Development of a unified mathematical framework for modelling molecular and structural changes in free-radical homopolymerization reactions

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In the present study, a unified mathematical framework is developed for modelling molecular and structural changes in free-radical homopolymerization reactions. Three modelling methods – namely, the instantaneous property method (IPM), the method of moments (MM) and a new hybrid method, the so-called property moments method (PMM) – are derived using a unified approach. A critical analysis is carried out to determine the conditions under which each of the above methods can be applied to a given polymerization system. This is achieved through the application of the three modelling methods to several experimentally investigated free-radical polymerization systems leading to linear and branched polymers. Polymerizations are examined in bulk and in solution, both in the presence and in the absence of strong diffusional limitations in the termination and propagation reactions.

(Keywords: modelling; homopolymerization; free-radical polymerization; kinetics; method of moments; instantaneous property method; property moments method)

INTRODUCTION

A major objective of polymerization reaction engineering is to understand how the reactor operating conditions affect the 'polymer quality' of the final product. The term 'polymer quality' refers to all molecular and structural characteristics of a polymer, such as molecular-weight distribution (*MWD*), degree-of-branching distribution (*DBD*), etc., which can influence the end-use properties of the polymer[1]. The ability of a mathematical model to predict accurately the molecular properties of a polymer produced in a polymerization reactor in terms of operating conditions is of great economic importance to the polymer industry.

The mathematical modelling of polymerization kinetics has been the subject of numerous publications over the past 45 years[2–10]. The mathematical approaches that have been proposed for modelling free-radical polymerization reactions can be broadly classified into three categories: black-box models, statistical models and detailed kinetic models. The black-box models, relying on empirical regression correlations, can generally be established using planned experiments. The statistical models view chain growth as a stochastic process having possible states resulting from the kinetic mechanism and state transition probabilities dependent on the kinetic parameters[11,12]. In this way, the *MWD* of the final polymer can easily be obtained. By far the most powerful modelling approach is that based on the detailed kinetic mechanism of polymerization. This modelling approach presupposes a clear understanding of the polymerization kinetics and knowledge of the individual rate constants of the various elementary reactions. Subsequently, an infinite set of algebraic or differential–difference equations, depending on the reactor type, are derived to describe the conservation of the individual macromolecular species in the reactor. Several solution procedures have been developed for solving the resulting species conservation equations. These have been reviewed by Tirrell *et al.*[8], Biesenberger and Sebastian[5] and Ray[4].

In spite of the large number of publications on polymerization kinetics, a comparative study on the main kinetic modelling methods has not yet been published. Furthermore, very often, a kinetic model is applied to a polymerization system despite its obvious limitations. In the present investigation, three kinetic modelling methods – namely, the method of moments (MM), the instantaneous property method (IPM) and a new kinetic modelling approach called the property moments method (PMM) – are described in relation to the production of linear and branched polymers. Polymerizations are studied in bulk and in solution, both in the presence and in the absence of strong diffusional limitations. A systematic analysis is carried out to determine the conditions under which each of the above kinetic modelling methods can be applied to a given polymerization system. This is achieved through the application of the three modelling methods to several free-radical polymerization systems for which experimental data on conversion and molecular-weight averages are available.

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Both IPM and PMM utilize two commonly used assumptions, namely, the long-chain hypothesis (LCH) and the quasi-steady-state approximation (QSSA), to obtain analytical expressions for the rate of polymerization and the instantaneous molecular-weight distribution. The LCH implies that monomer is solely consumed through propagation reactions. thus neglecting monomer consumption by the initiation reaction. The QSSA assumes that the net rate of formation of growing radical chains is approximately zero. It should be pointed out that, contrary to the IPM and PMM, the MM does not rely on the application of the two simplifying approximations, and therefore it can be used to verify the validity of LCH and QSSA.

Note that the IPM can only be applied to polymerizations leading to the formation of linear polymers. For branched polymers involving 'chain transfer to polymer' reactions, one has to resort to the method of moments. The moment equations are usually derived from the original molar species balance equations through well established mathematical techniques and the definition of the moments of the differential number chain-length distributions (*NCLD*) of the 'live' and 'dead' polymer macromolecules. The numerical solution of the resulting moment equations is straightforward and readily leads to the calculation of the instantaneous and cumulative polymer molecular properties (i.e. molecular-weight averages, degree-of-branching averages, etc.). It should be pointed out that the method of moments can be applied to both linear and branched polymers. Finally, it can be shown that, for linear polymers, the IPM modelling equations can be derived directly from the corresponding moment equations by invoking the LCH and the QSSA.

