Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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Håvard Nordhus[a]; Øsivind Moen[b]; Peter Singstad[c]
[a] Statoil's Research Centre, Trondheim, Norway [b] Borealis A/S, Stathelle, Norway [c] SINTEF Electronics and Cybernetics, Trondheim, Norway

To cite this Article Nordhus, Håvard , Moen, Øsivind and Singstad, Peter(1997) 'Prediction of Molecular Weight Distribution and Long-Chain Branching Distribution of Low-Density Polyethylene from a Kinetic Model', Journal of Macromolecular Science, Part A, 34: 6, 1017 — 1043

To link to this Article: DOI: 10.1080/10601329708015008

URL: http://dx.doi.org/10.1080/10601329708015008

J.M.S.—PURE APPL. CHEM., A34(6), pp. 1017–1043 (1997)

PREDICTION OF MOLECULAR WEIGHT DISTRIBUTION AND LONG-CHAIN BRANCHING DISTRIBUTION OF LOW-DENSITY POLYETHYLENE FROM A KINETIC MODEL

HÅVARD NORDHUS

Statoil's Research Centre
N-7005 Trondheim, Norway

ØIVIND MOEN*

Borealis A/S
N-3960 Stathelle, Norway

PETER SINGSTAD

SINTEF Electronics and Cybernetics
N-7034 Trondheim, Norway

Key Words: Polyethylene; Molecular weight distribution; Long-chain branching distribution

ABSTRACT

The molecular weight distribution and the long-chain branching distribution of low-density polyethylene are predicted as a function of the synthesis conditions from a kinetic model for an autoclave reactor. The model includes initiations, propagation, termination by combination and disproportionation, and chain transfer to monomer, solvent, and polymer. Recursion formulas are developed to calculate the whole distribution density functions. A numerical method for solving the model equations is proposed. Several simulations have been performed to demonstrate the method, and predictions of long-chain branching distributions of an industrial autoclave reactor are compared with laboratory measurements.

INTRODUCTION

Low-density polyethylene is produced with the free-radical mechanism in high-pressure reactors, and are characterized by a relatively high degree of long-chain branching. The end-use properties of polyethylene are highly sensitive to the degree of branching. Experimental studies show that branching strongly affects the character of the molecular weight distribution and its rheological behavior, such as solution viscosity and viscoelastic properties (Billmeyer [1], Sperati et al. [2], Bovey et al. [3], Cudby and Bunn [4], Yamamoto and Sugimoto [5], Gianotti et al. [6], Romanini et al. [7], Luft et al. [8], Yamamoto [9], Rudin et al. [10], Santamaria [11], Bugada and Rudin [12], and Shiga [13]).

To be able to design specified resins of high quality at minimized production costs, a lot of effort has been made to develop mathematical models which describe the relations between the synthesis conditions and the structure of the polymer. A large number of publications deal with predictions of the molecular weight distribution and the degree of long-chain branching. Beasley [14] demonstrated that branch formation due to intermolecular chain transfer will broaden the distribution. The molecular weight averages can be estimated by use of the statistical moments, which can either be developed directly from kinetic rate expressions (Bamford and Tomba [15], Chen et al. [16], Shirodkar and Tsien [17], Zabisky et al. [18], Chan et al. [19], Kiparissides et al. [20]) or from a statistical approach where the fundamental parameters are the probabilities for propagation and long-chain branching (Mullikin and Mortimer [21, 22]). The zero-, first-, and second-order moments are used to express the mean value and the variance of the distribution (or the average degree of polymerization and the polydispersity, using polymer terminology). One important advantage of describing the molecular weight distributions by statistical moments is the significant reduction in complexity. The overall long-chain branching density can be calculated from the kinetic model by establishing a conservation balance for the number of branching points.

There is growing interest, however, in obtaining more detailed structural information of the polymer such as the full molecular weight distribution (MWD) and the long-chain branching distribution (LCBD). The calculation is required to take into account the history of the generated branch structure due to the nature of the chain transfer to polymer reaction. This has been a tough barrier to the development of theoretical analysis. Although the equations describing the distribution density functions are of a discrete nature, the large dimension of the chain length makes numerical solutions very time consuming. Teymour and Campell [23] presented a method called "Numerical Fractionation" which splits the polymer into fractions or classes, where molecules with the same number of long-chain branches belong to the same class. From a fundamental model the equations for the moments within each class are derived, and the MWD for each class is calculated by assuming that each polymer fraction may be described as a given statistical distribution. The overall

MWD is achieved from a weighted sum of MWDs for different fractions. Yamaguchi et al. [24], Feucht et al. [25], and Singstad [26] have all published reactor models where the full MWD is calculated directly from recursion expressions, where a polymer of a given length is a function of smaller polymer molecules. Another approach, suggested by Tobita [27] and Tobita and Hatanaka [28], utilizes the Monte Carlo simulation technique to investigate MWD and the branched structure formation during free-radical polymerization that involves chain transfer to polymer.

The method presented in this paper was proposed by Singstad [26], but the model is extended to also describe the LCBD. From a kinetic scheme and a description of the mixing within the reactor, analytical expressions are derived for the polymer molecular weight distribution (MWD) and the distribution of branches frequency versus molecular weight for polymer chains in the MWD. A numerical method for solving the equations efficiently is presented.

MODEL FORMULATIONS

Kinetic Model

The following reaction steps are used to describe the long-chain branching of the free-radical polymerization:

Initiation:

$$I \xrightarrow{k_{\mathrm{I}}} 2R_{0,0} \tag{1}$$

Initiator degradation:

$$I \xrightarrow{k_{\mathrm{L}}} L \tag{2}$$

Propagation:

$$R_{m,b} + M \xrightarrow{k_{\mathrm{p}}} R_{m+1,b} \tag{3}$$

Termination by combination:

$$R_{m,b} + R_{i,j} \xrightarrow{k_{\mathrm{tc}}} P_{m+i,b+j} \tag{4}$$

Termination by disproportionation:

$$R_{m,b} + R_{i,j} \xrightarrow{k_{\mathrm{td}}} P_{m,b} + P_{i,j} \tag{5}$$

Chain transfer to monomer:

$$R_{m,b} + M \xrightarrow{k_{\mathrm{tm}}} R_{1,0} + P_{m,b} \tag{6}$$

Chain transfer to solvent or chain transfer agent:

$$R_{m,b} + S \xrightarrow{k_{\text{ts}}} R_{0,0} + P_{m,b} \tag{7}$$

Chain transfer to polymer:

$$P_{m,b} + R_{i,j} \xrightarrow{k_{\text{tp}}(1 + am)} R_{m,b+1} + P_{i,j} \tag{8}$$

The molar concentration of radicals (or "living" polymers) and polymer (or "dead" polymer) are denoted by $R_{m,b}$ and $P_{m,b}$, respectively, where m is the number of monomer groups and b is the number of long-chain branching points.

Chain transfer to polymer is the only reaction that can create new long-chain branches (LCB), see Eq. (8), where the LCB subscript of the new radical is increased by 1. The radicals created from this reaction are the only ones containing LCB (sometimes referred to as 'secondary radicals').

Three of the reactions contribute to new "primary radicals": Initiation, chain transfer to solvent or transfer agent, and chain transfer to monomer (Eqs. 1, 7, and 6, respectively). While the former two reactions create radicals containing no monomer, $R_{0,0}$, the latter forms radicals with one unsaturated monomer molecule, $R_{1,0}$. There is no good reason for treating these radicals differently, but the model development can be simplified if the following modification of Eq. (6) is employed:

$$R_{m,b} + M \xrightarrow{k_{\text{tm}}} R_{0,0} + P_{m,b} \tag{9}$$

This approximation introduces loss of generality that is undetectable in the simulations.

Most authors assume that the rate of chain transfer to polymer is proportional to the chain length of the "dead" molecule involved. This implies an equal probability of hydrogen abstraction from all monomer groups in all "dead" molecules. As some of the polymer molecules are very large and highly branched, one could argue that the probability must be smaller for some of the groups on the larger molecules, simply because of reduced accessibility. There are good reasons for assuming that the true rate constant is a complex function of the chain length. It is, however, very difficult to incorporate a general expression for this particular dependency in the model, as the tractability of the resulting equations is strongly affected.

In this paper the rate of chain transfer to polymer is assumed to depend linearly on the polymer chain length, Eq. (8), as previously proposed by Feucht et al. [25]. This is perhaps a crude approximation, but still somewhat more general than the common practice of equal probability.

Component Balances

Based on the above-mentioned kinetic model, the following component balances are developed.

Initiator:

$$\Psi(I) = -k_{\text{I}}I - k_{\text{L}}I \tag{10}$$

Monomer:

$$\Psi(M) = -k_pMR - k_{tm}MR \tag{11}$$

Solvent or chain transfer agent:

$$\Psi(S) = -k_{ts}SR \tag{12}$$

Radicals:

$$\begin{aligned}\Psi(R_{m,b}) = &-[k_pM + k_{tc}R + k_{td}R + k_{tm}M + k_{ts}S \\ &+ k_{tp}(1 + a\mu_1)P]R_{m,b} + k_pMR_{m-1,b} + k_{tp}(1 + am)RP_{m,b-1}\end{aligned} \tag{13}$$

where it is assumed that $m > 0$ and $b > 0$. If $m > 0$ and $b = 0$, the last term in Eq. (13) is omitted, giving

$$\begin{aligned}\Psi(R_{m,0}) = &-[k_pM + k_{tc}R + k_{td}R + k_{tm}M + k_{ts}S \\ &+ k_{tp}(1 + a\mu_1)P]R_{m,0} + k_pMR_{m-1,0}\end{aligned} \tag{14}$$

If both $m = 0$ and $b = 0$, Eq. (13) is replaced by

$$\begin{aligned}\Psi(R_{0,0}) = &-[k_pM + k_{tc}R + k_{td}R + k_{tm}M + k_{ts}S \\ &+ k_{tp}(1 + a\mu_1)P]R_{0,0} + 2k_II + k_{tm}MR + k_{ts}SR\end{aligned} \tag{15}$$

Dead polymer chains:

$$\begin{aligned}\Psi(P_{m,b}) = &[k_{td}R + k_{tm}M + k_{ts}S + k_{tp}(1 + a\mu_1)P]R_{m,b} \\ &- k_{tp}(1 + am)RP_{m,b} + \frac{1}{2}k_{tc}\sum_{i=0}^{m}\sum_{j=0}^{b} R_{i,j}R_{m-i,b-j}\end{aligned} \tag{16}$$

