CALCULATION OF THE MOLECULAR WEIGHT – LONG CHAIN BRANCHING DISTRIBUTION IN BRANCHED POLYMERS

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Abstract: In the present study a population balance approach is described to follow the time evolution of molecular polymer properties in free-radical polymerizations. The model formulation is based on the fixed pivot technique (FPT) which was properly adapted to calculate the combined molecular weight - long chain branching distribution. At first the predictive capabilities of the proposed model were tested against experimental measurements and simulation results taken from the open literature, on molecular weight distribution (MWD) of branched polymers. Then the MWD calculated by the FPT was compared with the MWD calculated by the method of classes. However the FPT proved to be a faster method for the calculation of the MWD. Copyright © 2006 IFAC.

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1. INTRODUCTION

The molecular properties (e.g., molecular weight distribution, MWD, copolymer composition distribution, CCD, long chain branching distribution, LCBD, etc.) of polymers are directly related to their end-use properties (e.g., mechanical, rheological, etc.). Hence, the ability to control accurately the molecular architecture of polymer chains in a polymerization reactor is of profound interest to the polymer industry. This presupposes a thorough knowledge of the polymerization kinetics and the availability of advanced mathematical models to quantify the effects of process operating conditions on the molecular polymer properties.

Branched polymers are characterized by the presence of long or/and short branches attached to the main backbone of a polymer chain. Thus, the end-use properties of branched polymers will also depend on the number, the type and the distribution of the branches. Long chain branching has a strong impact on the rheological behavior of the polymer. In fact, it affects the flow properties of the polymer melt (e.g., extensional viscosity, shear viscosity and elasticity) as well as the polymer solid state properties (e.g., orientation effects and stress induced crystallization). Thus, the elucidation of the LCB formation and its correlation with the various rheological and physical polymer properties are two subjects of significant research interest.

The free-radical polymerization of vinyl acetate (VAc) is a typical system that leads to the formation of long chain branching that largely affect the MWD and thus, the polymer rheological properties. In this system, transfer to monomer and to polymer reactions as well as terminal double bond polymerization largely control the molecular weight developments via the formation of highly branched polymer chains.

In the past twenty years, several mathematical models dealing with the calculation of the MWD of branched polymers have been published (Lorenzini et al., 1992; Tobita and Hatanaka, 1996; Nordhus et al., 1997; Thomas, 1998; Pladis and Kiparissides, 1998, Iedema et al., 2000). A variety of numerical methods have been employed to calculate the MWD of branched polymers, including ‘numerical fractionation’ (Teymour and Campbell, 1992, 1994), Monte-Carlo simulations (Tobita, 1996; Tobita and Hatanaka, 1996), global orthogonal collocation (Canu and Ray, 1991; Nele et al., 1999) and discrete weighted Galerkin (Wulkow, 1995). In general, the above numerical attempts suffer from two key kinetic limitations, (e.g., the use of the quasi steady state approximation (QSSA) for ‘live’ radical chains and the absence of gel and glass effect).

The ‘numerical fractionation’ method can provide information on the full MWD of branched polymers by dividing the total polymer chain population into a finite number of classes of polymer chains having narrow MWDs. The method assumes that the transition from one class of polymer chains to a higher one occurs exclusively by a geometric growth mechanism (e.g., termination by combination polymer and terminal double bond reactions are
reactions). However, in systems in which transfer to important, this assumption will not be sufficient. The use of global orthogonal collocation methods for the prediction of the MWD in free-radical polymerization systems is partially successful because a single interpolation polynomial is only employed for the entire collocation domain. As a result, prior knowledge on the type of the approximated distribution is required. Furthermore, global collocation schemes have been proved inadequate in accommodating complex MWDs (e.g., bimodal distributions, MWDs for branched polymers, etc.). Pladis and Kiparissides (1998) employed a polymer chain fractionation approach to calculate the molecular weight – long chain branching bivariate distribution for branched polymers. The total population of the polymer chains was divided into a number of classes with respect to the number of long chain branches. However, in addition to the well-known problem of closure of the ‘higher order’ moments, the reconstruction of the overall MWD at high monomer conversions and high LCB content, requires a very large number of classes to reduce the approximation errors associated with the high molecular weight fractions of the distribution. Monte Carlo simulations are straightforward techniques that can generally handle complex kinetic mechanisms but usually require significant computational effort for the determination of the MWD. Finally, the discrete weighted Galerkin formulation, even though is computationally demanding, provides a powerful tool for the prediction of the MWD in complex polymerization systems. However, the approximation of the infinite summation terms (e.g., resulting from termination by combination reactions) requires special treatment.