Contrary to the MM, the PMM does not consider balances on the individual species present in the reaction mixture. Instead, mass balance equations are directly derived for some selected quantities of interest (i.e. the leading moments of the *NCLD*, the number of long-chain branching points, the number of terminal double bonds, etc.) that characterize the polymer quality.

Subsequently, the general rate functions describing the net production of the various macromolecular species present in a free-radical polymerization system are derived.

POLYMERIZATION RATE FUNCTIONS

The following mechanism is assumed to represent the general kinetics of chemically initiated free-radical polymerizations[6,7,13–15]:

Initiation

$$\mathrm{I} \xrightarrow{k_d} 2\mathrm{PR}^{\bullet} \tag{1}$$

$$\mathrm{PR}^{\bullet} + \mathrm{M} \xrightarrow{k_I} \mathrm{P}_{1,0} \tag{2}$$

Propagation

$$\mathrm{P}_{n,b} + \mathrm{M} \xrightarrow{k_p} \mathrm{P}_{n+1.b} \tag{3}$$

$$\mathrm{P}^{=}_{n,b} + \mathrm{M} \xrightarrow{k_p} \mathrm{P}^{=}_{n+1,b} \tag{4}$$

Chain transfer to monomer

$$\mathrm{P}_{n,b} + \mathrm{M} \xrightarrow{k_{fm}} \mathrm{D}_{n,b} + \mathrm{M}^{\bullet} \tag{5}$$

$$\mathrm{P}^{=}_{n,b} + \mathrm{M} \xrightarrow{k_{fm}} \mathrm{D}^{=}_{n,b} + \mathrm{M}^{\bullet} \tag{6}$$

$$\mathrm{M}^{\bullet} + \mathrm{M} \xrightarrow{k_{pm}} \mathrm{P}^{=}_{1,0} \qquad \text{(reinitiation)} \tag{7}$$

Chain transfer to modifier

$$\mathrm{P}_{n.b} + \mathrm{S} \xrightarrow{k_{fs}} \mathrm{D}_{n,b} + \mathrm{S}^{\bullet} \tag{8}$$

$$\mathrm{P}^{=}_{n,b} + \mathrm{S} \xrightarrow{k_{fs}} \mathrm{D}^{=}_{n,b} + \mathrm{S}^{\bullet} \tag{9}$$

$$\mathrm{S}^{\bullet} + \mathrm{M} \xrightarrow{k_{ps}} \mathrm{P}_{1,0} \qquad \text{(reinitiation)} \tag{10}$$

Chain transfer to polymer

$$P_{n,b} + \mathrm{D}_{r,q} \xrightarrow{k_{fp}} \mathrm{P}_{r,q+1} + \mathrm{D}_{n,b} \tag{11}$$

$$\mathrm{P}^{=}_{n,b} + \mathrm{D}_{r,q} \xrightarrow{k_{fp}} \mathrm{P}_{r,q+1} + \mathrm{D}^{=}_{n,b} \tag{12}$$

$$\mathrm{P}_{n,b} + \mathrm{D}^{=}_{r,q} \xrightarrow{k_{fp}} \mathrm{P}^{=}_{r,q+1} + \mathrm{D}_{n,b} \tag{13}$$

$$\mathrm{P}^{=}_{n,b} + \mathrm{D}^{=}_{r,q} \xrightarrow{k_{fp}} \mathrm{P}^{=}_{r,q+1} + \mathrm{D}^{=}_{n,b} \tag{14}$$

Reaction of a terminal double bond

$$\mathrm{P}_{n,b} + \mathrm{D}^{=}_{r,q} \xrightarrow{k_p^*} \mathrm{P}_{n+r,b+q+1} \tag{15}$$

$$\mathrm{P}^{=}_{n,b} + \mathrm{D}^{=}_{r,q} \xrightarrow{k_p^*} \mathrm{P}^{=}_{n+r,b+q+1} \tag{16}$$