$\Psi(\,)$ is a linear operator in time and space describing accumulation, convection, and possibly diffusion. To simplify the notation, some definitions are introduced. By eliminating the information of the branching, the total concentration of radicals and polymers of length m will be

$$R_m = \sum_{b=0}^{\infty} R_{m,b} \tag{17}$$

$$P_m = \sum_{b=0}^{\infty} P_{m,b} \tag{18}$$

The total radical concentration, R, and the total polymer concentration, P, are defined as

$$R = \sum_{m=0}^{\infty}\sum_{b=0}^{\infty} R_{m,b} \tag{19}$$

$$P = \sum_{m=0}^{\infty}\sum_{b=0}^{\infty} P_{m,b} \tag{20}$$

The average number of monomer groups in a polymer molecule (number-average degree of polymerization) is equal to the dimensionless first moment, μ_1, where

$$\mu_1 = \frac{1}{P} \sum_{m=0}^{\infty} m \sum_{b=0}^{\infty} P_{m,b} \tag{21}$$

Mixing within the Reactor

A model for describing a complex industrial reactor must take into account varying process conditions within the reactor. The following model formulation describes the reactor by a number of perfectly mixed control volumes, which is the natural choice for stirred autoclaves, but can easily be adapted to tubular reactors. For a perfectly mixed control volume, the accumulation and convection operator $\Psi(\;)$ can be formulated

$$\Psi(\xi) = \frac{d}{dt}\xi + \frac{1}{V}\sum_{o} \xi q_o - \frac{1}{V}\sum_{i} \xi_i q_i \tag{22}$$

where the summations are made for every outlet stream o and every inlet stream i, respectively. If only stationary reactor conditions are considered, the first term on the right-hand side will be zero.

Molecular Size Formulas

The free radicals have much higher reactivity than the other reactants. The quasi steady-state assumption (QSSA) is therefore applied to the radicals:

$$\Psi(R_{m,b}) = 0 \tag{23}$$

Use of the QSSA in the form of Eq. (23) implies that the total radical concentration obeys the relation

$$2k_1 I = k_{tc} R^2 + k_{td} R^2 \tag{24}$$

By use of Eqs. (13), (14), (15), and (23), the following recursive formulas for the radicals are derived:

$$R_{m,b} = \sum_{i=0}^{m} \frac{[k_p M]^{m-i} k_{tp}[1 + ai] R P_{i,b-l}}{[k_p M + k_{tc} R + k_{td} R + k_{tm} M + k_{ts} S + k_{tp}(1 + a\mu_1)P]^{m-i+1}} \tag{25}$$

for $b > 0$. For $m > 0$ and $b = 0$:

$$R_{m,0} = \frac{[k_p M]^m R_{0,0}}{[k_p M + k_{tc} R + k_{td} R + k_{tm} M + k_{ts} S + k_{tp}(1 + a\mu_1)P]^m} \tag{26}$$

Otherwise, for both $m = 0$ and $b = 0$:

$$R_{0,0} = \frac{2k_1 I + k_{tm} M R + k_{ts} S R}{[k_p M + k_{tc} R + k_{td} R + k_{tm} M + k_{ts} S + k_{tp}(1 + a\mu_1)P]} \tag{27}$$

Note that only radicals formed from the chain transfer to polymer reaction, Eq. (8), contain long-chain branches.

These expressions can be simplified if the analysis is restricted to account for the total number of monomer groups only. The simplification does not imply loss of accuracy, but the information about the branching distribution is eliminated. From Eqs. (17), (18), and (25)-(27) it follows that

$$R_m = \frac{[k_pM]^m[2k_II + k_{tm}MR + k_{ts}SR]}{[k_pM + k_{tc}R + k_{td}R + k_{tm}M + k_{ts}S + k_{tp}(1 + a\mu_1)P]^{m+1}} + \sum_{i=0}^{m} \frac{[k_pM]^{m-i}k_{tp}[1 + ai]RP_i}{[k_pM + k_{tc}R + k_{td}R + k_{tm}M + k_{ts}S + k_{tp}(1 + a\mu_1)P]^{m-i+1}} \tag{28}$$

Similarly, the polymer description without the branching information is

$$\Psi(P_m) = [k_{td}R + k_{tm}M + k_{ts}S + k_{tp}(1 + a\mu_1)P]R_m - k_{tp}(1 + am)RP_m + \frac{1}{2}k_{tc}\sum_{i=0}^{m} R_iR_{m-i} \tag{29}$$

Further simplification of the MWD model is done by introducing the dimensionless parameters

$$\alpha = \frac{k_pMR}{r} \tag{30}$$

$$\beta = \frac{k_{tp}P(1 + a\mu_1)R}{r} \tag{31}$$

$$\gamma = \frac{k_{tc}R^2 + k_{td}R^2 + k_{tm}MR + k_{ts}SR}{r} \tag{32}$$

$$\delta = \frac{0.5k_{tc}R^2}{r} \tag{33}$$

The common denominator r is the total reaction rate:

$$r = k_pMR + k_{tc}R^2 + k_{td}R^2 + k_{tm}MR + k_{ts}SR + k_{tp}(1 + a\mu_1)PR \tag{34}$$

The following physical interpretation can be given to these variables:

α is the probability that a certain radical molecule will propagate at least one more reaction step.

β is the probability that a certain radical molecule will participate in a chain transfer to polymer reaction.

γ is the probability that a certain radical molecule will terminate at its current size—either by combination, disproportionation, or by chain transfer to monomer or solvent.

2δ is the probability that a certain radical molecule will terminate by combination.

These parameters obey the following relation:

$$\alpha + \beta + \gamma = 1 \tag{35}$$

The model, Eqs. (28) and (29), is reduced to the following simple form:

$$\frac{R_m}{R} = \sum_{i=1}^{m} \alpha^{m-i}\beta\frac{1 + ai}{P(1 + a\mu_1)}P_i + \alpha^m\gamma \tag{36}$$

$$\Psi(P_m) = r\left\{[\gamma - 2\delta + \beta]\frac{R_m}{R} + \frac{\delta}{R^2}\sum_{i=0}^{m} R_iR_{m-i} - \beta\frac{(1 + am)}{P(1 + a\mu_1)}P_m\right\} \tag{37}$$

The initial condition is given by

$$R_0/R = \gamma \tag{38}$$

Long-Chain Branching Distribution

Bookkeeping of the total number of long chain branches (LCB) yields

$$\Psi(c_{\mathrm{LCB}}) = k_{\mathrm{tp}}(1 + \alpha\mu_1)RP \tag{39}$$

where c_{LCB} is a LCB concentration.

To be able to calculate the long-chain branching distribution as a function of the molecular weight, component balances of the long-chain branches for each chain length are established. The concentration of LCB belonging to radicals and polymers of length m are defined by the relations

$$c_{\mathrm{LCB},m}^{\mathrm{R}} = \sum_{b=1}^{\infty} bR_{m,b} \tag{40}$$

$$c_{\mathrm{LCB},m} = \sum_{b=1}^{\infty} bP_{m,b} \tag{41}$$

Since only radicals generated by chain transfer to polymer contain long-chain branches, $c_{\mathrm{LCB},m}^{\mathrm{R}}$ can be calculated by inserting Eq. (25) into (40):

$$c_{\mathrm{LCB},m}^{\mathrm{R}} = \sum_{i=0}^{m} \frac{[k_{\mathrm{p}}M]^{m-i}k_{\mathrm{tp}}(1 + ai)R(c_{\mathrm{LCB},i} + P_i)}{[k_{\mathrm{p}}M + k_{\mathrm{tc}}R + k_{\mathrm{td}}R + k_{\mathrm{tm}}M + k_{\mathrm{ts}}S + k_{\mathrm{tp}}(1 + a\mu_1)P]^{m-i+1}} \tag{42}$$

Replacing the molar LCB concentration with the average number of LCB per molecule:

$$\bar{n}_{\mathrm{LCB},m} = \frac{c_{\mathrm{LCB},m}}{P_m} \tag{43}$$

in Eq. (42) yields

$$c_{\mathrm{LCB},m}^{\mathrm{R}} = \sum_{i=0}^{m} \frac{[k_{\mathrm{p}}M]^{m-i}k_{\mathrm{tp}}(1 + ai)RP_i(\bar{n}_{\mathrm{LCB},i} + 1)}{[k_{\mathrm{p}}M + k_{\mathrm{tc}}R + k_{\mathrm{td}}R + k_{\mathrm{tm}}M + k_{\mathrm{ts}}S + k_{\mathrm{tp}}(1 + a\mu_1)P]^{m-i+1}} \tag{44}$$

By carefully examining Eq. (44), it can be seen from the factor $(\bar{n}_{\mathrm{LCB},i} + 1)$ that the number of LCB is equal to the number of LCB of the polymers participating in the chain transfer to polymer reaction, but in addition one new branching point per molecule is created, which is in agreement with Eq. (8).

The component balances of the number of LCB belonging to the polymers of length m are derived from Eqs. (16), (40), and (41):

$$\begin{aligned}\Psi(c_{\mathrm{LCB},m}) = {} & [k_{\mathrm{td}}R + k_{\mathrm{tm}}M + k_{\mathrm{ts}}S + k_{\mathrm{tp}}P(1 + a\mu_1)]c_{\mathrm{LCB},m}^{\mathrm{R}} \\ & + k_{\mathrm{tc}} \sum_{i=0}^{m} R_{m-i}c_{\mathrm{LCB},i}^{\mathrm{R}} - k_{\mathrm{tp}}(1 + am)Rc_{\mathrm{LCB},m}\end{aligned} \tag{45}$$

The first term on the right-hand side represents the formation of LCB from radicals of length m terminated by disproportionation and chain transfer to monomer, modifier, and polymer. The second term is the formation of LCB from termination by combination. The last term represents the consumption of LCB from polymer of length m by chain transfer to polymer.

