

An Approach for Complete Molecular Weight Distribution Calculation: Application in Ethylene Coordination Polymerization

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ABSTRACT: The objective of this article is to present an approach to ascertain the molecular weight distribution (MWD) of polymeric systems and its application to an industrial polyethylene reactor. Ascertaining the complete MWD can provide more reliable predictions of polymer end-use properties, as some of them may depend on specific molecular weight ranges, instead of solely on the averages of the distribution. The proposed method is based on differentiation of the cumulative MWD, where the accumulated concentrations, evaluated at a finite number of chain lengths, are considered components in a reaction medium. Therefore, the dimension of the mathematical model may be suited to the desired level of detail on

the MWD. The ethylene polymerization in solution with Ziegler–Natta catalyst is taken as a case study because of the lack of studies in this field. The reaction takes place in continuously stirred and tubular reactors. The results show the potential of the proposed approach and its usefulness in ascertaining the whole MWD, which in turn can be used to predict the polymer end-use properties. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2176–2186, 2008

Key words: computer modeling; simulations; Ziegler–Natta polymerization; polymerization; molecular weight distribution

INTRODUCTION

Polymerization reaction engineering may satisfy not only yield and purity specifications but also the desired polymer processing characteristics and end-use properties. In the polymer industry, these properties are the real measure of polymerization reactor performance. On the other hand, polymer chains produced in polymerization reactors do not have the same length or molecular weight (MW), i.e., there are many species in the reaction medium with different concentrations. Therefore polymers are characterized by a molecular weight distribution (MWD) which determines the polymer's final properties. It is important to identify this distribution to develop representative and useful mathematical models.

End-use properties are usually related to MWD mean values and dispersion.¹ However, it is important to note that in many cases these two properties fail to describe polymer end-use properties satisfactorily. Rheological and processing properties might show significant differences in cases where there is a high concentration of high or low molecular weight fractions.² Studies such as those carried out by Hinchliffe et al.² show the importance of specific molecular weight fractions in polymer end-use properties. A polymer property Q can be determined by molecular weight fractions (A_i is the area under the curve and α_i are constants estimated through experimental data-fitting) as Figure 1 illustrates.

As MWD affects polymer rheology and end-use properties, there has been considerable interest in controlling the MWD of synthetic polymers during polymerization processes. In recent years, therefore, much effort has gone into developing procedures to estimate or to model MWD, as well as to control such properties in polymer production.

Wells and Ray³ studied the effects of operating conditions on the polyethylene produced in a perfectly mixed autoclave. The MWD is obtained with a stationary simulation through linear expansions of polymer concentration ranges. Tobita⁴ used a power-law distribution to represent the MWD at the gel

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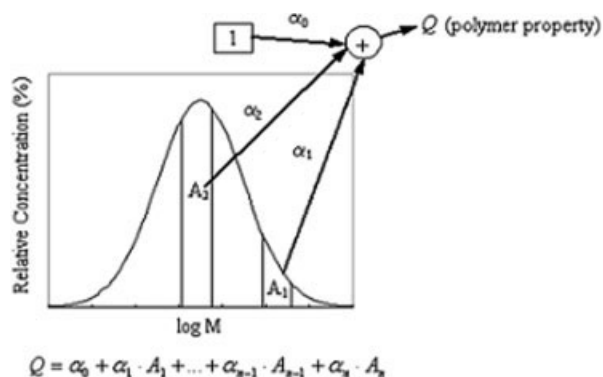


Figure 1 Relationship between polymer end-use properties and some molecular weight fractions.

point during emulsion polymerization of ethylene. The results were compared with experimental data reported in literature. Fang et al.⁵ developed a mathematical model for gas-phase butadiene polymerization. The model is based on the multilayer model of polymeric particles and on new intrinsic kinetics. The authors used a weight distribution function to obtain the MWD of each layer.

Despite this interest in calculating the whole MWD, few authors have written about complete MWD for ethylene coordination polymerization in solution. Thus, the main contribution of this work is to present an approach to calculate the complete MWD for coordination polymerization. It is based on the differentiation of the cumulative MWD, where the accumulated concentration up to a given chain length is considered a component in reaction medium and hence has an associated component mass balance. This technique has been applied to the ethylene polymerization process in solution with Ziegler-Natta catalyst in continuous stirred tank reactor (CSTR) and plug flow reactor (PFR).

PROCEDURES TO COMPUTE MWDs

Deterministic modeling of polymerization systems involves the solution of an infinite number of mass balance equations given the great number of species in the reaction medium. There are some techniques that attempt to overcome this difficulty to obtain the MWD or at least some of its parameters, as Figure 2 depicts.

Because of difficulties usually found in the calculation of the whole MWD, it is sometimes more useful to use the leading moments of the distribution to characterize it. They reduce the infinite number of equations in the mass balance to just a few ones. Despite the fact that moments give only the mean molecular weight and polydispersity, they are well suited in many cases and constitute a widely used technique. The *k*th-order moment, μ_k , is defined as

$$\mu_k = \sum_{p=1}^{\infty} p^k \cdot P_p, \quad k = 0, 1, 2, \dots \quad (1)$$

where *p* is the number of monomeric units in polymer chain and P_p is the concentration of polymer with *p* monomer units.