Termination by combination

$$\mathrm{P}_{n,b} + \mathrm{P}_{r,q} \xrightarrow{k_{tc}} \mathrm{D}_{n+r,b+q} \tag{17}$$

$$\mathrm{P}^{=}_{n,b} + \mathrm{P}_{r,q} \xrightarrow{k_{tc}} \mathrm{D}^{=}_{n+r,b+q} \tag{18}$$

$$\mathrm{P}_{n,b} + \mathrm{P}^{=}_{r,q} \xrightarrow{k_{tc}} \mathrm{D}^{=}_{n+r,b+q} \tag{19}$$

$$\mathrm{P}^{=}_{n,b} + \mathrm{P}^{=}_{r,q} \xrightarrow{k_{tc}} \mathrm{D}^{=}_{n+r,b+q} \tag{20}$$

Termination by disproportionation

$$\mathrm{P}_{n,b} + \mathrm{P}_{r,q} \xrightarrow{k_{td}} \tfrac{1}{2}\mathrm{D}^{=}_{n,b} + \tfrac{1}{2}\mathrm{D}_{n,b} + \tfrac{1}{2}\mathrm{D}^{=}_{r,q} + \tfrac{1}{2}\mathrm{D}_{r,q} \tag{21}$$

$$\mathrm{P}^{=}_{n,b} + \mathrm{P}_{r,q} \xrightarrow{k_{td}} \mathrm{D}^{=}_{n,b} + \tfrac{1}{2}\mathrm{D}^{=}_{r,q} + \tfrac{1}{2}\mathrm{D}_{r,q} \tag{22}$$

$$\mathrm{P}_{n,b} + \mathrm{P}^{=}_{r,q} \xrightarrow{k_{td}} \tfrac{1}{2}\mathrm{D}^{=}_{n,b} + \tfrac{1}{2}\mathrm{D}_{n,b} + \mathrm{D}^{=}_{r,q} \tag{23}$$

$$\mathrm{P}^{=}_{n,b} + \mathrm{P}^{=}_{r,q} \xrightarrow{k_{td}} \mathrm{D}^{=}_{n,b} + \mathrm{D}^{=}_{r,q} \tag{24}$$

Here I, PR$^{\bullet}$, M and S represent the initiator, primary radicals, monomer and modifier (i.e. solvent) molecules, respectively. To identify a polymer chain we introduce a general notation $G_{n,b}$, which denotes the concentration of 'live' ($G_{n,b} \equiv P_{n,b}$) or 'dead' ($G_{n,b} \equiv D_{n,b}$) polymer molecules having n monomer units and b long-chain branches (LCB). The superscript '=' indicates the presence of a terminal double bond incorporated into the 'live' or 'dead' polymer chain. It is assumed that each polymer chain has at most one terminal double bond[6,7]. The mechanism described by equations (1)–(24) is sufficiently general to cover most free-radical chain addition polymerizations.

Let $r_{\mathrm{P}_{n,b}}$, $r_{\mathrm{P}^{=}_{n,b}}$ and $r_{\mathrm{D}_{n,b}}$, $r_{\mathrm{D}^{=}_{n,b}}$ denote the net rates of production of 'live' radicals and 'dead' polymer molecules, respectively. The expressions for these rate functions can be obtained by combining the reaction rates of the various elementary reactions describing the generation and consumption of 'live' and 'dead' polymer molecules. Based on the kinetic mechanism of free-radical polymerization, the following general rate functions can be derived[6,7] (using *italics* to represent concentrations of corresponding species):

$$\begin{aligned} r_{\mathrm{P}_{n,b}} = {} & (k_{\mathrm{I}} PR^{\bullet} M + k_{\mathrm{fs}} S P^{\mathrm{T}}_{00})\,\delta(n-1,b) \\ & + k_{\mathrm{p}} M (P_{n-1,b} - P_{n,b}) - A P_{n,b} + k_{\mathrm{fp}} n D_{n,b-1} P^{\mathrm{T}}_{00} \\ & + k^{*}_{\mathrm{p}} \sum_{r=1}^{n-1} \sum_{q=0}^{b-1} P_{r,q} D^{=}_{n-r,b-q-1} - k^{*}_{\mathrm{p}} P_{n,b} \sum_{r=0}^{\infty} \sum_{q=0}^{\infty} D^{=}_{r,q} \end{aligned} \tag{25}$$