A closer look at the termination by combination term is given below. Substituting the concentration of LCB with the average number of LCB per radical molecule:

$$\bar{n}^{\mathrm{R}}_{m} = \frac{c^{\mathrm{R}}_{\mathrm{LCB},m}}{R_m} \tag{46}$$

the termination by combination term can be rewritten as

$$\begin{aligned} k_{\mathrm{tc}} \sum_{i=0}^{m} R_{m-i} c^{\mathrm{R}}_{\mathrm{LCB},i} &= k_{\mathrm{tc}} \sum_{i=0}^{m} R_i R_{m-i} \bar{n}^{\mathrm{R}}_{\mathrm{LCB},i} \\ &= \frac{1}{2} k_{\mathrm{tc}} \sum_{i=0}^{m} R_i R_{m-i} [\bar{n}^{\mathrm{R}}_{\mathrm{LCB},i} + \bar{n}^{\mathrm{R}}_{\mathrm{LCB},m-i}] \end{aligned} \tag{47}$$

This equation states that the number of LCB in a polymer molecule formed by combinative termination will be the sum of the LCB of the two radicals, see reaction Eq. (4).

Finally, as for the MWD model, the LCBD model can be reduced to the following simple form:

$$\frac{c^{\mathrm{R}}_{\mathrm{LCB},m}}{R} = \sum_{i=0}^{m} \alpha^{m-i} \beta \frac{(1 + ai)}{P(1 + a\mu_1)} (c_{\mathrm{LCB},i} + P_i) \tag{48}$$

$$\Psi(c_{\mathrm{LCB},m}) = r\left\{[\gamma - 2\delta + \beta] \frac{c^{\mathrm{R}}_{\mathrm{LCB},m}}{R} + \frac{2\delta}{R^2} \sum_{i=0}^{m} R_{m-i} c^{\mathrm{R}}_{\mathrm{LCB},i} - \beta \frac{(1 + am)}{P(1 + a\mu_1)} c_{\mathrm{LCB},m}\right\} \tag{49}$$

where the parameters α, β, γ, and δ are given by Eqs. (30)-(33).

The initial condition will be

$$c_{\mathrm{LCB},0} = 0 \tag{50}$$

Remarks

By examining the model Eqs. (36), (37), (48), and (49), two observations have been made. First, the MWD and LCBD models are linear with respect to the polymer concentration, P_m, and LCB concentration, $c_{\mathrm{LCB},m}$. Second, the models are only dependent on the smaller polymers and the LCB belonging to shorter molecules,

$$\begin{aligned} P_m &= f_1(P_{m-1}, P_{m-2}, \ldots, P_0) \\ c_{\mathrm{LCB},m} &= f_2(c_{\mathrm{LCB},m-1}, c_{\mathrm{LCB},m-2}, \ldots, c_{\mathrm{LCB},0}) \end{aligned} \tag{51}$$

This implies that the MWD and LCBD can be calculated by recursion starting at $m = 0$ and with the initial conditions in Eqs. (38) and (50).

SIMULATION ALGORITHM

The MWD and the LCBD equations are not well suited for direct implementation in a computer simulator, even though they are in discrete form. The reason for this is the large size of the polymer molecules combined with the convolution sum resulting from the termination by combination reactions. The convolution sums have to be recalculated for each polymer length. If the reactor model consists of v

control volumes, then two sets of ν linear equations have to be solved for each polymer length. Extensive computational resources are therefore required in order to calculate the distributions by a direct approach. A more efficient way of performing the numerical calculation is proposed below.

Continuous Model Formulation

In order to use suitable numerical tools for the calculation, the model is transformed into a continuous differential-algebraic relation. The integer chain length variable m is replaced by the continuous variable x, with the same unit. Let the dimensionless variable λ be defined by

$$\alpha^m = e^{-\lambda x} \tag{52}$$

λ^{-1} can be interpreted as a characteristic chain length for a single polymeric chain.

$$\lambda = -\ln \alpha \approx 1 - \alpha \tag{53}$$

Steady state is assumed, and the convection in a perfectly mixed control volume is formulated:

$$\Psi(\xi) = \frac{1}{V} \sum_o \xi\, q_o - \frac{1}{V} \sum_i \xi_i q_i \tag{54}$$

where the summations are made for every outlet stream o and every inlet stream i, respectively. The following two dimensionless parameters are defined:

$$\zeta = \frac{P}{Vr} \sum_o q_o \tag{55}$$

$$\varepsilon_i = \frac{(P)_i}{Vr\zeta} q_i \tag{56}$$

In addition, the normalized concentration-based chain length distribution density functions of radical, polymer, long-chain branching of polymer, and long-chain branching of radicals are introduced:

$$\mathcal{R}_m = \frac{R_m}{R} \tag{57}$$

$$\mathrm{P}_m = \frac{P_m}{P} \tag{58}$$

$$\mathrm{C}_{\mathrm{LCB},m} = \frac{c_{\mathrm{LCB},m}}{P} \tag{59}$$

$$\mathrm{C}^{\mathrm{R}}_{\mathrm{LCB},m} = \frac{c^{\mathrm{R}}_{\mathrm{LCB},m}}{R} \tag{60}$$

To differ between the continuous and the discrete representation, the notation $\mathrm{P}(x)$ is introduced to represent a polymer of length x in the continuous model formulation. The same convention is used for radicals and long chain branches. Approximating the sums in Eqs. (36) and (37) with integrals, the continuous form of the MWD model can be written

$$\mathrm{P}(x)\left\{\zeta + \beta\frac{(1+ax)}{(1+a\mu_1)}\right\} - \zeta\sum_i \varepsilon_i \mathrm{P}_i(x) = [\gamma - 2\delta + \beta]\mathcal{R}(x) + \delta\int_0^x \mathcal{R}(x')\mathcal{R}(x-x')dx' \tag{61}$$

$$\frac{d}{dx}\mathcal{R}(x) = \lambda\mathcal{R}(x) + \beta\frac{(1+ax)}{(1+a\mu_1)}\mathrm{P}(x) \tag{62}$$

with initial conditions

$$\mathcal{R}(0) = \gamma \tag{63}$$

Similarly, the continuous form of the LCBD model in Eqs. (48) and (49) is

$$\mathrm{C}_{\mathrm{LCB}}(x)\left\{\zeta + \beta\frac{(1+ax)}{(1+a\mu_1)}\right\} - \zeta\sum_i \varepsilon_i \mathrm{C}_{\mathrm{LCB},i}(x) = [\gamma - 2\delta + \beta]\mathrm{C}^{\mathrm{R}}_{\mathrm{LCB}}(x) + 2\delta\int_0^x \mathcal{R}(x-x')\,\mathrm{C}^{\mathrm{R}}_{\mathrm{LCB}}(x')dx' \tag{64}$$

$$\frac{d}{dx}\mathrm{C}^{\mathrm{R}}_{\mathrm{LCB}}(x) = -\lambda\mathrm{C}^{\mathrm{R}}_{\mathrm{LCB}}(x) + \beta\frac{(1+ax)}{(1+a\mu_1)}\{\mathrm{C}_{\mathrm{LCB}}(x) + \mathrm{P}(x)\} \tag{65}$$

with initial conditions

$$\mathrm{C}^{\mathrm{R}}_{\mathrm{LCB}}(0) = 0 \tag{66}$$

Calculation Scheme

A solution method for solving the differential-algebraic set of equations was proposed by Singstad [26] who used a spectral method. The Fourier transformed set of equations becomes ordinary, complex differential equations and quadratic algebraic relations. The main advantage of this method is that the convolution integral in the "time domain" corresponds to a multiplication in Fourier transformed "frequency domain," which reduces the calculation time. An alternative method is presented below. The efficiency of this algorithm seems to be quite similar. The convolution integrals have to be calculated, but the transformation to and from the "frequency domain" is omitted.

The MWD and LCBD models must be linked to a model which supplies numerical values of the reactant concentration, the rate constants, and the internal flow rates. The calculation procedure starts with taking a "snapshot" of the reactor, where the values of all needed parameters are collected. The process model is not focused in this presentation. The further calculations follow these steps:

1. Calculate the dimensionless kinetic parameters α, β, γ, δ, ζ, μ_1, and (ε_i, $\forall i$) for each control volume.
2. Solve the differential-algebraic set of equations in Eqs. (61), (62), (64), and (65) with the initial conditions given by Eqs. (63) and (66). At each integration step:
   - 2.1 Receive from the integration procedure updated radical concentrations $\mathcal{R}(x)$ and LCB concentrations $\mathrm{C}^{\mathrm{R}}_{\mathrm{LCB}}(x)$ for each control volume.
   - 2.2 Solve the convolution integrals in Eqs. (61) and (64) for each control volume (requires a separate integration procedure).
   - 2.3 Calculate the polymer concentration $\mathrm{P}(x)$ and the LCB concentration $\mathrm{C}_{\mathrm{LCB}}(x)$ of the polymer by solving two linear sets of ν equations given by

Eqs. (61) and (64). (ν is the number of control volumes.) If the chain length x is equal to the final length, stop calculations.

2.4 Calculate increments in the radical and LCB concentrations [$\mathcal{R}(x)$ and $C^{R}_{LCB}(x)$], and return these values to the integration procedure.

2.5 Perform a new integration step, and go to 2.1.

An Euler scheme is used for the integration, while the convolution integrals are solved by the trapezoidal rule. Euler was chosen because the discretized continuous equations reduce to the exact discrete relations when the integration step equals unity.

The model Eqs. (61) to (66) describe the concentrations in one control volume. A model with several control volumes requires one set of equations for each volume, and the internal flow rates yield linear couplings between the different volumes. They are described by the left sides of Eqs. (61) and (64). Gaussian elimination has been performed to solve the two sets of linear equations. Note that the left side coefficients of the linear MWD and LCBD equations are equal. This may be exploited in order to speed up the calculations. By solving the two set simultaneously, the number of arithmetic operations is decreased from $\approx 2/3\nu^3$ to $\approx 1/3\nu^3 + \nu^2$ compared to solving them separately, Strang [29].

To further speed up the calculations, the following approaches have been used with success:

- The Gauss–Seidel iterative method is used for solution of the linear set of flow equations (Step 2.3).
- The implementation of the Gauss–Seidel algorithm takes advantage of the sparse structure of the flow matrix.
- Larger discretization intervals are used in the solution of the convolution integrals as compared to the discretization intervals of the integration procedure. (The convolution integrals are not calculated at each integration step.)

The accuracy of the MWD and LCBD calculations have been tested by comparing precalculated values of the number-average molecular weight, the polydispersity, and the overall LCB concentration with values postcalculated from the resulting distribution density functions. The overall LCB concentration is given as

$$c_{LCB} = \sum_{m=1}^{\infty} \sum_{b=1}^{\infty} bP_{m,b} = \sum_{m=1}^{\infty} c_{LCB,m} \qquad (67)$$

which can be compared to the precalculated value given by Eq. (39).