The direct sequential solution is based on sequential integration of the differential equations in mass balance, as the concentration P_p depends on P_{p-1} . According to Dotson et al.,⁷ in some systems, a general expression can be obtained by induction of initial integrations, without having to integrate infinite equations. They apply this technique to an anionic batch polymerization, obtaining a Poisson distribution to represent the complete MWD. However, in more complex systems, it is not possible to obtain a single expression for the distribution by induction. Verros⁸ developed a method to calculate the MWD in free radical copolymerization in a batch isothermal reac-

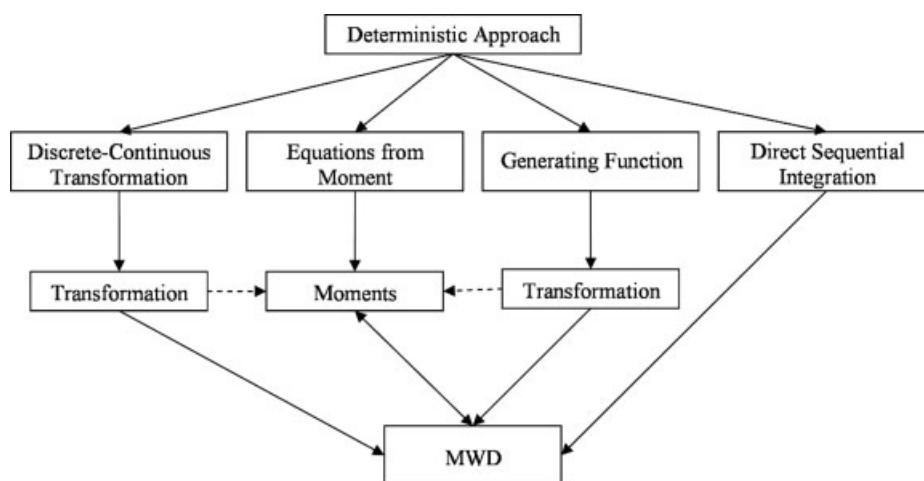


Figure 2 Deterministic techniques used to estimate the MWD of polymerization systems.⁶

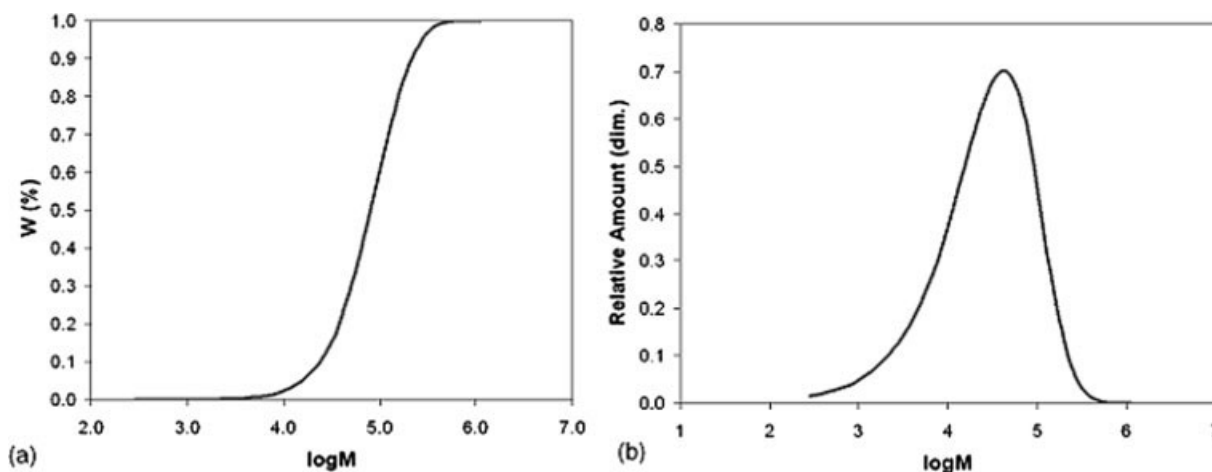


Figure 3 (a) Cumulative and (b) differential molecular weight distributions.

tor. The method is based on the direct sequential integration of the infinite mass balance equations for the dead polymer. To reduce the number of equations to be integrated, an approximation for continuous variable through Taylor series was used.

McCoy and Madras⁹ compared a continuous and a discrete model for polymerization and its reverse, depolymerization. They concluded that both approaches are equivalent and that the discrete model is a special case of the continuous one.

Crowley and Choi¹⁰ proposed a method, named Finite Molecular Weight Moments, which calculates the mass fraction in a finite chain length range, as well as the moments of the distribution. This method can be viewed as an extension to the method of molecular weight moments as some low order moments are calculated. It was applied to methyl methacrylate polymerization in solution (free radical) in a pilot batch reactor. The obtained results were validated with gel permeation chromatography data, considering 20 chain length ranges.

Brandolin and Sarmonia¹¹ presented a mathematical model able to describe the whole MWD for ethylene and vinyl acetate copolymers in autoclave reactors (free radical). The generating function was used to transform the infinite number of ordinary equations into a finite number of equations. The resulting function was inverted, providing the complete MWD, which was compared with experimental data. Another example of complete MWD computation through generating functions and their inversion is reported by Austeasuain et al.,¹² which concerns a model for polypropylene with controlled rheology.

Canut and Ray¹³ applied the discrete weighted residual method to a free-radical polymerization batch reactor, to obtain the complete MWD. Sayer et al.¹⁴ applied orthogonal collocation to calculate the complete MWD in emulsion polymerization. They also presented a survey on the computation of the com-

plete MWD and the various techniques used to accomplish this task.

As can be seen from the literature, the studies related to the whole MWD have mainly been applied to free radical polymerization. McAuley et al.¹⁵ and Carvalho et al.¹⁶ developed mathematical models for ethylene polymerization with Ziegler–Natta heterogeneous catalyst. Cozewith,¹⁷ Kim and Choi,¹⁸ and Embiruçu et al.^{19,20} also studied ethylene polymerization systems with Ziegler–Natta catalyst, but in solution. All these models use the moments of the distribution to calculate molecular weight mean values and polydispersity. Thus, apart from the few models concerning coordination ethylene polymerization, none of them so far have calculated the whole MWD. Within this context, this study presents a technique to calculate the complete MWD applied to such systems.