The present study deals with the numerical solution of the dynamic bivariate population balance equations (PBEs) for ‘live’ and ‘dead’ polymer chains, arising in highly branched polymer systems. The fixed pivot technique (Kumar and Ramkrishna, 1996) is employed to solve the resulting system of bivariate population balance equations. The validity of the proposed numerical method is tested by a direct comparison of model predictions with experimental data on the number average degree of branching, the number and weight average molecular weights for the free-radical polymerization of VAc (Thomas, 1998). The calculated bivariate MW-LCB distribution is also compared with simulations obtained by an improved method of classes (Pladis and Kiparissides, 1998) as well as with predictions of MWD obtained by Monte Carlo Simulations (Tobita and Hatanaka, 1996).

2. KINETIC MECHANISM AND RATE FUNCTIONS

In the present study, the following kinetic mechanism was employed to describe the formation of highly branched polymers:

Initiator decomposition:

\[ I \xrightarrow{k_i} 2PR^* \]

Chain initiation:

\[ PR^* + M \xrightarrow{k_i} P_{b,1} \]

Propagation:

\[ P_{b,n} + M \xrightarrow{k_p} P_{b,n+1} \]

Chain transfer to monomer:

\[ P_{b,n} + M \xrightarrow{k_{tn}} D_{b,n} + P_{b,0} \]

Chain transfer to solvent:

\[ P_{b,n} + S \xrightarrow{k_{ts}} D_{b,n} + P_{b,1} \]

Reaction with terminal double bond:

\[ P_{b,n} + D_{r,m} \xrightarrow{k_o} P_{b,r+1,n+m} \]

Chain transfer to polymer:

\[ P_{b,n} + D_{r,m} \xrightarrow{k_o} D_{b,n} + P_{r+1,m} \]

Termination by combination:

\[ P_{b,n} + P_{r,m} \xrightarrow{k_d} D_{b+n+r+1,m} \]

Termination by disproportionation:

\[ P_{b,n} + P_{r,m} \xrightarrow{k_d} 2D_{b+n-m} \]

The symbols \( P_{b,n} \) and \( D_{b,n} \) denote the respective ‘live’ and ‘dead’ polymer chains with ‘b’ long chain branches and a chain length equal to ‘n’. The above kinetic mechanism includes initiation and propagation reactions, termination by combination and disproportionation, molecular weight control reactions via transfer to monomer and chain transfer agent (solvent) and long chain branching formation via transfer to polymer and terminal double bond reactions. Polymer chains with terminal double bonds, formed via termination by disproportionation and transfer to monomer reactions, can react with ‘live’ polymer chains to produce long chain branches. Transfer to polymer reactions involve the transfer of reactivity from a growing polymer chain to a ‘dead’ polymer chain. More specifically, a hydrogen atom abstracted from the backbone of a ‘dead’ polymer chain leads to the formation of a new ‘live’ polymer chain with an internal radical center and a ‘dead’ polymer chain.

In the present study, to reduce the number of bivariate population balances to be numerically solved, it was assumed that the concentration of the ‘dead’ polymer chains having a terminal double bond, was some known fraction of the ‘dead’ polymer chains (Baltasas et. al., 1996). Based on the above kinetic mechanism and assumptions, the following dynamic population balance equations for the ‘live’, \( P(b,n,t) \), and ‘dead’, \( D(b,n,t) \), polymer chains can be derived:

\[ \frac{1}{V} \frac{\partial P(b,n,t)}{\partial t} = r_P(b,n,t) \quad (1) \]

\[ \frac{1}{V} \frac{\partial D(b,n,t)}{\partial t} = r_D(b,n,t) \quad (2) \]