The models were implemented on a HP750 Unix work station. One MWD and LCBD calculation for a CSTR model takes approximately 1–2 minutes, while calculating these distributions of a more complex reactor configuration of 31 control volumes typically requires 15–20 minutes.

SIMULATION RESULTS

To illustrate the behavior of the LCBD model, several simulations of simple and more complicated reactor configurations have been performed. The focus of these simulations is set on the prediction of the long-chain branching distribution, and the following three cases are examined:

Case 1: An ideal continuously stirred tank reactor (CSTR).
Case 2: A reactor model of 3 CSTRs in series.
Case 3: A 31 volumes reactor model.

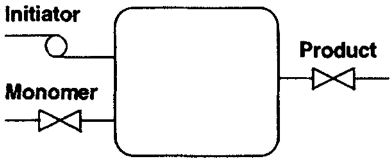

FIG. 1. Schematic sketch of the CSTR simulation model.

The model in Case 3 represents an industrial autoclave similar to the one at Borealis Rønningen.

Case 1: A Continuously Stirred Tank Reactor (CSTR)

For a CSTR all the polymers are produced at the same reactor condition, and the simplicity of this configuration is well suited for analyzing the sensitivity of the model to the choice of kinetic parameters. A schematic sketch of the CSTR simulation model is given in Fig. 1. In these simulations the reactor pressure is 1700 bar, the reactor temperature is 230°C, and the mean residence time is 60 seconds. The monomer temperature and pressure are 30°C and 1950 bar, respectively. The reactor temperature is controlled by the feed rate of the initiator di-*tert*-butyl peroxide. The kinetic parameters used in the simulations are given in Table 1. The frequency factor of the chain transfer to monomer is selected to predict a number-average degree of polymerization of 450, which is a typical value for single phase resins produced without modifier. The frequency factor of the chain transfer to polymer is chosen so that the number of LCB per 1000C is approximately 1.0. All the other parameters are taken from Singstad [26]. Other choices of kinetic parameters will be specified in the text.

The chain transfer to polymer parameter a is used to make this reaction dependent on the polymer chain length, see Eq. (8). This reaction will be size independent by setting a equal 0, as some authors do (e.g., Agrawal and Han [30] and Gupta et al. [31]). The most common choice in the literature is assuming the

TABLE 1. Kinetic Parameters. All Parameters Except $k_{\mathrm{tm},0}$ Are Taken from Singstad [26]

		$k_{\mathrm{x}0}$, $\mathrm{s}^{-1}\cdot\mathrm{m}^{3n-3}\cdot\mathrm{mol}^{1-n}$	E_{x}, J/mol	V_{x}, m^3/mol
Di-*tert*-butyl peroxide	k_{I}	1.7×10^{15}	152,000	13.4×10^{-6}
	k_{L}	5.3×10^{26}	275,000	0.0
Propagation	k_{p}	5.0×10^{4}	30,000	0.0
Termination:				
Combination	k_{tc}	1.6×10^{6}	10,000	0.0
Disproportionation	k_{td}	0.0	0	0.0
Chain transfer:				
To monomer	k_{tm}	5.9×10^{3}	42,000	0.527×10^{-6}
To polymer	k_{tp}	1.6×10^{2}	38,000	0.0

rate of chain transfer to polymer will be proportional to the chain length of the "dead" molecules involved, and this will be achieved by specifying a large a ($a > 1$). The constant part of the linear expression in Eq. (8) will then be negligible compared to the term am. Simulations with $a = 0$, $a = 0.02$, and $a = 1.0$ have been done. Note that the frequency factor is selected such that the overall number of LCB will be approximately the same in all the simulations. The following sets of kinetic parameters are used:

$$k_{\mathrm{tp,0}} = 4.2 \times 10^6\ (\mathrm{m^3 \cdot mol^{-1} \cdot s^{-1}});\ \Delta E_{\mathrm{tp}} = 38{,}000\ (\mathrm{kJ/kmol});\ \Delta V_{\mathrm{tp}} = 0;\ a = 0$$

$$k_{\mathrm{tp,0}} = 4.2 \times 10^5\ (\mathrm{m^3 \cdot mol^{-1} \cdot s^{-1}});\ \Delta E_{\mathrm{tp}} = 38{,}000\ (\mathrm{kJ/kmol});\ \Delta V_{\mathrm{tp}} = 0;\ a = 0.02$$

$$k_{\mathrm{tp,0}} = 9.3 \times 10^4\ (\mathrm{m^3 \cdot mol^{-1} \cdot s^{-1}});\ \Delta E_{\mathrm{tp}} = 38{,}000\ (\mathrm{kJ/kmol});\ \Delta V_{\mathrm{tp}} = 0;\ a = 1.0$$

Second, the sensitivity to the choice of the termination reactions is examined. Neglecting the termination by combination reaction and assuming termination by disproportionation as the only termination reaction will simplify the model, because then the convolution sum will disappear. The LCBD is calculated for the two cases where the termination reaction is either combination only or disproportionation only. The kinetic parameters for these two reactions are chosen equal so that the overall consumption of radicals will be unchanged.

Figures 2a–c present the calculated MWDs. A relatively large rate of chain transfer to monomer causes most radical chains to terminate by this reaction, and

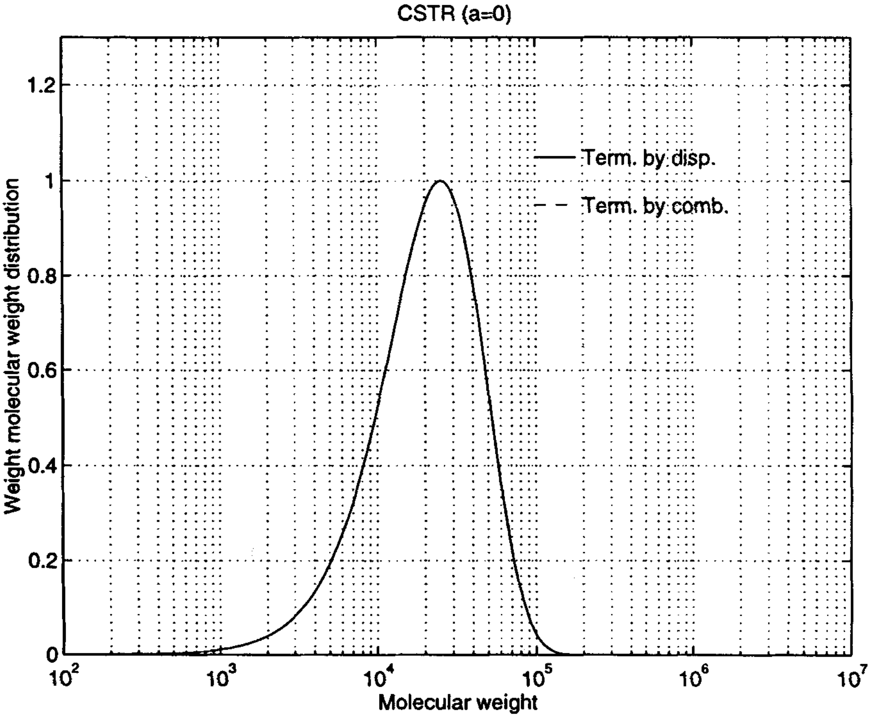

FIG. 2a. The MWDs. CSTR model. The kinetic parameter $a = 0$. The two cases nearly fall on top of each other.

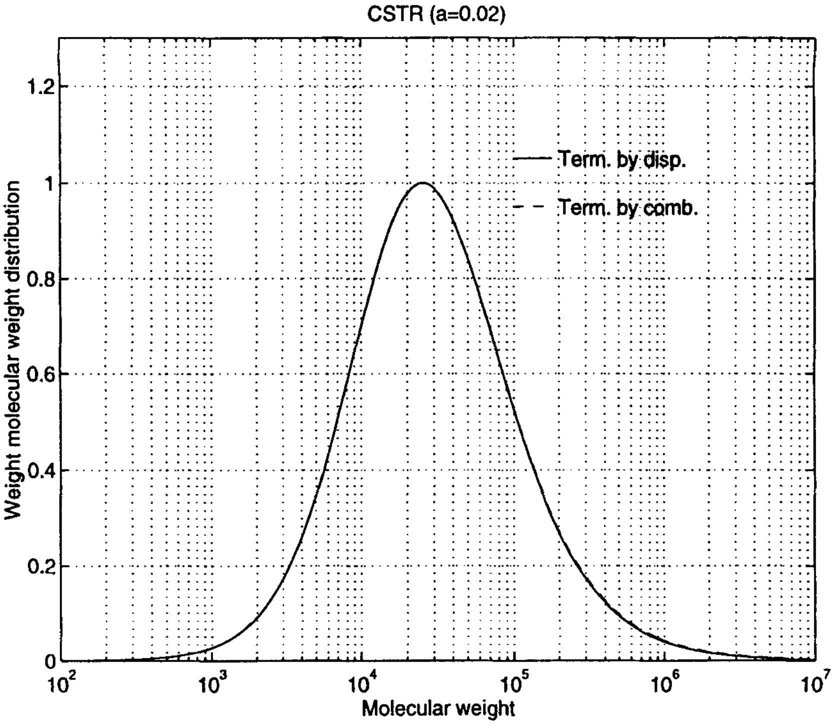

FIG. 2b. The MWDs. CSTR model. The kinetic parameter $a = 0.02$. The two cases nearly fall on top of each other.