$$\begin{aligned} r_{\mathrm{P}^{=}_{n,b}} = {} & k_{\mathrm{fm}} M P^{\mathrm{T}}_{00}\,\delta(n-1,b) + k_{\mathrm{p}} M (P^{=}_{n-1,b} - P^{=}_{n,b}) \\ & - A P^{=}_{n,b} + k_{\mathrm{fp}} n D^{=}_{n,b-1} P^{\mathrm{T}}_{00} \\ & + k^{*}_{\mathrm{p}} \sum_{r=1}^{n-1} \sum_{q=0}^{b-1} P^{=}_{r,q} D^{=}_{n-r,b-q-1} - k^{*}_{\mathrm{p}} P^{=}_{n,b} \sum_{r=0}^{\infty} \sum_{q=0}^{\infty} D^{=}_{r,q} \end{aligned} \tag{26}$$

$$\begin{aligned} r_{\mathrm{D}_{n,b}} = {} & (A - k_{\mathrm{t}} P^{\mathrm{T}}_{00}) P_{n,b} - k_{\mathrm{fp}} n D_{n,b} P^{\mathrm{T}}_{00} \\ & + \tfrac{1}{2} k_{\mathrm{tc}} \sum_{r=1}^{n-1} \sum_{q=1}^{b-1} P_{r,q} P_{n-r,b-q} + \tfrac{1}{2} k_{\mathrm{td}} P_{n,b} P^{\mathrm{T}}_{00} \end{aligned} \tag{27}$$

$$\begin{aligned} r_{\mathrm{D}^{=}_{n,b}} = {} & (A - k_{\mathrm{t}} P^{\mathrm{T}}_{00}) P^{=}_{n,b} - k_{\mathrm{fp}} n D^{=}_{n,b} P^{\mathrm{T}}_{00} - k^{*}_{\mathrm{p}} D^{=}_{n,b} P^{\mathrm{T}}_{00} \\ & + \tfrac{1}{2} k_{\mathrm{tc}} \sum_{r=1}^{n-1} \sum_{q=1}^{b-1} P^{=}_{r,q} (P^{=}_{n-r,b-q} + 2P_{n-r,b-q}) \\ & + \tfrac{1}{2} k_{\mathrm{td}} P^{\mathrm{T}}_{00} (P_{n,b} + 2P^{=}_{n,b}) \end{aligned} \tag{28}$$

where:

$$A = k_{\mathrm{fm}} M + k_{\mathrm{fs}} S + k_{\mathrm{t}} P^{\mathrm{T}}_{00} + k_{\mathrm{fp}} \sum_{r=0}^{\infty} \sum_{q=0}^{\infty} r D^{\mathrm{T}}_{r,q} \tag{29}$$

P^{T}_{00} is the concentration of total 'live' macroradicals given by the expression:

$$P^{\mathrm{T}}_{00} = \sum_{n=0}^{\infty} \sum_{b=0}^{\infty} P^{\mathrm{T}}_{n,b} \tag{30}$$

and $\delta(n,b)$ is the Kronecker delta:

$$\delta(n,b) \equiv \delta(n)\delta(b) \qquad \delta(i) \equiv \begin{cases} 1 & \text{for } i = 0 \\ 0 & \text{for } i \neq 0 \end{cases} \tag{31}$$

To describe the conservation of individual polymer chains in a polymer reactor, an infinite set of algebraic or differential–difference equations depending upon the reactor type and mode of operation (dynamic or steady state) are derived. For a batch polymerization reactor, one can write the following general population balance equation for both 'live' and 'dead' polymer molecules:

$$\frac{1}{V}\frac{\mathrm{d}(VG_{n,b})}{\mathrm{d}t} = r_{\mathrm{G}_{n,b}} \qquad \begin{matrix} n = 1,\ldots,N \\ b = 1,\ldots,B \end{matrix} \tag{32}$$

Application of the general design equation (32) to the various individual species present in the reacting mixture results in a prohibitively large set of differential equations, which must be solved numerically to obtain desired information on *MWD* and *DBD*[16,17]. In an attempt to reduce the high dimensionality of the numerical problem, several mathematical techniques have been developed to recast the 'infinite' set of equations into a low-order system, which can easily be solved. These techniques have been recently reviewed by Tirrell *et al.*[8] and include the use of generating functions[4], z-transforms[18] and the continuous variable approximation[1,19–21]. In addition to these computational techniques, three well established methods, namely, the IPM, MM and PMM, have been used in the kinetic modelling of free-radical polymerization reactions. In what follows, the three kinetic modelling methods are derived using a unified mathematical framework and the necessary conditions for the application of each method to a free-radical polymerization are established.