The net formation rates for the ‘live’ and ‘dead’ polymer chains are given by the following equations:
Net formation rate of ‘live’ polymer chains of length ‘n’ with ‘b’ branches:

\[ r_{P(n,b)} = k_P [M] P(n-1) b \delta(n) + k_P [S] \sum_{z=0}^{N_n} \sum_{b=0}^{N_b} P(z,x,t) \delta(n-1) b \delta(z) + \]

\[ k_P [M] \sum_{z=0}^{N_n} \sum_{b=0}^{N_b} P(z,x,t) \delta(n-1) b \delta(z) + k_P [S] \sum_{z=0}^{N_n} \sum_{b=0}^{N_b} P(z,x,t) \delta(n) b \delta(z) - \]

\[ k_P [M] [P(n-1) Dt] - P(n,n)] - \]

\[ (k_P [M] + k_P [S]) P(n,ni) + k_P [S] \sum_{z=0}^{N_n} \sum_{b=0}^{N_b} P(z,x,t) \delta(n) b \delta(z) - \]

\[ k_P [M] \sum_{z=0}^{N_n} \sum_{b=0}^{N_b} P(z,x,t) - k_P [S] \sum_{z=0}^{N_n} \sum_{b=0}^{N_b} P(z,x,t) \]

\[ k_P [M] \sum_{z=0}^{N_n} \sum_{b=0}^{N_b} P(z,x,t) - k_P [S] \sum_{z=0}^{N_n} \sum_{b=0}^{N_b} P(z,x,t) + \]

\[ k_P [S] \sum_{z=0}^{N_n} \sum_{b=0}^{N_b} P(z,x,t) (z-z_i,ni) \]

Net formation rate of ‘dead’ polymer chains of length ‘n’ with ‘b’ branches:

\[ r_{D(n,b)} = \{ k_P [M] + k_P [S] \} P(n,ni) + k_P [S] \sum_{z=0}^{N_n} \sum_{b=0}^{N_b} P(z,x,t) \delta(n) b \delta(z) - \]

\[ k_P [M] \sum_{z=0}^{N_n} \sum_{b=0}^{N_b} P(z,x,t) - k_P [S] \sum_{z=0}^{N_n} \sum_{b=0}^{N_b} P(z,x,t) \]

\[ k_P [M] \sum_{z=0}^{N_n} \sum_{b=0}^{N_b} P(z,x,t) - k_P [S] \sum_{z=0}^{N_n} \sum_{b=0}^{N_b} P(z,x,t) + \]

\[ k_P [S] \sum_{z=0}^{N_n} \sum_{b=0}^{N_b} P(z,x,t) (z-z_i,ni) \]

where \( \delta(n) \) is the Kronecker’s delta function [e.g., \( \delta(n) = 1 \) if \( n = 0 \) and \( \delta(n) = 0 \) if \( n \neq 0 \)]. \( N_b \) and \( N_n \) denote the maximum number of branches and the maximum chain length, respectively. It should be pointed out that the actual number of rate equations for the ‘live’ and ‘dead’ polymer chains will depend on the total degree of polymerization, that may be of the order of hundreds or-and thousands monomer units. Consequently, the computational effort associated with the solution of the complete set of differential equations becomes prohibitively high for the most cases of interest and makes the on-line application of such a model unrealistic. To deal with the above high-dimensionality problem, several methods have been proposed to reduce the infinite system of differential equations into a low-order system of DAEs.

In the present work the fixed pivot technique was applied for the solution of the bivariate PBEs [see eqs. (3) and (4)] to predict the joint MW-LCB distribution of branched polymers.

3. FIXED PIVOT TECHNIQUE

The fixed pivot technique was properly adapted for solving the bivariate population balance equations for the ‘live’ and ‘dead’ polymer chains [see eqs (3) and (4)]. The method assumes that the overall polymer chain population can be assigned to selected discrete points, also called ‘grid’ points. The bivariate PBEs which are derived from the application of the proposed method are then solved at the discrete points. Thus, the initial infinite system of PBEs, is reduced to a system of discrete-continuous differential equations. Since the chain populations in various chain lengths and number of branches are assumed to exist only at the representative discrete points, specific reaction steps (i.e., termination by combination, propagation, chain transfer to polymer and terminal double bond), involving such chain populations, can result in the formation of new polymer chains whose chain lengths and/or number of branches do not correspond to the representative grid points. According to the 2-D FPT, the polymer chains that do not correspond to specific grid points are incorporated in the set of discrete-continuous dynamic PBEs in such a way that any four moments (two in each dimension), of the joint MW-LCB distribution, are exactly preserved.