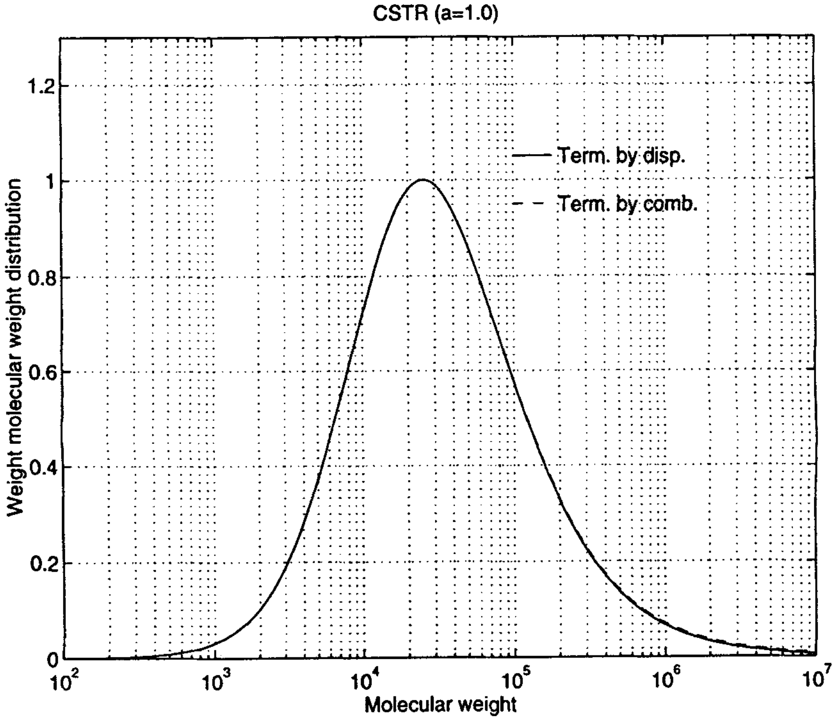

FIG. 2c. The MWDs. CSTR model. The kinetic parameter $a = 1.0$. The two cases nearly fall on top of each other.

the MWDs become insensitive to selecting either the combination or the disproportionation reaction. Assuming a chain-length-dependent chain transfer to polymer reaction gives a broader MWD.

Figures 3a–c show the LCBDs expressed as number of LCB per 1000C as a function of the molecular weight. As expected, the density of LCB will increase for larger molecules if the chain transfer to polymer is size dependent. The LCBDs for a equal to 0.02 and 1.0 are quite similar, except that the amount of LCB in smaller molecules will be less when a is increased (and the frequency factor is reduced). If the chain transfer to polymer reaction is size independent, the LCB density is constant for molecular weights between 10^3 and 10^5. The border condition of the LCBD calculation, Eq. (50), defines the number of long-chain branches belonging to a polymer of length zero to be zero. Therefore, the LCB density will start at zero and increase to a level equal to the overall number of LCB per 1000C when about 10 monomer groups have been added to the polymer. If the termination by combination reaction is omitted, the density will be constant for higher molecular weights (above 10^5).

From Eq. (13) the ratio of the amount of radicals of length x having the reactive point at the end of the chain $R^{\mathrm{p}}(x)$, which is created by the propagation reaction, and the amount of radicals of the same length having the reactive point at a branching point, $R^{\mathrm{tp}}(x)$, see Fig. 4, can be written

$$\frac{R^{\mathrm{tp}}(x)}{R^{\mathrm{p}}(x)} = \frac{\beta \mathrm{P}(x)}{\alpha \mathcal{R}(x-1)} \approx \frac{\beta \mathrm{P}(x)}{\alpha \mathcal{R}(x)} \tag{68}$$

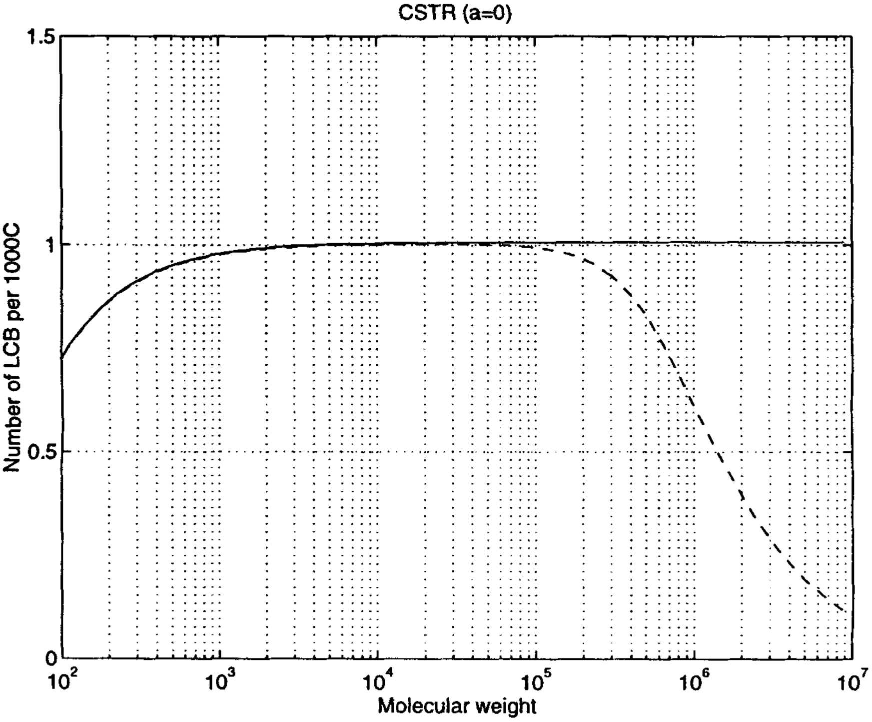

FIG. 3a. The #LCB/1000C. CSTR model. The kinetic parameter a = 0.

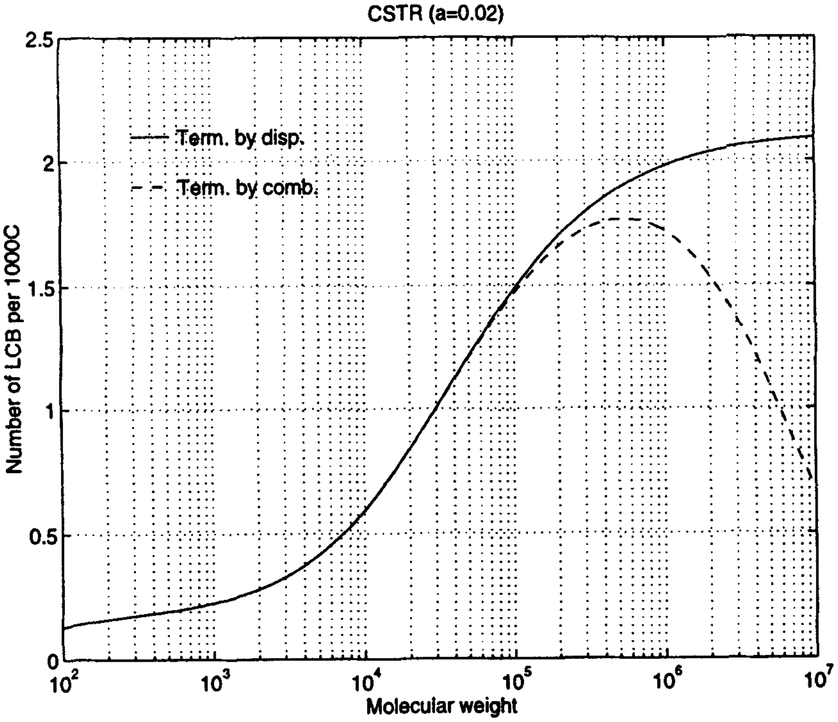

FIG. 3b. The #LCB/1000C. CSTR model. The kinetic parameter $a = 0.02$.

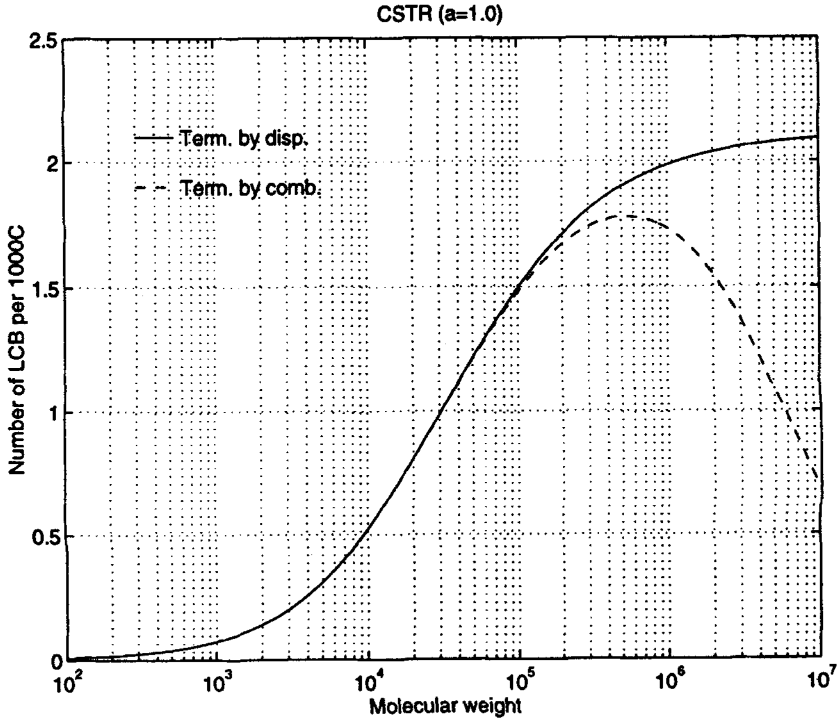

FIG. 3c. The #LCB/1000C. CSTR model. The kinetic parameter $a = 1.0$.

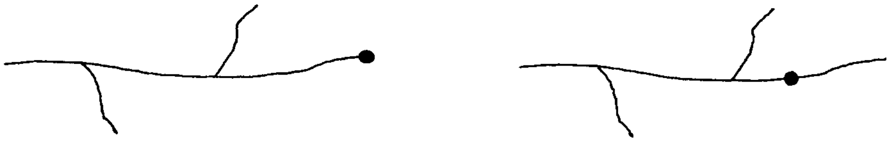

FIG. 4. Molecules with a radical point at the end of a chain (left) and with a radical point at a branching point (right).

where it is assumed $a = 0$. For a CSTR model the ratio of the polymer and radicals of length x is given by the MWD model Eq. (61). Using this equation, Eq. (68) can be rewritten as

$$\frac{R^{\text{tp}}(x)}{R^{\text{p}}(x)} = \frac{\beta}{\alpha}\,\frac{[\gamma - 2\delta + \beta] + \dfrac{2\delta}{\mathcal{R}(x)}\displaystyle\int_0^x \mathcal{R}(x')\mathcal{R}(x - x')dx'}{\zeta + \beta} \tag{69}$$

If the termination by combination reaction is omitted, i.e., $\delta = 0$, this ratio will be constant, and the ratio in Eq. (68) becomes constant, which proves that the LCB density of the radicals and polymers will be constant. This corresponds to the solid LCB density in Fig. 3a. Otherwise, if the combination reaction is present, the convolution term in Eq. (69) will in general change this ratio as a function of the molecular weight.