INSTANTANEOUS PROPERTY METHOD

A detailed description of the instantaneous property method (IPM) can be found in several polymer textbooks[2,5,11]. However, it should be pointed out that the IPM is strictly valid for linear polymers. Hence, all those reactions leading to branch formation, namely chain transfer to polymer and terminal double-bond polymerization, cannot be accounted for by the IPM. The IPM employs both the LCH and QSSA to obtain analytical expressions for the rate of polymerization and molecular-weight distribution.

Following the general developments of the IPM, the cumulative 'live' radical distribution can be expressed as[2,11,22]:

$$\bar{w}(i)^{\mathrm{r}} = (\tau + \beta)\exp[-(\tau + \beta)i] \tag{33}$$

where $\bar{w}(i)^{\mathrm{r}}$ denotes the cumulative chain-length distribution of 'live' growing polymer chains, and τ and β are two dimensionless parameters defined as:

$$\tau = k_{\mathrm{td}} R_{\mathrm{p}}/(k_{\mathrm{p}}M)^2 + k_{\mathrm{fm}}/k_{\mathrm{p}} + k_{\mathrm{fs}} S/k_{\mathrm{p}} M \tag{34}$$

$$\beta = k_{\mathrm{tc}} R_{\mathrm{p}}/(k_{\mathrm{p}}M)^2 \tag{35}$$

where:

$$R_{\mathrm{p}} = k_{\mathrm{p}} M P_0 \qquad P_0 = (2fk_{\mathrm{d}}I/k_{\mathrm{t}})^{1/2} \tag{36}$$

All symbols are explained in the nomenclature section at the end of the paper.

From equation (33), the cumulative number- and weight-average chain lengths of 'live' polymer chains can be calculated:

$$\bar{X}^{\mathrm{r}}_{\mathrm{N}} = 1 + \frac{1}{\tau + \beta} \simeq \frac{1}{\tau + \beta} \qquad \bar{X}^{\mathrm{r}}_{\mathrm{W}} = 1 + \frac{2}{\tau + \beta} \simeq \frac{2}{\tau + \beta} \tag{37}$$

The instantaneous number chain-length distribution (*INCLD*) of 'dead' polymer chains at conversion x, $w(i,x)$, will be given by[2,11,22]:

$$w(i,x) = (\tau + \beta)[\tau + \tfrac{1}{2}\beta(\tau + \beta)i]\,i\exp[-(\tau + \beta)i] \tag{38}$$

Accordingly, one can calculate the instantaneous number- and weight-average chain lengths of the *INCLD* of 'dead' polymer chains:

$$X_{\mathrm{n}} = 1 \Big/ \sum_i [w(i,x)/i] = 1/(\tau + \beta/2) \qquad (39)$$

$$X_{\mathrm{w}} = \sum_i [iw(i,x)] = 2(\tau + 3\beta/2)/(\tau + \beta)^2 \qquad (40)$$

The cumulative number chain-length distribution of the 'dead' polymer chains is obtained by integrating the instantaneous number chain-length distribution (*INCLD*) over the total variation of monomer conversion $(0, x)$:

$$\bar{w}(i,x) = \frac{1}{x}\int_0^x w(i,x)\,\mathrm{d}x \qquad (41)$$

Similarly, the corresponding cumulative number- and weight-average chain lengths will be given by[2,11,22]:

$$\bar{X}_{\mathrm{n}} = x \Big/ \int_0^x \frac{\mathrm{d}x}{X_{\mathrm{n}}} = x \Big/ \int_0^x (\tau + \beta/2)\,\mathrm{d}x \qquad (42)$$

$$\bar{X}_{\mathrm{w}} = \frac{1}{x}\int_0^x X_{\mathrm{w}}\,\mathrm{d}x = \frac{2}{x}\int_0^x (\tau + 3\beta/2)/(\tau + \beta)^2\,\mathrm{d}x \qquad (43)$$

The physical meaning of the two dimensional parameters, namely τ and β, is discussed next. The parameter τ includes all those reactions (i.e. chain transfer to monomer, chain transfer to modifier, and termination by disproportionation) which lead to the production of 'dead' macromolecules having exactly the same distribution as that of the deactivated growing macroradicals.

On the other hand, the parameter β accounts for termination of radicals by combination. According to this type of reaction, macromolecules containing x units can be produced by the reaction of a radical containing y units with a radical containing $(x - y)$ units. Note that the distribution of macromolecules obtained by this process will be narrower than the distribution of macromolecules produced by the reactions included in the parameter τ.