In the bivariate PBEs, the distribution of polymer chains with a specific number of branches is considered to be continuous over the chain length domain and the number of long chain branches domain. Based on the original developments of Kumar and Ramkrishna (1996), the total branch and chain length domains, are divided into a number of finite elements \( N_{e,b} \) and \( N_{e,n} \) respectively. Let \( P(j,i,t) \) and \( D(j,i,t) \), be the concentrations of the ‘live’ and ‘dead’ polymer domain, which correspond to the discrete point \( u(j,i) \) of the 2-D domain (see Fig. 1).

**Fig. 1**: The two-dimensional grid which can be used with the FPT.

Let \( b(i) \) and \( n(i) \) be the corresponding middle points in the \( i^{th} \) element \( (u_i(i),u_i(i+1)) \) and \( j^{th} \) element \( (u_j(i),u_j(i+1)) \), respectively. When a new polymer chain is formed within the 2-D discrete element (e.g., due to termination by combination or transfer to polymer reactions), its concentration is assigned to the four neighboring grid points in such a way so that selected moments of the MWD are exactly preserved. On the other hand, polymer chains formed via initiation, transfer to monomer, transfer to solvent or termination by disproportionation reactions, are always assigned to the existing grid points. From the application of the FPT to the bivariate PBEs of the ‘live’ and ‘dead’ polymer chains [see eqs (3) and (4)] we obtain the following system of continuous-discrete differential equations:
Continuous-discrete differential equations for linear 'live' polymer chains:

\[
\frac{1}{\nu} \frac{d}{dt} \left[ TP(0,i,t) \right] = 2J_0 [T] \delta(i-1) + k_p[M] \left[ \sum_{j=0}^{N_b} \sum_{k=0}^{N_c} P(j,k,t) \right] \delta(i-1)
\]

\[+ k_p[M] \frac{N_b N_c}{N_b} \sum_{j=0}^{N_b} \sum_{k=0}^{N_c} P(j,k,t) \delta(i-1) - k_p[M] P(0,i,t) \delta(i-1) - k_p[M] P(0,i,t)
\]

Continuous-discrete differential equations for branched 'live' polymer chains:

\[
\frac{1}{\nu} \frac{d}{dt} \left[ TP(i,j,t) \right] = k_p[M] \left[ \sum_{k=0}^{N_c} P(j,k,t) \right] - k_p[M] P(i,j,t)
\]

\[+ k_p[M] P(i,j,t) \sum_{k=0}^{N_c} \sum_{l=0}^{N_b} B(i,k,m) \left( C(j,l) P(l,k,t) D(k,l,t) + D(k,l,t) P(l,k,t) \right)
\]

\[+ k_p[M] P(i,j,t) \sum_{l=0}^{N_b} \sum_{k=0}^{N_c} B(i,k,m) \left( C(j,l) P(l,k,t) D(k,l,t) + D(k,l,t) P(l,k,t) \right)
\]

Continuous-discrete differential equations for 'dead' polymer chains:

\[
\frac{1}{\nu} \frac{d}{dt} \left[ TD(0,i,t) \right] = k_p[M] \left[ \sum_{j=0}^{N_b} \sum_{k=0}^{N_c} P(j,k,t) \right] - k_p[M] P(0,i,t)
\]

\[+ k_p[M] P(0,i,t) \sum_{j=0}^{N_b} \sum_{k=0}^{N_c} P(j,k,t) - k_p[M] P(0,i,t) \sum_{j=0}^{N_b} \sum_{k=0}^{N_c} P(j,k,t)
\]

Continuous-discrete differential equations for branched 'dead' polymer chains:

\[
\frac{1}{\nu} \frac{d}{dt} \left[ DV(j,i,t) \right] = k_p[M] \left[ \sum_{j=0}^{N_b} \sum_{k=0}^{N_c} P(j,k,t) \right] - k_p[M] P(j,i,t)
\]

\[+ k_p[M] P(j,i,t) \sum_{j=0}^{N_b} \sum_{k=0}^{N_c} P(j,k,t) - k_p[M] P(j,i,t) \sum_{j=0}^{N_b} \sum_{k=0}^{N_c} P(j,k,t)
\]