The accuracy of the LCBD calculations is evaluated by comparing the precalculated overall number of LCB per 1000C with this property achieved directly from the calculated LCBDs by use of Eq. (67), which is denoted postcalculated. Table 2 shows that the deviations are relatively small in these simulations.

Case 2: A Reactor Model of 3 CSTRs in Series

In Case 2 the influence of inhomogeneous reactor conditions on the calculated LCBD is examined. The inhomogeneities are modeled by dividing the reactor model in Case 1 into three equal-sized control volumes in series with no backmixing (Fig.

TABLE 2. Comparison between the Pre- and Postcalculated, Number-Average Degree of Polymerization (N_n), and the Number of LCB per 1000C for the Single CSTR Case

		Precalculated		Postcalculated	
a	Termination reaction	N_n	#LCB/1000C	N_n	#LCB/1000C
0	Disproportionation	451	1.008	452	1.006
	Combination	451	1.007	453	1.003
0.02	Disproportionation	451	1.010	453	1.011
	Combination	451	1.010	453	0.997
1.0	Disproportionation	451	1.009	451	1.004
	Combination	452	1.009	451	0.989

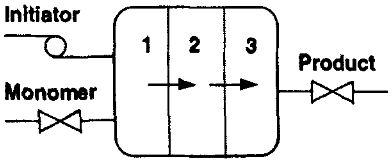

FIG. 5. Schematic sketch of the 3 volumes simulation model.

5). The LCBD calculation has to take into account the history of the polymer entering a control volume. The size of the reactor volume and the throughput is unchanged, i.e., the mean residence time of each control volume will be 20 seconds. The monomer and the initiator are fed into the first volume and the product outlet is at the last one. The temperature of the last volume is controlled by the initiator feed rate to 230°C. The kinetic parameters are the same as in Case 1. Termination by disproportionation is the only termination reaction, and the chain transfer to polymer is assumed to be independent of the chain length, i.e., $a = 0$. For a single CSTR this choice of parameters results in a flat LCBD function, see Figs. 3. Therefore, these kinetic parameters are well suited to demonstrate the effect of including several control volumes in the model.

Figure 6 presents the calculated MWD of the polymer out of the reactor. Figure 7 shows the number of LCB per 1000C of the polymer in each of the three control volumes. In the first one the LCBD is flat (except for smaller molecules) as

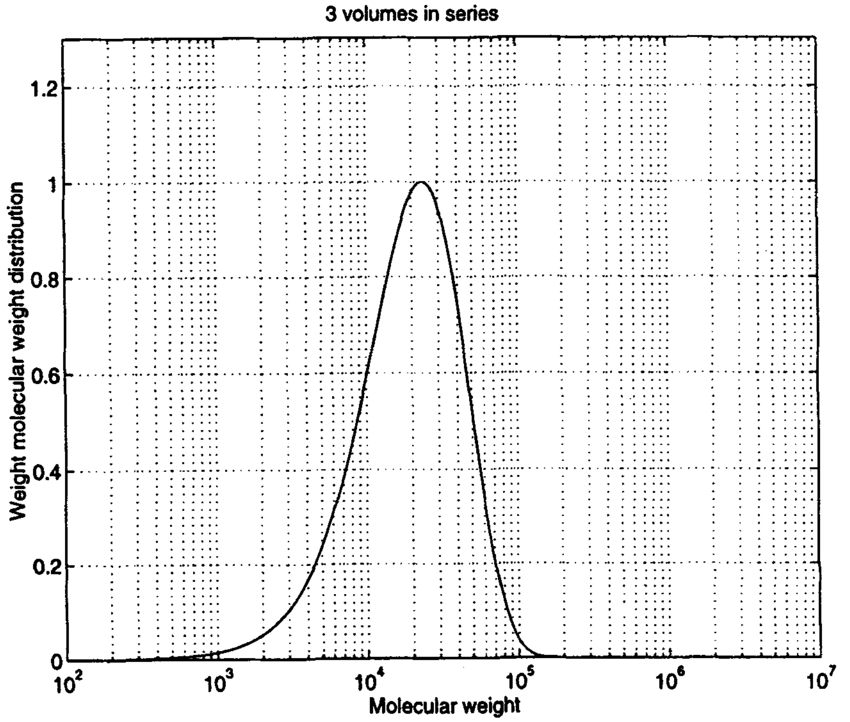

FIG. 6. The MWD. 3 volumes reactor model.

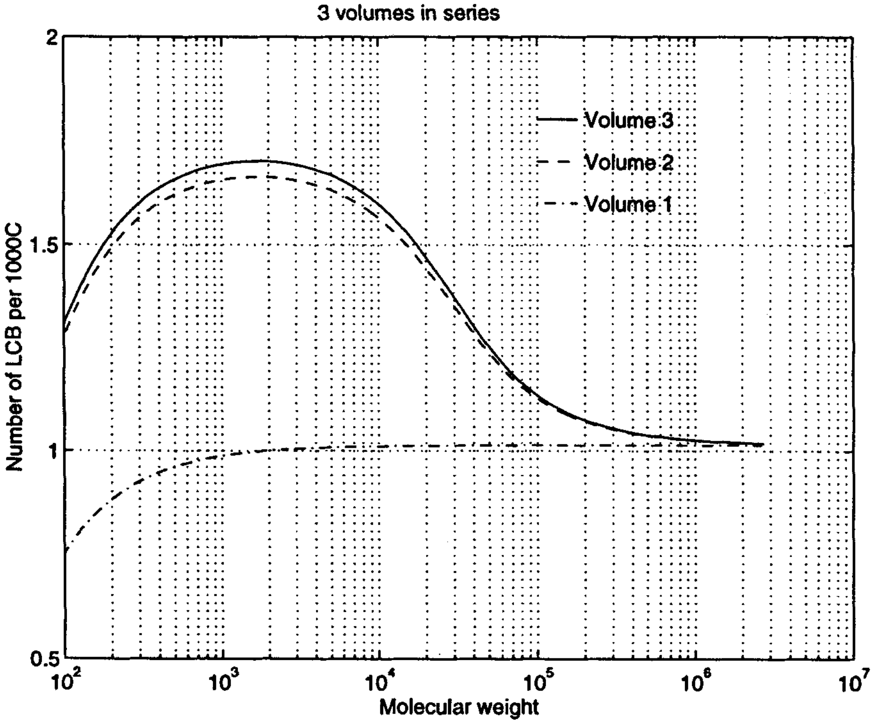

FIG. 7. The #LCB/1000C. 3 volumes reactor model.

expected from the results of Case 1. The amount of LCB increases as the polymer is transported through the reactor. However, the transportation of polymer from one volume to another seems to give less increase in LCB at higher molecular weights than at lower molecular weights. The overall number of LCB per 1000C of the product is 1.47. In other words, inhomogeneous reactor conditions influence both the overall amount of LCB and the shape of the LCBD.

Case 3: A 31 Volumes Reactor Model

In Case 3 the LCBD is calculated for a more realistic reactor configuration. This model represents an industrial autoclave similar to the one at Borealis Rønningen. Thirty-one control volumes are selected to describe the mixing within the reactor. Smaller control volumes are used near the initiator inlets to achieve a good representation of the concentration gradients of initiator and radicals. This influences both the initiator consumption and the product quality. In addition, the model allows for inhomogeneities in the radial direction. A circulating flow is induced by the impeller with a downward flow near the reactor wall and an upward flow in the center. This is quite similar to the model described by Donati et al. [32]. A sketch of one part of the reactor model is given in Fig. 8. The kinetic parameters are partly taken from the literature and partly estimated from measurements at the Borealis plant.

The following parameters for the chain transfer to polymer reaction are chosen

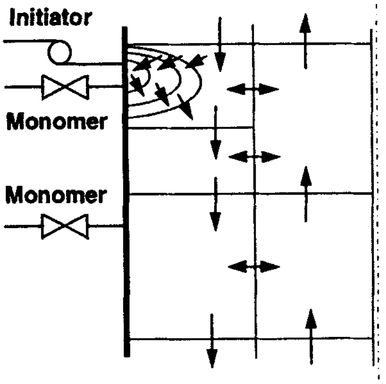

FIG. 8. Schematic sketch of a part of the 31 volumes simulation model.

$k_{tp,0} = 8 \times 10^5$ (m^3·mol^{-1}·s^{-1}); $\Delta E_{tp} = 38{,}000$ (kJ/kmol); $\Delta V_{tp} = 0$; $a = 0.02$

All the other kinetic parameters are kept unchanged in these simulations. The LCBDs of the single phase resins L500, LE4510, LE7520, LE6100, and LE6200 are estimated, and the number of LCB per 1000C is plotted in Fig. 9a. The resin LE6200 has a large amount of LCB compared to the others, which is in agreement with measurements.

No direct way to measure the number of LCB is known to the authors. The intrinsic viscosity is used to indirectly measure the amount of LCB as a function of the molecular weight. The relation between the number of LCB per 1000C and the g' property is given by

$$g' = G^B \tag{70}$$

and the Zimm-Stockmayer equation

$$G = f(n_w) = \frac{6}{n_w}\left[\frac{1}{2}\frac{(2+n_w)^{0.5}}{n_w^{0.5}}\ln\left(\frac{(2+n_w)^{0.5}+n_w^{0.5}}{(2+n_w)^{0.5}-n_w^{0.5}}-1\right)\right] \tag{71}$$

where n_w is the number of branching points per molecule (Rudin et al. [10]). The g' is the ratio of the intrinsic viscosity of branched and linear molecules of the same molecular weight, and G is the corresponding ratio of the mean square radii of gyration. The value of the exponent B is reported to vary between 0.5 and 1.5, (Yamamoto [9]). The LCBDs presented as g' plots are shown in Fig. 9b. The B factor is set equal to 1.0. The LE6200 curve is the first one to decrease, then LE6100 and LE7520 follow, and finally L500 and LE4510. The changes of g' and the number of LCB per 1000C curves are in accordance with the measurements, see Fig. 10a.