Notice that the sum $(\tau + \beta)$ is simply the inverse kinetic chain length of the 'live' polymer chains. Besides, the expression $(\tau + \beta/2)$ represents the inverse instantaneous number-average chain length of the 'dead' polymer chains. As can be seen, as $\beta \to 0$, the instantaneous number-average chain length (*NACL*) of the polymer, X_{n}, becomes equal to the kinetic chain length of the 'live' radicals. Furthermore, as $\tau \to 0$, the instantaneous *NACL* of the polymer will be twice the kinetic chain length of the 'live' radicals.

Because of the simplicity of the IPM, it has been applied by several authors to the kinetic modelling of many free-radical polymerizations[22–24]. Finally, it can be easily shown that the rate of monomer conversion will be given by:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_{\mathrm{p}}(1-x)P_0 = \left(\frac{2fk_{\mathrm{d}}k_{\mathrm{p}}^2}{k_{\mathrm{t}}}\right)^{1/2} I^{1/2}(1-x) \qquad (44)$$

THE METHOD OF MOMENTS

The method of moments (MM) is based on the statistical representation of the *MWD* (*NCLD*) or other distributions of interest (i.e. *DBD*) through the use of some averages of the distributions. These averages can be found in terms of the leading moments of the respective distribution[4,9,25,26].

In many polymer reactor studies, it is often sufficient to know how the leading moments of the total differential *NCLD* of various polymer populations present in the reaction mixture are influenced by the reactor operating conditions. Based on the general kinetic mechanism described before, one can identify four distributions related to the populations of P_n, $\mathrm{P}_n^{=}$, D_n and $\mathrm{D}_n^{=}$ species. Accordingly, the moments of these distributions are defined as:

$$\lambda_k = \sum_{n=1}^{\infty} n^k \mathrm{P}_n \qquad \lambda_k^{=} = \sum_{n=1}^{\infty} n^k \mathrm{P}_n^{=} \qquad (45)$$

$$\mu_k = \sum_{n=1}^{\infty} n^k D_n \qquad \mu_k^{=} = \sum_{n=1}^{\infty} n^k D_n^{=} \qquad (46)$$

where λ_k, μ_k, $\lambda_k^{=}$, $\mu_k^{=}$ denote the respective kth moments of the 'live' and 'dead' polymer *NCLD*s. The superscript '=' identifies the corresponding moments of 'live' and 'dead' polymer molecules with a terminal double bond.

The corresponding net production rates for the kth moments of *NCLD*s can be obtained by multiplying each term in equations (25)–(28) by n^k and summing the resulting equations over the total variation of n. The final expressions for the moment rate functions are:

$$r_{\lambda_k} = k_{\mathrm{I}}PR^{\bullet}M + k_{\mathrm{fs}}S\lambda_0^{\mathrm{T}} + k_{\mathrm{p}}M\left[\sum_{i=0}^{k}\binom{k}{i}\lambda_i - \lambda_k\right] - A''\lambda_k + k_{\mathrm{fp}}\lambda_0^{\mathrm{T}}\mu_{k+1} - k_{\mathrm{p}}^{*}\lambda_k\mu_0^{=} + k_{\mathrm{p}}^{*}\sum_{i=0}^{k}\binom{k}{i}\lambda_i\mu_{k-i}^{=} \qquad (47)$$

$$r_{\lambda_k^{=}} = k_{\mathrm{fm}}M\lambda_0^{\mathrm{T}} + k_{\mathrm{p}}M\left[\sum_{i=0}^{k}\binom{k}{i}\lambda_i^{=} - \lambda_k^{=}\right] - A''\lambda_k^{=} + k_{\mathrm{fp}}\lambda_0^{\mathrm{T}}\mu_{k+1}^{=} + k_{\mathrm{p}}^{*}\sum_{i=0}^{k}\binom{k}{i}\lambda_i^{=}\mu_{k-i}^{=} - k_{\mathrm{p}}^{*}\lambda_k^{=}\mu_0^{=} \qquad (48)$$