PROPOSED APPROACH TO DETERMINE MWD

The main idea in the proposed approach is that the differential MWD [Fig. 3(b)] is obtained through differentiation of the cumulative distribution [Fig. 3(a)].²¹ The cumulative distribution may be obtained through computation of accumulated concentrations (UA) at a finite number of chain lengths in a finite domain (N), as given by

$$UA_m = \sum_{p=1}^m U_p, \quad m \in \Psi, \quad (2)$$

$$\Psi = \{a_1, a_2, \dots, a_{nr}\}, \quad a_{nr} = N, \quad (3)$$

$$M = m \cdot MW, \quad (4)$$

$$W_m = \frac{\sum_{p=1}^m p \cdot MW \cdot U_p}{\sum_{p=1}^N p \cdot MW \cdot U_p} = \frac{UA_{1,m}}{UA_{1,N}}, \quad (5)$$

TABLE I
Kinetic Mechanism of Ethylene Polymerization by Coordination

Description	Reaction	Kinetic constant	
Activation	$C_n + CC \xrightarrow{k_f',n} C_n^*$	k_f'	
Poisoning	$I_{CC} + CC \xrightarrow{k_{icc}'} CCD$	k_{icc}'	
	$I_C + C_n^* \xrightarrow{k_{ic}'} CD_n$	k_{ic}'	
Initiation	$C_n^* + M \xrightarrow{k_i,n} P_{1,n}$	k_i	
Propagation	$P_{p,n} + M \xrightarrow{k_p,n} P_{p+1,n}$	k_p	
Transfer	Monomer	$P_{p,n} + M \xrightarrow{k_{fm,n}} P_{1,n} + U_p$	k_{fm}
	Hydrogen	$P_{p,n} + H_2 \xrightarrow{k_{fh,n}} C_n^* + U_p$	k_{fh}
	Organometallic	$P_{p,n} + CC \xrightarrow{k_{fcc,n}} C_n^* + U_p$	k_{fcc}
Spontaneous	Deactivation	$P_{p,n} \xrightarrow{k_f,n} C_n^* + U_p$	k_f
	Spontaneous	$C_n^* \xrightarrow{k_d,n} CD$	k_d
Termination	Monomer	$P_{p,n} + M \xrightarrow{k_{tm,n}} CD + U_p$	k_{tm}
	Hydrogen	$P_{p,n} + H_2 \xrightarrow{k_{th,n}} CD + U_p$	k_{th}
	Organometallic	$P_{p,n} + CC \xrightarrow{k_{tcc,n}} CD + U_p$	k_{tcc}
	Spontaneous	$P_{p,n} \xrightarrow{k_t,n} CD + U_p$	k_t

where U_p is the concentration of dead polymer with p monomeric units, a_i are chain lengths at which the accumulated concentrations are computed, nr is the number of bins or the finite number of points in the domain N , MW and M are, respectively, the monomer and the polymer molecular weights and W_m is the normalized mass fraction of polymer up to chain length m . Cubic splines interpolation²² is used to obtain the smooth cumulative distribution. This method fits a cubic polynomial between each pair of data points. The differentiation of these polynomials therefore yields the desired MWD, as illustrated in Figure 3(b). The degree of detail of the calculated distribution is given by the number of bins (nr) and the selected chain lengths in Ψ .

For the implementation of the method, therefore, it is sufficient to know how to calculate the accumulated concentrations. They are considered species and hence should have a mass balance associated.

MWD for ethylene polymerization with Ziegler–Natta

The proposed procedure was applied to ethylene polymerization process with Ziegler–Natta catalyst, given the lack of studies on it, as mentioned earlier. According to previous works,²⁰ the kinetic mechanism of this polymerization is shown in Table I, where C is catalyst, CC cocatalyst, C^* active specie, I_C poison to catalyst, I_{CC} poison to cocatalyst, CCD cocatalyst deactivated by poisoning, CD catalyst

deactivated, H_2 hydrogen, M monomer, P_p live polymer with p monomer units, and U_p dead polymer with p monomer units. The multiple active sites theory was considered and n denotes the site type.

The process model as well as the kinetic and physical parameters have been detailed in previous works.²⁰ The ethylene polymerization reaction takes place in PFRs and CSTRs operating in solution with a Ziegler–Natta catalyst. A schematic diagram of these reactors is depicted in Figure 4. The tubular reactor is split into smaller segments to simulate side feeds of hydrogen, which is the chain transfer agent. The nonideal CSTR is modeled through smaller ideal CSTR zones with back-mixing streams between them to represent the mixing pattern inside the nonideal CSTR. As this article focuses on computing the whole MWD, further details about the process model may be found elsewhere.²⁰

The component mass balance for each ideal CSTR zone and each PFR segment can be given, respectively, by

$$V \cdot \rho \cdot \frac{dC_i}{dt} = \sum_{in=1}^{nin} F_{in} \cdot C_{i,in} - \sum_{out=1}^{nout} F_{out} \cdot C_{i,out} + V \cdot \rho \cdot r_i, \quad i = 1, \dots, nc + nr, \quad (6)$$

$$\frac{\partial C_i}{\partial t} + \frac{\partial(v \cdot C_i)}{\partial z} = r_i, \quad i = 1, \dots, nc + nr, \quad (7)$$

where V is the reactor constant volume (m^3), ρ is the mixture specific mass (kg/m^3), C_i is the molar concentration of component i (mol/m^3), F is the mass flow rate (kg/s), A is the transversal section area (m^2), v is defined as $v = F / (\rho \cdot A)$, r_i is the production rate of the component i ($mol m^{-3} s^{-1}$), nin and

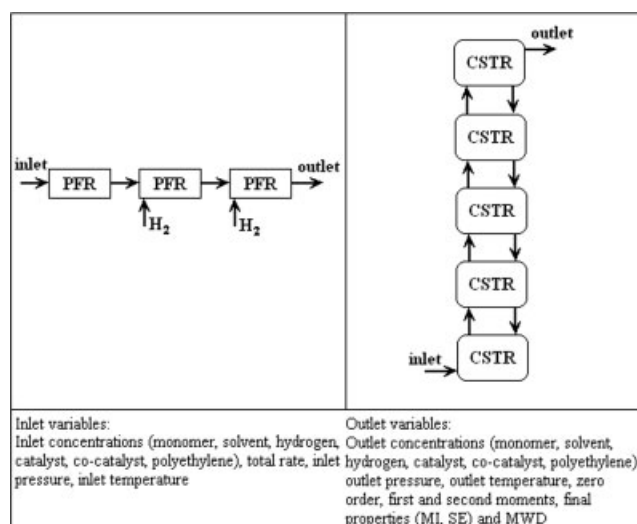


Figure 4 Schematic diagram of (a) PFR and (b) CSTR reactors.