Alternatively, the number of long-chain branches may be calculated from the measured g' by use of Eqs. (70) and (71). This way of plotting the distribution permits one to use intuition when evaluating the curves. It is the g' which is measured directly however, and the accuracy of the number of LCB calculated from g' will depend on the goodness of the correlation model used to transform the viscosity measurement g' to the number of LCB. The number of LCB per 1000C calculated

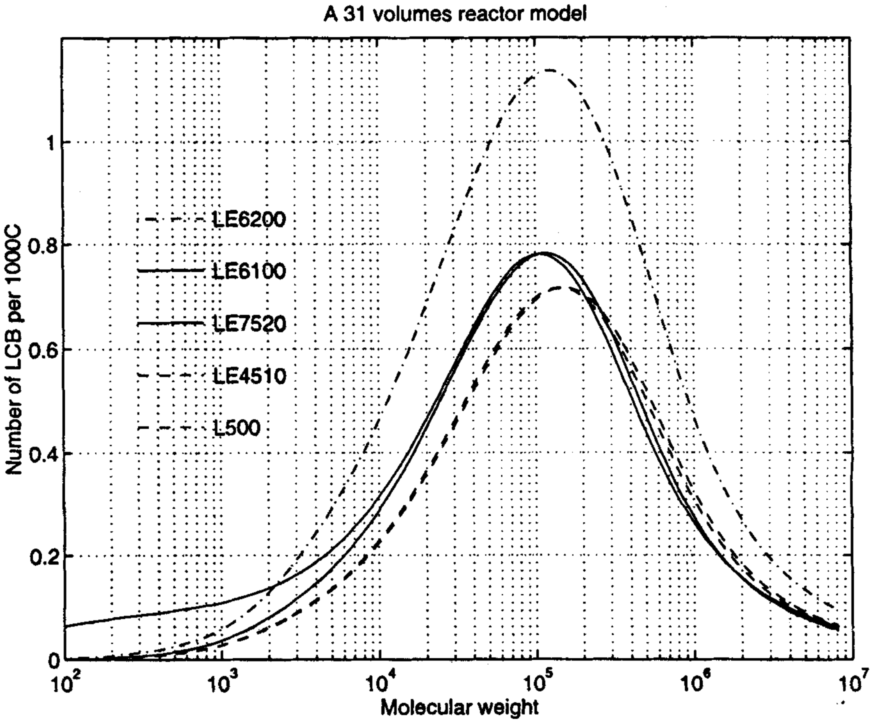

FIG. 9a. The #LCB/1000C of the resins L500, LE4510, LE7520, LE6100, and LE6200.

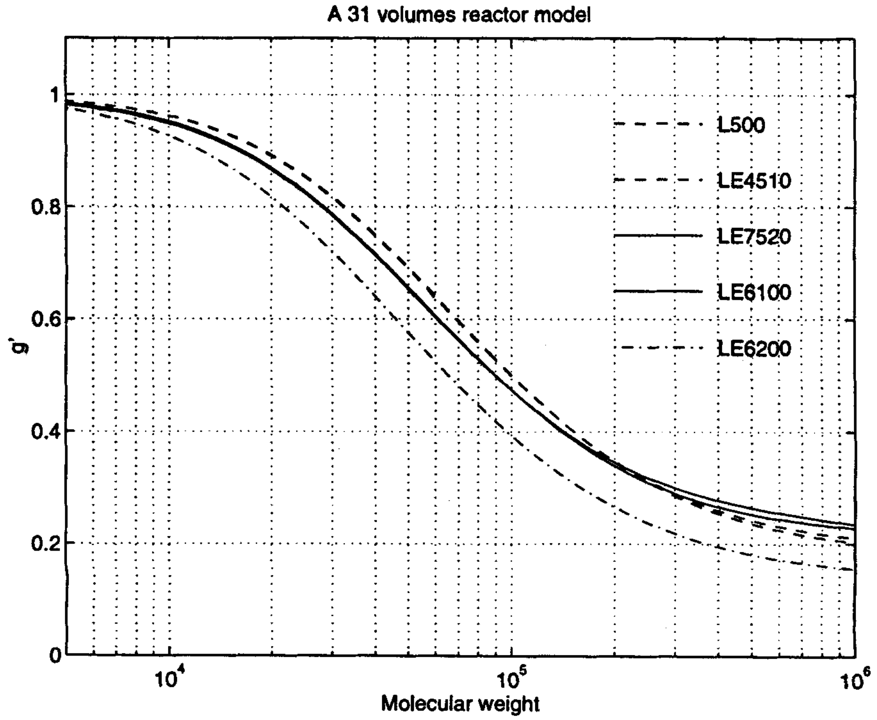

FIG. 9b. The g' of the resins L500, LE4510, LE7520, LE6100, and LE6200.

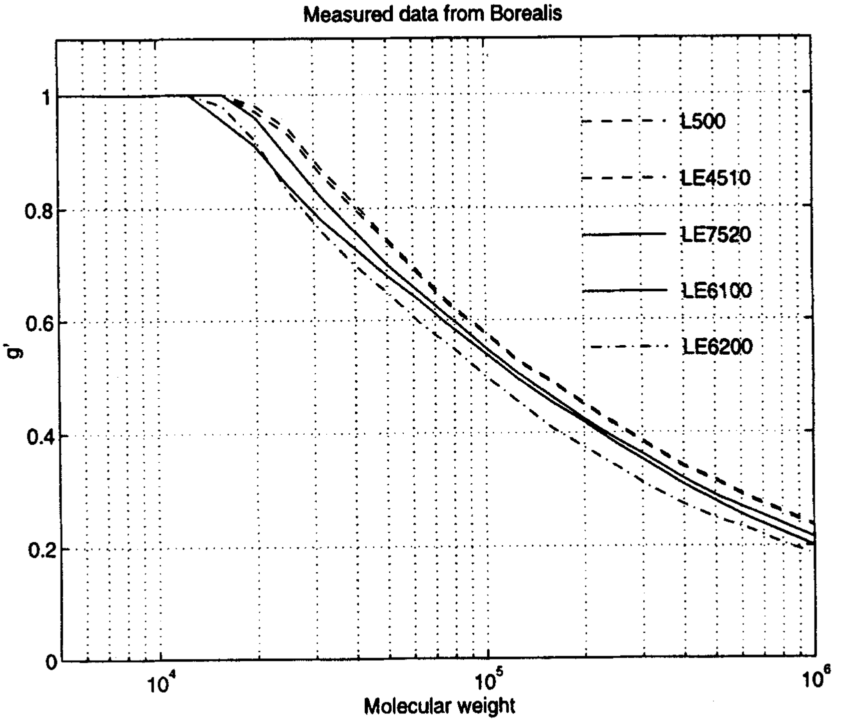

FIG. 10a. Measurements of g' for the resins L500, LE4510 LE7520, LE6100, and LE6200.

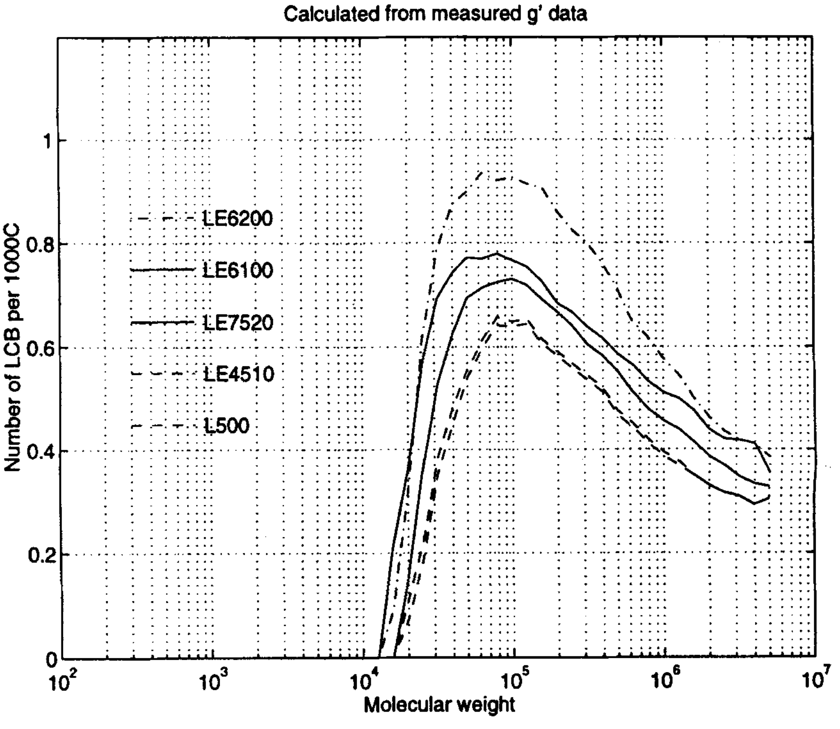

FIG. 10b. The #LCB/1000C calculated from measured g' for the resins L500, LE4510, LE7520, LE6100, and LE6200. (The g' measurements are insensitive to long-chain branches for molecular weights below 10^4.)

TABLE 3. Comparison between the Pre- and Postcalculated, Number-Average Degree of Polymerization (N_n), and the Number of LCB per 1000C

		Precalculated		Postcalculated	
a	Resin	N_n	#LCB/1000C	N_n	#LCB/1000C
0	L500	543	1.08	563	0.98
	LE4510	531	1.08	549	1.06
	LE7520	498	1.42	517	1.30
	LE6100	456	1.42	475	1.28
	LE6200	449	2.13	468	1.98
0.02	L500	543	0.50	572	0.45
	LE4510	531	0.51	560	0.45
	LE7520	498	0.63	541	0.51
	LE6100	456	0.57	484	0.49
	LE6200	449	0.85	490	0.74

from the measured g' are presented in Fig. 10b. Although the measurements have no sensitivity for molecular weight below 10^4, the shapes and the relative positions of the different product qualities are in accordance to the estimated ones in Fig. 9a for molecular weights above 10^4.

To examine the numerical accuracy of the LCBD calculation, the precalculated and postcalculated number of LCB per 1000C is compared, see Table 3. The agreement between the pre- and postcalculated values is relatively good. It seems that the postcalculated value systematically lies about 0.1 lower than the precalculated one.