$$r_{\mu_k} = (A'' - k_{\mathrm{t}}\lambda_0^{\mathrm{T}})\lambda_k + \tfrac{1}{2}k_{\mathrm{tc}}\sum_{i=0}^{k}\binom{k}{i}\lambda_i\lambda_{k-i} + \tfrac{1}{2}k_{\mathrm{td}}\lambda_k\lambda_0^{\mathrm{T}} - k_{\mathrm{fp}}\mu_{k+1}\lambda_0^{\mathrm{T}} \qquad (49)$$

$$r_{\mu_k^{=}} = (A'' - k_{\mathrm{t}}\lambda_0^{\mathrm{T}})\lambda_k^{=} + \tfrac{1}{2}k_{\mathrm{tc}}\sum_{i=0}^{k}\binom{k}{i}\lambda_i^{=}(\lambda_{k-i}^{=} + 2\lambda_{k-i}) - k_{\mathrm{p}}^{*}\mu_k^{=}\lambda_0^{\mathrm{T}} + \tfrac{1}{2}k_{\mathrm{td}}\lambda_0^{\mathrm{T}}(2\lambda_k^{=} + \lambda_k) - k_{\mathrm{fp}}\mu_{k+1}^{=}\lambda_0^{\mathrm{T}} \qquad (50)$$

where:

$$A'' = k_{\mathrm{fm}}M + k_{\mathrm{fs}}S + k_{\mathrm{t}}\lambda_0^{\mathrm{T}} + k_{\mathrm{fp}}\mu_1^{\mathrm{T}} \qquad (51)$$

$$\lambda_k^{\mathrm{T}} = \lambda_k + \lambda_k^{=} \qquad \mu_k^{\mathrm{T}} = \mu_k + \mu_k^{=} \qquad k = 0, 1, 2 \ (52)$$

One can easily show that the instantaneous number- and weight-average chain lengths of the polymer *NCLD* will be given by[4]:

$$X_{\mathrm{N}} = (\mathrm{d}\mu_1 + \mathrm{d}\lambda_1)/(\mathrm{d}\mu_0 + \mathrm{d}\lambda_0) \simeq \mathrm{d}\mu_1/\mathrm{d}\mu_0 \qquad (53)$$

$$X_{\mathrm{W}} = (\mathrm{d}\mu_2 + \mathrm{d}\lambda_2)/(\mathrm{d}\mu_1 + \mathrm{d}\lambda_1) \simeq \mathrm{d}\mu_2/\mathrm{d}\mu_1 \qquad (54)$$

On the other hand, the cumulative number- and weight-average chain lengths will be given by the following ratios of the leading moments of the polymer *NCLD*:

$$\bar{X}_{\mathrm{N}} = (\mu_1 + \lambda_1)/(\mu_0 + \lambda_0) \simeq \mu_1/\mu_0 \qquad (55)$$

$$\bar{X}_{\mathrm{W}} = (\mu_2 + \lambda_2)/(\mu_1 + \lambda_1) \simeq \mu_2/\mu_1 \qquad (56)$$

Similarly, the polydispersity indices D and $\bar{D}$ will be given by the ratios of the weight- to the number-average chain length, $(X_{\mathrm{W}}/X_{\mathrm{N}})$ and $(\bar{X}_{\mathrm{W}}/\bar{X}_{\mathrm{N}})$, respectively.

For branched polymers, a bivariate distribution of $G_{n,b}$ defined in terms of the total chain length, n, and the number of branch points per polymer molecule, b, is introduced to characterize the molecular weight and branching frequency of polymer chains. Accordingly, the moments of the joint (*CLDB*) distributions of 'live' and 'dead' polymer chains are defined:

$$\lambda_{k,l} = \sum_{n=1}^{\infty} \sum_{b=0}^{\infty} n^k b^l P_{n,b} \qquad \bar{\bar{\lambda}}_{k,l} = \sum_{n=1}^{\infty} \sum_{b=0}^{\infty} n^k b^l \bar{\bar{P}}_{n,b} \qquad (57)$$

$$\mu_{k,l} = \sum_{n=1}^{\infty} \sum_{b=0}^{\infty} n^k b^l D_{n,b} \qquad \bar{\bar{\mu}}_{k,l} = \sum_{n=1}^{\infty} \sum_{b=0}^{\infty} n^k b^l \bar{\bar{D}}_{n,b} \qquad (58)$$