Assuming that the zero and first moment of the MWD are preserved, the matrices \( A(i,k) \), \( B(i,k,m) \), \( C(j,l) \), \( T(j,l,q) \) and \( O(j,l,q) \), can be calculated by the following expressions:

\[
A(i,k) = \begin{cases} \frac{n(i+1) - n(i)}{n(i)} & n = n(k) \\ \frac{n(i+1) - n(i)}{n(i)} & n = n(k) + 1 \end{cases}
\]

\[
B(i,k,m) = \begin{cases} \frac{n(i+1) - n(i)}{n(i)} & n = n(k) \\ \frac{n(i+1) - n(i)}{n(i)} & n = n(k) + 1 \end{cases}
\]

\[
C(j,l) = \begin{cases} \frac{b(j+1) - b(j)}{b(j)} & b = b(l) + 1 \\ \frac{b(j+1) - b(j)}{b(j)} & b = b(l) + b(q) + 1 \end{cases}
\]

\[
T(j,l,q) = \begin{cases} \frac{b(j+1) - b(j)}{b(j)} & b = b(l) + b(q) \\ \frac{b(j+1) - b(j)}{b(j)} & b = b(l) + b(q) + 1 \end{cases}
\]

\[
O(j,l,q) = \begin{cases} \frac{b(j+1) - b(j)}{b(j)} & b = b(l) + b(q) \\ \frac{b(j+1) - b(j)}{b(j)} & b = b(l) + b(q) + 1 \end{cases}
\]

where \( \delta \) is the Kronecker’s delta function.

The resulting differential-discrete equations were integrated in time to calculate the dynamic behavior of the ‘live’ and ‘dead’ bivariate number chain length distributions. The concentrations of the ‘dead’ polymer chains at the grid points were then used to reconstruct the weight chain length distribution (WCLD) that corresponds to a specific grid point of the branch domain:

\[
W(j,i,t) = n(i) D(j,i,t) \left[ u_n(i+1) - u_n(i) \right]
\]

The overall WCLD was then calculated by the weighted sum of all polymer branch distributions:

\[
W_{\text{total}}(i,t) = \sum_{j=0}^{N_b} \sum_{k=0}^{N_c} \left[ n(i) D(j,i,t) \left[ u_n(i+1) - u_n(i) \right] \right]
\]

For the discretization of the chain length and branch domains a logarithmic discretization rule was employed. Typically, the chain length and branch domains were partitioned into 50 and 8 finite elements, respectively, leading to a total number of 800 discrete-continuous differential equations.

To ensure that the selected number of elements was sufficient for the accurate reconstruction of the
MWD, the following convergence criterion was established:

$$\left( \mu_1 - \sum_{i=0}^{N_{x,z}} \sum_{k=1}^{N_{x,z}} n(k)D(l,k,i) \right) / \mu_1 \leq \varepsilon$$  \hspace{1cm} (16)$$

$\varepsilon$ is a convergence parameter with typical values in the range of (0, 0.03).

Finally, the number and weight average molecular weights and the number and weight average degrees of branching are calculated using the following equations:

**Number average molecular weight:**

$$M_n = \frac{\sum_{i=0}^{N_{x,z}} \sum_{k=1}^{N_{x,z}} n(k) D(l,k,i)}{\sum_{i=0}^{N_{x,z}} \sum_{k=1}^{N_{x,z}} D(l,k,i)} MW_n$$  \hspace{1cm} (17)$$

**Weight average molecular weight:**

$$M_w = \frac{\sum_{i=0}^{N_{x,z}} \sum_{k=1}^{N_{x,z}} n(k)^2 D(l,k,i)}{\sum_{i=0}^{N_{x,z}} \sum_{k=1}^{N_{x,z}} D(l,k,i)} MW_w$$  \hspace{1cm} (18)$$