CONCLUSIONS

A simulation model to predict the molecular weight distribution and long-chain branching distribution in the free-radical polymerization of LDPE is proposed. The predictions are based on a deterministic kinetic model, and recursion formulas are derived from the species balances for radicals and polymers. The reaction mechanisms initiation, propagation, termination by combination and disproportionation, and chain transfer to monomer, solvent, and polymer are included. The model also takes into account inhomogeneous reactor conditions. Therefore, it is well suited for calculation of MWDs and LCBDs for complex, industrial reactors. Simulations show that the shape of the LCBDs will depend on the choice of kinetics and the description of the flow pattern within the reactor. Promising results of prediction of the LCBDs for grades produced at the Borealis' autoclaves have been achieved.

NOTATION

a	kinetic constant for chain transfer to polymer (—)
b	number of long-chain branching points (—)
$c_{\mathrm{LCB},m}$	concentration of long-chain branching points belonging to polymer molecules of length m (mol/m^3)

$c^{\mathrm{R}}_{\mathrm{LCB},m}$	concentration of long-chain branching points belonging to radical molecules of length m (mol/m^3)
$\mathrm{C}_{\mathrm{LCB},m}$	dimensionless concentration of long-chain branching points belonging to polymer molecules of length m (–)
$\mathrm{C}^{\mathrm{R}}_{\mathrm{LCB},m}$	dimensionless concentration of long-chain branching points belonging to radical molecules of length m (–)
I	initiator concentration (mol/m^3)
k_{I}	reaction rate constant of initiation (1/s)
k_{L}	reaction rate constant of initiator degradation (1/s)
k_{p}	reaction rate constant of propagation [m^3/(mol s)]
k_{tc}	reaction rate constant of termination by combination [m^3/(mol s)]
k_{td}	reaction rate constant of termination by disproportion [m^3/(mol s)]
k_{tm}	reaction rate constant of chain transfer to monomer [m^3/(mol s)]
k_{tp}	reaction rate constant of chain transfer to polymer [m^3/(mol s)]
k_{ts}	reaction rate constant chain transfer to modifier [m^3/(mol s)]
m	number of monomer groups (–)
n	order of reaction (Table 1)
M	monomer concentration (mol/m^3)
P	total polymer concentration (mol/m^3)
P_m	concentration of polymer molecules of length m (mol/m^3)
$P_{m,b}$	concentration of polymer molecules of length m and with b long-chain branches (mol/m^3)
P_m	dimensionless concentration of polymer molecules of length m (–)
R	total radical concentration (mol/m^3)
R_m	concentration of radical molecules of length m (mol/m^3)
$R_{m,b}$	concentration of radical molecules of length m and with b long-chain branches (mol/m^3)
$\mathcal{R}_m$	dimensionless concentration of radical molecules of length m (–)
S	modifier concentration (mol/m^3)
q_j	volumetric flow j into volume (m^3/s)
q_0	volumetric flow out of volume (m^3/s)
V	volume (m^3)
x	chain length (used in the continuous model formulation) (–)
α	dimensionless kinetic parameter (–)
β	dimensionless kinetic parameter (–)
γ	dimensionless kinetic parameter (–)
δ	dimensionless kinetic parameter (–)
ε	dimensionless kinetic parameter (–)
ζ	dimensionless kinetic parameter (–)
μ_1	dimensionless first moment polymer (–)
λ	inverse of the characteristic chain length of a polymer chain (–)
$\Psi(\cdot)$	operator for convection and accumulation in a reactor model

ACKNOWLEDGMENTS

We thank Merete Skar and Espen Ommundsen at Borealis and Svein Olav Hauge at Statoil for their valuable comments and discussion. We also thank Adam Jackson at Statoil for his help with the intricacies of the English language.

REFERENCES

[1] F. W. Billmeyer Jr., "The Molecular Structure of Polyethylene. III. Determination of Long Chain Branching," *J. Am. Chem. Soc., 75,* 6118-6122 (1953).

[2] C. A. Sperati, W. A. Franta, and H. W. Starkweather Jr., "The Molecular Structure of Polyethylene. V. The Effect of Chain Branching and Molecular Weight on Physical Properties," *Ibid., 75,* 6127-6133 (1953).

[3] F. A. Bovey, F. C. Schilling, F. L. McCrackin, and H. L. Wagner, "Short-Chain and Long-Chain Branching in Low-Density Polyethylene." *Macromolecules, 9,* 76-80 (1976).

[4] M. E. A. Cudby and A. Bunn, "Determination of Chain Branching in Low Density Polyethylene by ^{13}C Nuclear Magnetic Resonance and Infra-red Spectroscopy," *Polymer, 17,* 345-347 (1976).

[5] K. Yamamoto and M. Sugimoto, "Rate Constant for Long-Chain Branch Formation in Free-Radical Polymerization of Ethylene," *J. Macromol. Sci.-Chem., A13*(8), 1067-1080 (1979).

[6] G. Gianotti, A. Cicuta, and D. Romanini, "Long Chain Branching in Low Density Polyethylene: 1. Molecular Structure," *Polymer, 21,* 1087-1091 (1980).

[7] D. Romanini, A. Savadori, and G. Gianotti, "Long Chain Branching in Low Density Polyethylene: 2. Rheological Behaviour of the Polymers," *Ibid., 21,* 1092-1011 (1980).

[8] G. Luft, R. Kämpf, and H. Seidl, "Synthesis Conditions and Structure of Low Density Polyethylene. I. Short and Long Chain Branching," *Makromol. Chem., 109*(1708), 203-217 (1982).

[9] K. Yamamoto, "An Analytical Method for Long-Chain Branching in Free-Radical Polymerization of Ethylene," *J. Macromol. Sci.—Chem., A17*(3), 415-431 (1982).

[10] A. Rudin, V. Grinshpun, and K. F. O'Driscoll, "Long Chain Branching in Polyethylene," *J. Liq. Chromatogr., 7*(9), 1809-1821 (1984).

[11] A. Santamaria, "Influence of Long Chain Branching in Melt Rheology and Processing of Low Density Polyethylene," *Mater. Chem. Phys., 12,* 1-28 (1985).

[12] D. C. Bugada and A. Rudin, "Sizes of Long Branching in Low Density Polyethylenes," *J. Appl. Polym. Sci., 33,* 87-93 (1987).

[13] S. Shiga, "Modern Characterization of Long-Chain Branching," *Polym.-Plast. Technol. Eng., 28*(1), 17-41 (1989).

[14] J. K. Beasley, "The Molecular Structure of Polyethylene. IV. Kinetic Calculation of the Effect of Branching on Molecular Weight Distribution," *J. Am. Chem. Soc., 75,* 6123-6127 (1953).

[15] C. H. Bamford and H. Tompa, "The Calculation of Molecular Weight Distribution from Kinetic Schemes," *Trans. Faraday Soc., 50,* 1097-1115 (1954).

[16] C. H. Chen, J. G. Vermeychuk, J. A. Howell, and P. Ehrlich, "Computer Model for Tubular High-Pressure Polyethylene Reactors," *AIChE J., 22*(3), 463-471 (1976).

[17] P. P. Shirodkar and G. O. Tsien, "A Mathematical Model for the Production of Low Density Polyethylene in a Tubular Reactor," *Chem. Eng. Sci., 41*(4), 1031-1038 (1986).

[18] R. C. M. Zabisky, W.-M. Chan, P. E. Gloor, and A. E. Hamielec, "A Kinetic Model for Olefin Polymerization in High-Pressure Tubular Reactors: A Review and Update," *Polymer, 33*(11), 2243-2262 (1992).

[19] W.-M. Chan, P. E. Gloor, and A. E. Hamielec, "A Kinetic Model for Olefin Polymerization in High-Pressure Autoclave Reactors," *AIChE J.*, *39*(1), 111-126 (1993).

[20] C. Kiparissides, G. Verros, and J. F. MacGregor, "Mathematical Modeling, Optimization, and Quality Control of High-Pressure Ethylene Polymerization Reactors," *J. Macromol. Sci.—Rev. Macromol. Chem. Phys., C33*(4), 437-527 (1993).

[21] R. V. Mullikin and G. A. Mortimer, "Another Look at Long-Chain Branching," *J. Macromol. Sci.—Chem. A4*(7), 1495-1505 (1970).

[22] R. V. Mullikin and G. A. Mortimer, "Long-Chain Branching under Conditions of Nonuniform Branching Probability," *Ibid., A6*(7), 1301-1310 (1972).

[23] F. Teymour and J. D. Campbell, "Analysis of the Dynamics of Gelation in Polymerization Reactors Using the 'Numerical Fractionation' Technique," *Macromolecules, 27*(9), 2460-2469 (1994).

[24] K. Yamaguchi, H. Kishi, and S. Taoka, "Molecular Weight Distribution of Polyethylene Polymerized by Free Radical Polymerization Including Chain Transfer Reaction to Polymer," *Kobunshi Kagaku, Engl. Ed., 1*(11), 1374-1391 (1972).

[25] P. Feucht, B. Tilger, and G. Luft, "Prediction of Molar Mass Distribution, Number and Weight Average Degree of Polymerization and Branching of Low Density Polyethylene," *Chem. Eng. Sci., 40*(10), 1935-1942 (1985).

[26] P. Singstad, "Modelling and Multivariable Control of High Pressure Autoclave Reactors for Polymerization of Ethene," Ph.D. Thesis, The University of Trondheim, The Norwegion Institue of Technology, 1992.

[27] H. Tobita, "Molecular Weight Distribution in Free Radical Polymerization with Long-Chain Branching," *J. Polym. Sci., 31,* 1363-1371 (1993).

[28] H. Tobita and K. Hatanaka, "Long-Chain Branching in Free-Radical Polymerization Due to Chain Transfer to Polymer," *J. Polym. Sci., Part B: Polym. Phys., 33*(5), 841-853 (1995).

[29] G. Strang, *Linear Algebra and Its Applications,* Academic Press, 1980.

[30] S. Agrawal and C. D. Han, "Analysis of the High Pressure Polyethylene Tubular Reactor with Axial Mixing," *AIChE J., 21*(3), 1097-1115 (1975).

[31] S. K. Gupta, A. Kumar, and M. V. G. Krishnamurthy, "Simulation of Tubular Low-Density Polyethylene," *Polym. Eng. Sci., 25*(1), 37-47 (1985).

[32] G. Donati, M. Gramondo, E. Lagianni, and L. Marini, "Low Density Polyethylene in Vessel Reactors. A Mathematical Model and Its Application to the Optimization of Industrial Reactors," *Ing. Chim. Ital., 17*(11-12), 88-96 (1981).

Received June 10, 1996
Revision received October 5, 1996