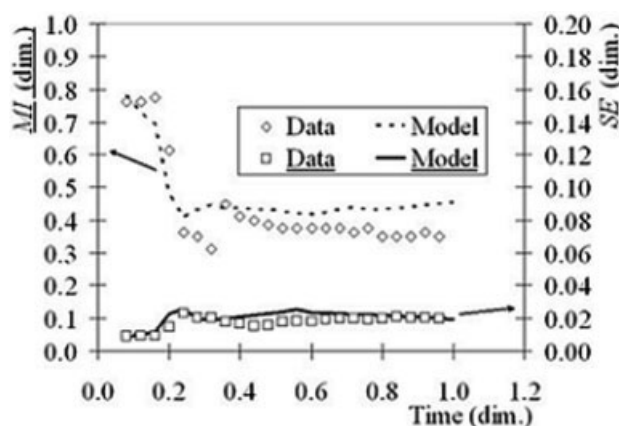


Figure 5 MI and SE experimental data versus model prediction.

nout are the number of inlet and outlet streams respectively, nc is the number of components, and nr is the number of bins of the distribution.

In Arrhenius' law, there are two kinetic constants associated with each reaction listed in Table I: the preexponential factor and the activation energy. Apart from the kinetic parameters, heat capacities, mixing parameters, and empirical constants for some polymer properties are unknown, making up a lot of parameters which have to be estimated. The case study is a real polymerization process. In industrial practice, the commonly measured polymer properties are the melt index (MI) and the stress exponent (SE).²⁰

$$MI = \alpha_1 \cdot (MW_w)^{\alpha_2}, \quad (8)$$

$$SE = \frac{1}{\beta_1 \cdot \exp(\beta_2 \cdot PD) + \beta_3}, \quad (9)$$

where α_1 , α_2 , α_3 , β_1 , β_2 , and β_3 are empirical constants to be estimated, PD is the polydispersity and MW_w is the weight average MW. The MI is a measure of the average molecular weight and the SE, a measure of the MWD broadness, i.e., a measure of polydispersity.

A methodology was then developed to fit the model predictions with the actual dynamic plant data, which covered the production of 15 different polymer grades. The MI and SE were used to validate the MWD through estimation of the empirical constants α_i and β_j . The numerical strategy combines data reconciliation procedures and standard parameter estimation techniques to filter the operation data sets and to improve the performance of the estimation process.²³ Figure 5 compares MI and SE experimental data with the model prediction, indicating a satisfactory adjustment of the model. The values are normalized for reasons of confidentiality. The estimated kinetic constants and empirical parameters for the MI and SE correlations are listed in Table II.

In the above equations, the term that distinguishes the kind of polymerization is the reaction rate, which includes the particularities of each kinetic mechanism. According to the proposed kinetic mechanism, the reaction rate for the dead polymer with length p (r_{U_p}) is given by

$$r_{U_p} = \sum_{n=1}^{ns} P_{p,n} \times \left(k_{fh,n} \cdot H_2^{\text{ofh}} + k_{fm,n} \cdot M + k_{f,n} + k_{fCC,n} \cdot CC^{\text{ofCC}} \right) + \left(k_{th,n} \cdot H_2^{\text{oth}} + k_{tm,n} \cdot M + k_{t,n} + k_{tCC,n} \cdot CC^{\text{otCC}} \right), \quad (10)$$

TABLE II
Estimated Parameters

Property	Parameter	Value	Unit
k_p, k_i	A_p, A_i	3.8896×10^2	$\text{m}^3/(\text{mol s})$
k_d, k_t	A_d, A_t	1.3382×10^1	1/s
k_{th}	A_{th}	8.7109×10^{-2}	$\text{m}^3/(\text{mol s})$
k_{tm}, k_{tCC}	A_{tm}, A_{tCC}	6.6522×10^{-6}	$\text{m}^3/(\text{mol s})$
k_f	A_f	6.8321×10^4	1/s
k_{fh}	A_{fh}	1.4503×10^1	$(\text{m}/\text{mol})^{0.5} \text{ s}$
k_{fm}	A_{fm}	1.3555×10^{-2}	$\text{m}^3/(\text{mol s})$
k_{fCC}	A_{fCC}	2.6252×10^{-2}	$(\text{m}/\text{mol})^{0.5} \text{ s}$
k_p, k_i	E_p, E_i	2.0531×10^4	J/mol
$k_d, k_t, k_{th}, k_{tm}, k_{tCC}$	$E_d, E_t, E_{th}, E_{tm}, E_{tCC}$	2.5111×10^4	J/mol
k_f	E_f	4.6450×10^4	J/mol
k_{fh}, k_{fm}, k_{fCC}	E_{fh}, E_{fm}, E_{fCC}	1.4550×10^4	J/mol
MI	α_1	4.1950×10^{19}	$(\text{g}/10 \text{ min}), (\text{g}/\text{mol})$
MI	α_2	-3.9252	$(\text{g}/10 \text{ min}), (\text{g}/\text{mol})$
SE	β_1	0.8728	-
SE	β_2	-0.048	-
SE	β_3	0.0103	-

A, Arrhenius preexponential factor; E, activation energy.

where n_s is the number of active site types and the superscripts ofh , $ofCC$, oth , and $otCC$ indicate reaction orders.

As discussed earlier, the accumulated concentration of dead polymer, UA_m , is considered a component in the mass balance for MWD calculations, then each accumulated concentration may have a reaction rate associated. Summing equation (10) up to chain length m , the reaction rate of the specie of interest is obtained:

$$r_{UA_m} = \sum_{n=1}^{n_s} \left(\begin{aligned} &k_{fh,n} \cdot H_2^{ofh} + k_{fm,n} \cdot M + k_{f,n} \\ &+ k_{fCC,n} \cdot CC^{ofCC} + k_{th,n} \cdot H_2^{oth} \\ &+ k_{tm,n} \cdot M + k_{t,n} + k_{tCC,n} \cdot CC^{otCC} \end{aligned} \right) \cdot PA_{m,n}, \quad (11)$$

where $PA_{m,n}$ is the live polymer accumulated concentration up to chain length m .