**Number average degree of branching:**

$$B_n = \frac{\sum_{i=0}^{N_{x,z}} \sum_{k=1}^{N_{x,z}} b(i) D(l,k,i)}{\sum_{i=0}^{N_{x,z}} \sum_{k=1}^{N_{x,z}} D(l,k,i)}$$  \hspace{1cm} (19)$$

**Weight average degree of branching:**

$$B_w = \frac{\sum_{i=0}^{N_{x,z}} \sum_{k=1}^{N_{x,z}} n(k)b(i) D(l,k,i)}{\sum_{i=0}^{N_{x,z}} \sum_{k=1}^{N_{x,z}} n(k) D(l,k,i)}$$  \hspace{1cm} (20)$$

where, $D(j,i,t)$, denotes the concentration of polymer chains with chain length $n(i)$ and number of branches $b(j)$.

### 4. RESULTS AND DISCUSSION

The free-radical polymerization of VAc was selected as a representative example for the production of branched polymers. In this system, transfer to monomer and polymer largely control the MWD of the poly(vinyl acetate) produced. Furthermore, the monomer radicals that are produced from the transfer to monomer reaction, propagate giving ‘live’ and ‘dead’ polymer chains with a terminal double bond. Thus, terminal double bond polymerization is an important reaction for this system, producing highly branched polymer chains.

It is well known that for the VAc polymerization system, the termination kinetic rate constant becomes gradually controlled by the diffusion phenomena as the monomer conversion and hence the viscosity of the mixture increases (Hamer and Ray, 1986). In order to account for this variation the termination rate constant was expressed as the sum of two terms, one taking into account the effect of the diffusion of polymer chains, $k_t^{diff}$, and the other describing the so-called ‘residual termination’, $k_t^{res}$:

$$k_t = k_t^{diff} + k_t^{res}$$  \hspace{1cm} (21)$$

The analytical calculation of the diffusion controlled termination rate constant is provided in the work of Keramopoulos and Kiparissides (2002).

The numerical performance of the FPT was first tested by a direct comparison of numerical results with experimental measurements on number average degree of branching $B_n$ for the free-radical polymerization of VAc (Thomas, 1998). Two temperatures (i.e., 60°C and 80°C) and different initiator concentrations (i.e., 2,2'-azobis(2-methylpropionitrile, AIBN) were used in the comparison analysis (see Fig. 2).

![Fig. 2: Predicted and experimental number average degree of branching with respect to monomer conversion (T=60°C and $[I_0] = 5 \times 10^{-3} \text{ mol/L}$; T=80°C and $[I_0] = 1 \times 10^{-4} \text{ mol/L}$).](image)

Figure 3 shows a comparison between the MWDs calculated by the FPT and the method of classes, at different monomer conversions. In both cases, the AIBN initial concentration was equal to $1.6 \times 10^{-3}$ mol/L while the polymerization temperature was 60°C. Notice that both methods are capable of predicting the MWDs up to very high monomer conversions. It was found that a number of 160 classes, leading to a total number of 960 differential equations, was sufficient for the convergence of the method of classes.

![Fig. 3: Predicted MWDs via the application of the FPT and the method of classes, at different monomer conversions](image)
Carlo simulation (Tobita and Hatanaka, 1996). The reactor temperature was 60°C, and the kinetic rate constants for the free-radical polymerization of VAc were taken from the original work of Tobita and Hatanaka (1996). The comparison was made for a specific value of monomer conversion equal to 85%. It can be seen that the MWD calculated by the FPT is in good agreement with the one obtained by the Monte Carlo simulation. The observed discrepancy in the tail of the distribution can be attributed to the use of the QSSA in the Monte Carlo simulation and to the inherent statistical difficulties of Monte Carlo simulations associated with the sampling of chains placed at the tail of the distribution.

Fig. 4: Comparison of the calculated total weight fraction distribution at monomer conversion equal to 85%. The discrete points are the calculated results by Tobita and Hatanaka (1996). The continue line represents the simulated results using the FPT.

The FPT is capable of predicting the entire joint molecular weight - long chain branching distribution. The calculated combined MW-LCB distributions are depicted at 60°C at a specific value of monomer conversion (i.e., 90%) as it can be seen in Figure 5.

Fig. 5: Predicted combined MW-LCB distribution at 90% monomer conversion (simulation conditions same as in Figure 3).

REFERENCES


