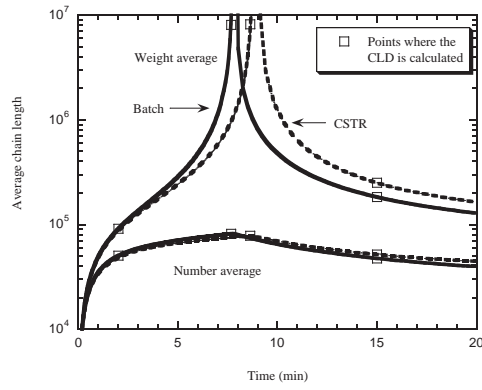


Figure 1: Predicted average chain lengths before and after gelation in metallocene-catalyzed copolymerization of an olefin with a non-conjugated diene for batch and CSTR operation. Feed composition (same in the Figs. 2-3: olefin=1 M; initiator = 10^{-6} M; chain transfer agent = 10^{-4} M; mole fraction of diene in feed $\frac{D}{M+D} = 0.002$).

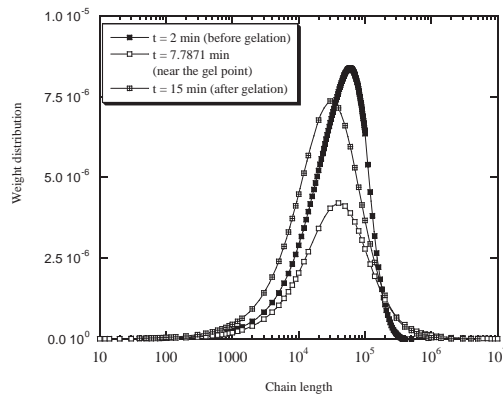


Figure 2: Predicted evolution of the chain length distribution in the metallocene-catalyzed copolymerization of an olefin with a non-conjugated diene for batch operation.

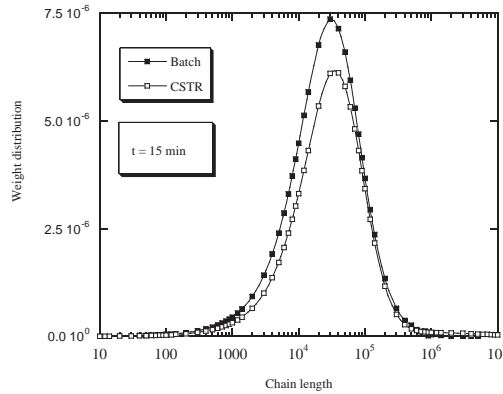


Figure 3: Predicted chain length distributions at $t=15$ min for batch and CSTR ($\tau=5$ min) operation in the metallocene catalyzed copolymerization of an olefin with a non-conjugated diene.