Therefore, the reaction rate for the accumulated dead polymer up to chain length m (UA_m) depends on the live polymer accumulated concentration up to the same chain length (PA_m). The reaction rates for live polymers with chain length 1 and p ($p/1$) are given, respectively, by

$$r_{P_{1,n}} = r_{i,n} - P_{1,n} \cdot f_{cP,n} + f_{m,n} \cdot \mu_{0,n}, \quad (12)$$

$$r_{P_{p,n}} = -f_{cP,n} \cdot P_{p,n} + f_{p,n} \cdot P_{p-1,n}, \quad (13)$$

where

$$f_{cP,n} = k_{p,n} \cdot M + k_{fh,n} \cdot H_2^{ofh} + k_{fm,n} \cdot M + k_{f,n} + k_{fCC,n} \cdot CC^{ofCC} + k_{th,n} \cdot H_2^{oth} + k_{tm,n} \cdot M + k_{t,n} + k_{tCC,n} \cdot CC^{otCC} \quad (14)$$

$$r_{i,n} = k_{i,n} \cdot C_n^* \cdot M, \quad (15)$$

$$f_{m,n} = k_{fm,n} \cdot M, \quad (16)$$

$$f_{p,n} = k_{p,n} \cdot M, \quad (17)$$

$$\mu_{0,n} = \sum_{p=1}^{\infty} P_p, \quad (18)$$

Assuming the quasi-steady state assumption for live polymers, it is possible to obtain P_1 and P_p by manipulating eqs. (12) and (13)

$$P_{1,n} = \frac{r_{i,n} + f_{m,n} \cdot \mu_{0,n}}{f_{cP,n}}, \quad (19)$$

$$P_{p,n} = P_{p-1,n} \cdot \frac{f_{p,n}}{f_{cP,n}}. \quad (20)$$

From eq. (20), it is worth noting that the concentration of live polymer with length p depends on the

concentration of polymer with length $p - 1$. It would therefore be unworkable to calculate the accumulated concentrations from this equation, as a mass balance for each chain length would be needed. Thus, to make this technique a feasible one, a solution for this equation must be found that eliminates this undesired backward dependence. Fortunately, it is possible to find a general expression for $PA_{m,n}$ given by the following geometric series:

$$PA_{m,n} = \sum_{p=1}^m P_{p,n} = \sum_{p=1}^m P_{1,n} \left(\frac{f_{p,n}}{f_{cP,n}} \right)^{p-1} = P_{1,n} \cdot \sum_{p=1}^m \left(\frac{f_{p,n}}{f_{cP,n}} \right)^{p-1}. \quad (21)$$

The accumulated concentration of live polymers can then be calculated by

$$PA_{m,n} = P_{1,n} \cdot \left\{ \frac{1 - \left(\frac{f_{p,n}}{f_{cP,n}} \right)^m}{1 - \left(\frac{f_{p,n}}{f_{cP,n}} \right)} \right\}. \quad (22)$$

The resulting expression depends only on variables already calculated by the model, which makes the present approach a feasible method to calculate the complete MWD.

It is sometimes useful to know not only the number of molecules, but also the mass of polymer that has a given chain length. The cumulative distribution in Figure 3(a), for example, requires the computation of the normalized mass fraction of polymer, given in eq. (5). To ascertain this quantity, it is important to know the accumulated product between polymer concentration and monomer mass, similar to the concept of k th-order moment, as written in

$$UA_{k,m} = \sum_{p=1}^m (p \cdot MW)^k \cdot U_p, \quad (23)$$

where MW is the monomer molecular weight. Since MW is a constant, it will be omitted from now on.

The reaction rate for the k th-order accumulated concentration of the dead polymer up to chain length m is then written according to

$$r_{UA_{k,m}} = \sum_{p=1}^m p^k \cdot r_{U_p} = \sum_{p=1}^m p^k \cdot \sum_{n=1}^{n_s} P_{p,n} \times \left(\begin{aligned} &k_{fh,n} \cdot H_2^{ofh} + k_{fm,n} \cdot M + k_{f,n} + k_{fCC,n} \cdot CC^{ofCC} \\ &+ k_{th,n} \cdot H_2^{oth} + k_{tm,n} \cdot M + k_{t,n} + k_{tCC,n} \cdot CC^{otCC} \end{aligned} \right), \quad (24)$$

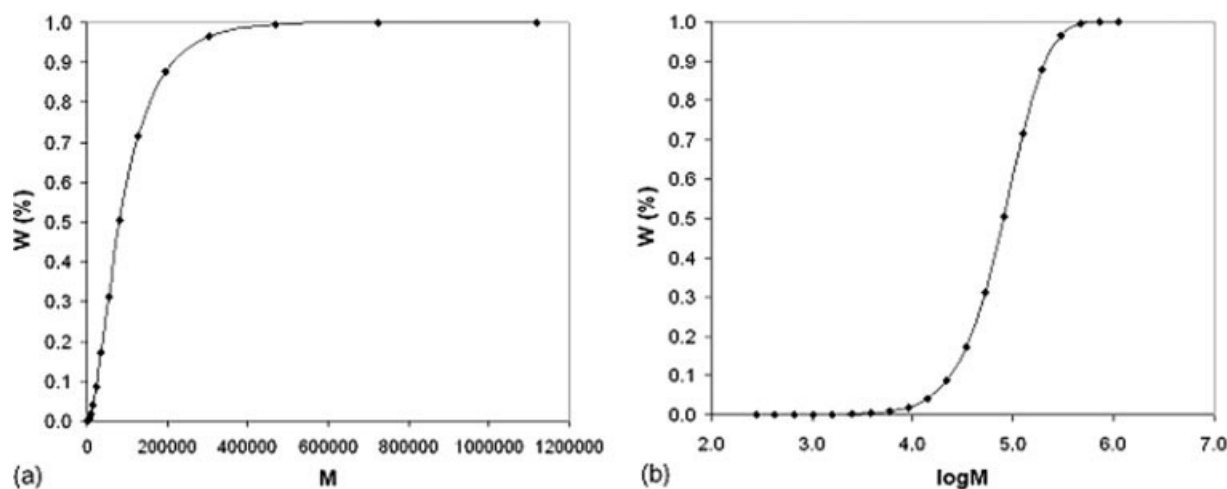


Figure 6 Cumulative distribution: (a) linear and (b) logarithm scales.

$$r_{UA_{k,m}} = \sum_{n=1}^{ns} \left(\begin{array}{l} k_{fh,n} \cdot H_2^{\text{ofh}} + k_{fm,n} \cdot M + k_{f,n} \\ + k_{fCC,n} \cdot CC^{\text{ofCC}} + k_{th,n} \cdot H_2^{\text{ofh}} \\ + k_{tm,n} \cdot M + k_{t,n} + k_{tCC,n} \cdot CC^{\text{ofCC}} \end{array} \right) \times PA_{k,m,n}, \quad (25)$$

where $PA_{k,m,n}$ is the k th-order accumulated concentration of the live polymer up to chain length m , which is further given by

$$PA_{k,m,n} = \sum_{p=1}^m p^k \cdot P_{p,n} = \sum_{p=1}^m p^k \cdot P_{1,n} \left(\frac{f_{p,n}}{f_{cP,n}} \right)^{p-1} = p_{1,n} \cdot \sum_{p=1}^m \left(\frac{f_{p,n}}{f_{cP,n}} \right)^{p-k}. \quad (26)$$

When $k = 1$, eq. (26) represents the first order accumulated concentration of live polymer up to chain length m and is an arithmetic-geometric series, which solution is given by

$$PA_{1,m,n} = P_{1,n} \cdot \frac{1 - \left(\frac{f_{p,n}}{f_{cP,n}} \right)^m}{1 - \left(\frac{f_{p,n}}{f_{cP,n}} \right)} + \frac{\left(\frac{f_{p,n}}{f_{cP,n}} \right) \cdot \left[1 - m \cdot \left(\frac{f_{p,n}}{f_{cP,n}} \right)^{m-1} + (m-1) \cdot \left(\frac{f_{p,n}}{f_{cP,n}} \right)^m \right]}{\left[1 - \left(\frac{f_{p,n}}{f_{cP,n}} \right) \right]^2}. \quad (27)$$

As well as eq. (22) for the accumulated concentration of live polymers with chain length of up to m , the above equation depends only on variables already calculated by the model. Therefore, the mass of polymer that has 1 to m monomer units can easily be ascertained.

With this approach, the final CSTR model comprises a set of $nz \cdot (1 + nc + nr)$ ordinary differential equations, among other algebraic equations, whereas the final tubular model comprises a set of $nj \cdot (1 + nc + nr)$ partial differential equations, as well as a set of algebraic equations, where nc is the number of components in mass balance (monomer, catalyst, cocatalyst, hydrogen and solvent, besides zero, first, and second order moments), nr is the number of bins of the MWD, nj is the number of segments of PFR, nz is the number of back-mixed zones of the CSTR and the additional equation is the energy balance.²⁰ The method of characteristics is used to solve the tubular model,²⁴ whereas LSODE code²⁵ is used to integrate ODEs. Algebraic equations comprise physical property models, such as density, heat capacity, and viscosity, as well as final property models, such as MI.

RESULTS AND DISCUSSION

The new species, i.e., the polymer accumulated concentration up to chain length m , given by eqs. (2) and (23), were incorporated into the ethylene polymerization model using the equations developed previously. It is therefore possible to obtain the cumulative distribution, depicted in Figure 6, where W is the normalized mass fraction of polymer and M is the polymer molecular weight.

The MWD can then be obtained by differentiating these cumulative distributions. The cubic splines interpolation²² is used to smooth and differentiate the cumulative distribution and the derivatives of the distributions in Figure 6 are illustrated in Figure 7.

As discussed in previous sections, the degree of detail of the calculated distribution is given by the number of bins (nr) and the selected chain lengths at

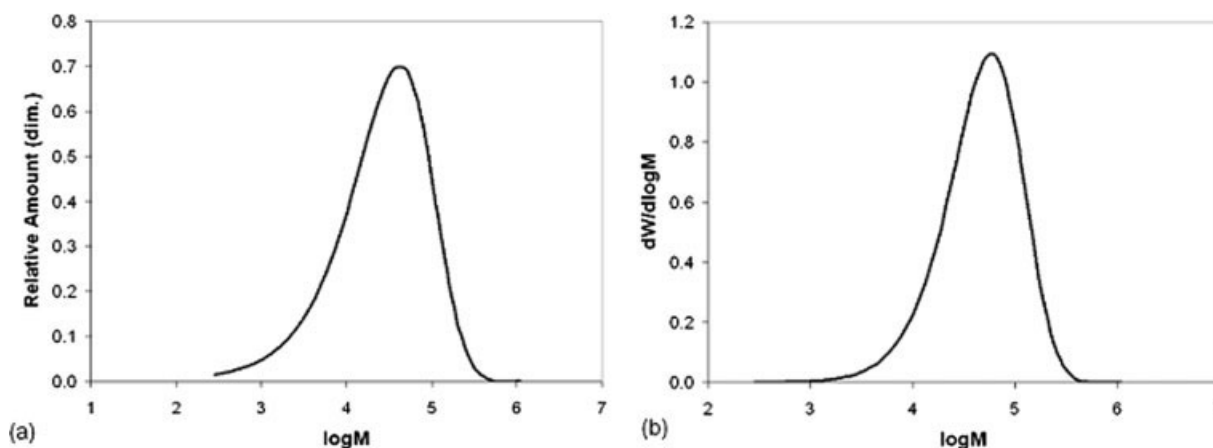


Figure 7 Differential molecular weight distribution: (a) derived from Figure 6(a); (b) derived from Figure 6(b).

which the accumulated concentrations are computed (Ψ). Indeed, two parameters are necessary for the proposed approach: the number of bins and the upper limit of the distribution (N). Both parameters can be selected *a priori*, if there is little experimental information about the resin investigated. The number of bins may be determined comparing distributions with an increasing number of bins (nr_1, nr_2, \dots), through a convergence criterion

$$e_j = \int_0^{x_{\max}} \left(P_{nr_{j+1}}(x) - P_{nr_j}(x) \right)^2 dx, \quad j = 1, 2, \dots, \quad (28)$$

where e is the tolerance criterion, j denotes a specific iteration, and x_{\max} represents the upper limit of the distribution. The MWD is represented by $P(x)$, and it may be obtained by differentiation of the cumulative distribution. Distributions with an increasing number of bins approximate the “real” distribution. Therefore the difference between successive distributions, expressed by eq. (28), goes to zero when the number

of bins is increased. When this difference is smaller than a prespecified tolerance, the procedure converges and the number of bins is then determined.

To compare different numbers of bins, Figure 8 illustrates MWD curves of polymers produced in CSTR and PFR reactors, with a chain length range from 10 to 40,000 ($N = 40,000$), i.e., polyethylene molecular weight from 280 to 1,120,000 g, which is a typical molecular weight range of the polymer simulated. The set of chain lengths (Ψ) is defined based on a logarithm-based scale with equal spaced points, but nonequal spaced points or other scales can be considered as well. The MWD with 20 bins matches very well the MWD with 30 bins. However, when this number is further reduced to 10, small deviation from the other two distributions can be observed. Therefore, 20 equal spaced chain lengths are considered satisfactory for simulation purposes. Figure 8 illustrates the CPU time, which considers a dynamic simulation, indicating, as expected, that the higher the numbers of bins the greater the computational time required.

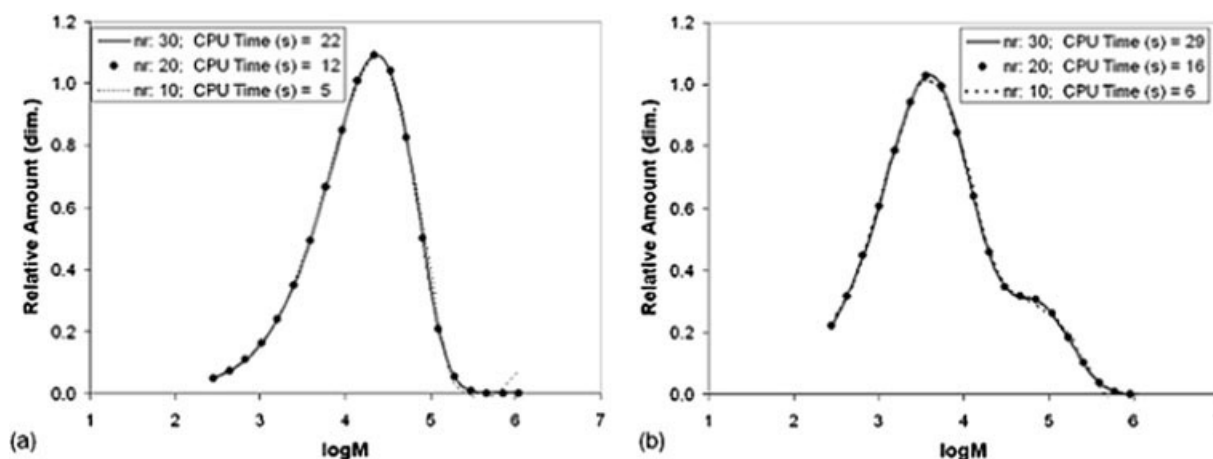


Figure 8 Comparison of different number of bins and the respective CPU time: (a) CSTR; (b) PFR.

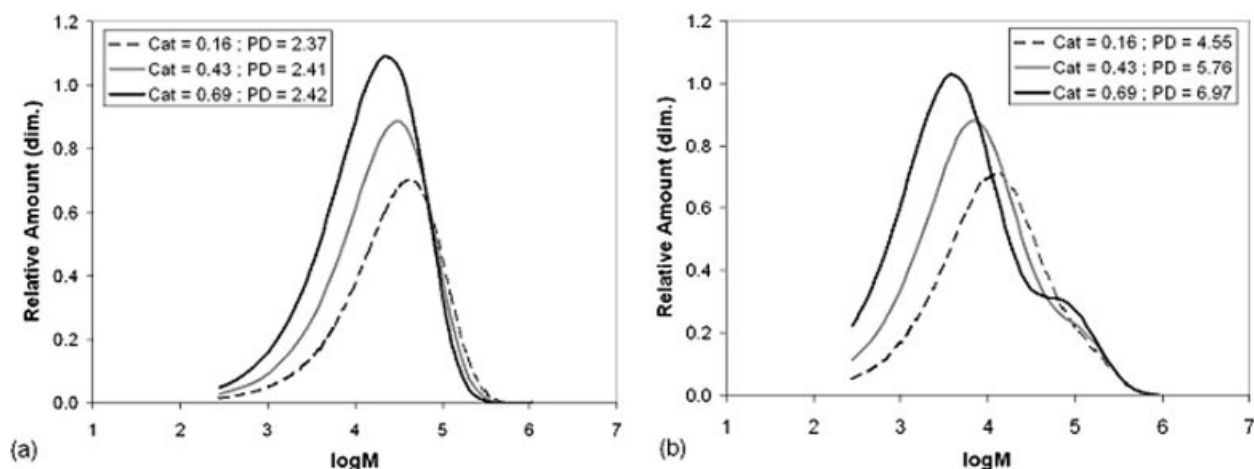


Figure 9 Effect of catalyst concentration on the MWD of (a) CSTR and (b) PFR reactors.

Some simulation studies are carried out to evaluate the effect of catalyst and hydrogen inlet concentrations on the MWD. As mentioned earlier, the results are presented here using normalized concentration values.

Figures 9 and 10 illustrate the effects of catalyst and H_2 concentration on the MWD of stirred and tubular reactors, respectively. The PFR is characterized by a higher polydispersity since polymer chains experience different reaction conditions during the residence time. This observation is verified when comparing the MWD curves of the two reactors. Furthermore, it is worth observing the effect of the catalyst on the shape of the distribution. In the PFR, increasing catalyst concentration leads to the formation of shoulders, i.e., higher molecular weights also have a considerable concentration in final polymer, unlike in the CSTR. The shoulders may be associated with the catalytic deactivation effect. Higher catalyst inlet concentration enhances propagation reactions, increasing temperature. At the first section of the

reactor, the higher temperature increases transfer reactions rate and then decreases the polymer molecular weight. On the other side, as reaction proceeds, high temperatures lead to the deactivation of the catalytic sites. With the smaller number of active species at the final section of the reactor, the polymer molecular weight tends to increase. As discussed previously, the presence of such shoulders in the MWD may be desirable to improve some end-use properties of the produced polymer. These observations are only possible with the knowledge of the complete MWD. In both reactors, a higher concentration of hydrogen (H_2), the chain transfer agent, produces preferentially low molecular weight chains and a narrower distribution, i.e., lower polydispersity. The hydrogen increases transfer reaction rates, reducing the molecular weight of the polymer and also the polydispersity.

The moments of the distribution can also predict some of the observed tendencies, for example, the decrease in the average molecular weight due to an

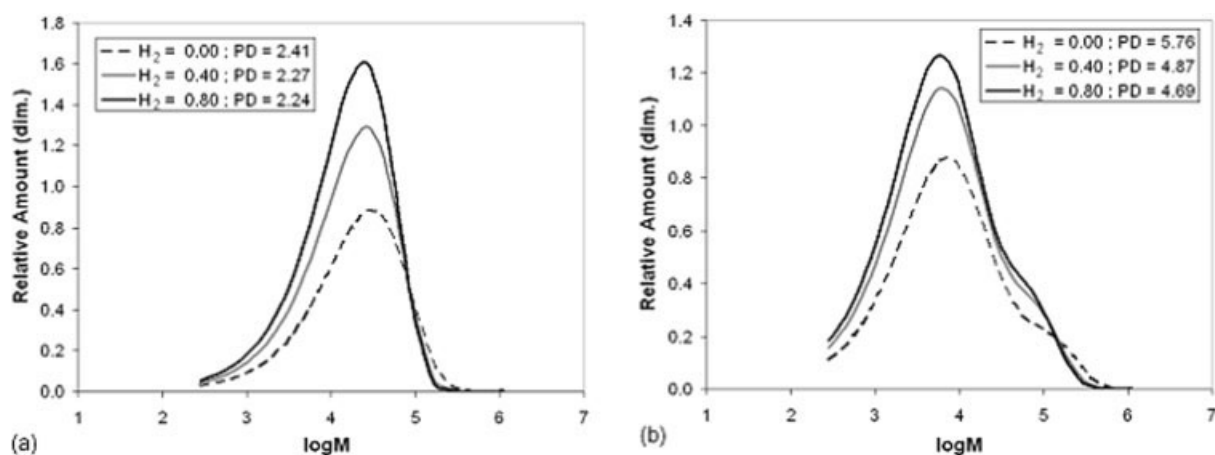


Figure 10 Effect of hydrogen concentration on the MWD of (a) CSTR and (b) PFR reactors.

increase in the hydrogen concentration. However, the shape of the distribution and in particular the formation of shoulders can only be predicted when the complete MWD is known. The proposed approach to compute the MWD is able to give the desired detail of the distribution, even predicting highly nonlinear behaviors.

CONCLUDING REMARKS

Some polymer end-use properties depend not only on average molecular weights and polydispersity but also on some specific fractions of the MWD. Therefore, it is of great importance to know the complete MWD, and in recent years, interest in predicting such polymer characteristics has increased.

This work presents a procedure to obtain the whole MWD, which is based on differentiating the cumulative MWD. Computational procedures are presented and this approach is applied to the ethylene polymerization in solution with a Ziegler–Natta catalyst in trains of PFR and CSTR reactors. The results show the potential use and versatility of the proposed procedure and the MWD curves obtained show that this approach is coherent and consistent.

The approach presented is a simple technique to implement because it does not require complex mathematical development and higher order differential equations as other techniques do. It can also be easily “tuned” to the desired detail of the MWD, providing information that the usual method of moments is unable to do. Indeed, it only depends on the kinetic mechanism. Furthermore, it can be applied to complex kinetics as in the case of coordination polymerization. This approach can also be extended to other polymer systems, depending only on the development of specific reaction rate expressions.

NOMENCLATURE

A	area under the curve
A	transversal section area
C	catalyst
C_i	molar concentration of component i
C^*	activated catalyst
CC	cocatalyst
CCD	deactivated cocatalyst
CD	deactivated catalyst
F	mass flow rate
H_2	hydrogen
I	poison
k	kinetic constant
m	maximum polymer chain length
M	monomer concentration

M	polymer molecular weight
MI	melt index
MW	monomer molecular weight
MW_w	average weight molecular weight
nc	number of components
nr	number of bins of the distribution
N	upper chain length
P	live polymer
P	live polymer concentration
PA	live polymer accumulated concentration
PD	polydispersity
Q	generic polymer property
r_i	reaction rate of component i
SE	stress exponent
U	dead polymer
U	dead polymer concentration
UA	dead polymer accumulated concentration
V	reactor volume
W	normalized mass fraction of polymer

Subscripts

C^*	activated catalyst
CC	cocatalyst
f	transfer reaction
h	hydrogen
i	initiation reaction
k	order of accumulated polymer concentration
m	maximum polymer chain length
m	monomer
n	activated catalytic site type
nc	number of catalytic site type
p	polymer chain length
t	termination reaction

Superscripts

CC	cocatalyst
f	transfer reaction
h	hydrogen
k	order of accumulated polymer concentration
k	order of polymer moment
o	reaction order
p	polymer chain length
t	termination reaction

Greek letters

α	empirical constants
β	empirical constants
λ	dead polymer moment
μ	live polymer moment
ρ	mixture specific mass

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