The associated net reaction rates of the moments of the bivariate (*CLDB*) distribution can be obtained from equations (25)–(28) by multiplying each term by $n^k b^l$ and summing the resulting expressions over the total variations of n and b. The final moment rate equations will be:

$$\begin{aligned} r_{\lambda_{k,l}} = {} & (k_{\mathrm{I}} PR^{\bullet} M + k_{\mathrm{fs}} S \lambda^{\mathrm{T}}_{0,0})\delta(l) \\ & + k_{\mathrm{p}} M \left[\sum_{i=0}^{k} \binom{k}{i} \lambda_{i,l} - \lambda_{k,l} \right] - A''' \lambda_{k,l} \\ & + k_{\mathrm{fp}} \lambda^{\mathrm{T}}_{0,0} \sum_{j=0}^{l} \binom{l}{j} \mu_{k+1,j} - k^*_{\mathrm{p}} \lambda_{k,l} \bar{\bar{\mu}}_{0,0} \\ & + k^*_{\mathrm{p}} \sum_{i=0}^{k} \binom{k}{i} \sum_{p=0}^{l} \binom{l}{p} \sum_{j=0}^{p} \binom{p}{j} \lambda_{i,j} \bar{\bar{\mu}}_{k-i,p-j} \end{aligned} \qquad (59)$$

$$\begin{aligned} r_{\bar{\bar{\lambda}}_{k,l}} = {} & k_{\mathrm{fm}} M \lambda^{\mathrm{T}}_{0,0} \delta(l) + k_{\mathrm{p}} M \left[\sum_{i=0}^{k} \binom{k}{i} \bar{\bar{\lambda}}_{i,l} - \bar{\bar{\lambda}}_{k,l} \right] \\ & - A''' \bar{\bar{\lambda}}_{k,l} + k_{\mathrm{fp}} \lambda^{\mathrm{T}}_{0,0} \sum_{j=0}^{l} \binom{l}{j} \bar{\bar{\mu}}_{k+1,j} - k^*_{\mathrm{p}} \bar{\bar{\lambda}}_{k,l} \bar{\bar{\mu}}_{0,0} \\ & + k^*_{\mathrm{p}} \sum_{i=0}^{k} \binom{k}{i} \sum_{p=0}^{l} \binom{l}{p} \sum_{j=0}^{p} \binom{p}{j} \bar{\bar{\lambda}}_{i,j} \bar{\bar{\mu}}_{k-i,p-j} \end{aligned} \qquad (60)$$

$$\begin{aligned} r_{\mu_{k,l}} = {} & (A''' - k_{\mathrm{t}} \lambda^{\mathrm{T}}_{0,0}) \lambda_{k,l} + \tfrac{1}{2} k_{\mathrm{tc}} \sum_{i=0}^{k} \binom{k}{i} \sum_{j=0}^{l} \binom{l}{j} \lambda_{i,j} \lambda_{k-i,l-j} \\ & + \tfrac{1}{2} k_{\mathrm{td}} \lambda_{k,l} \lambda^{\mathrm{T}}_{0,0} - k_{\mathrm{fp}} \mu_{k+1,l} \lambda^{\mathrm{T}}_{0,0} \end{aligned} \qquad (61)$$

$$\begin{aligned} r_{\bar{\bar{\mu}}_{k,l}} = {} & (A''' - k_{\mathrm{t}} \lambda^{\mathrm{T}}_{0,0}) \bar{\bar{\lambda}}_{k,l} + \tfrac{1}{2} k_{\mathrm{tc}} \sum_{i=0}^{k} \binom{k}{i} \sum_{j=0}^{l} \binom{l}{j} \bar{\bar{\lambda}}_{i,j} \\ & \times (\bar{\bar{\lambda}}_{k-i,l-j} + 2\lambda_{k-i,l-j}) - k^*_{\mathrm{p}} \bar{\bar{\mu}}_{k,l} \lambda^{\mathrm{T}}_{0,0} \\ & + \tfrac{1}{2} k_{\mathrm{td}} \lambda^{\mathrm{T}}_{0,0} (2\bar{\bar{\lambda}}_{k,l} + \lambda_{k,l}) - k_{\mathrm{fp}} \bar{\bar{\mu}}_{k+1,l} \lambda^{\mathrm{T}}_{0,0} \end{aligned} \qquad (62)$$

where:

$$A''' = k_{\mathrm{fm}} M + k_{\mathrm{fs}} S + k_{\mathrm{t}} \lambda^{\mathrm{T}}_{0,0} + k_{\mathrm{fp}} \mu^{\mathrm{T}}_{1,0} \qquad (63)$$

$$\lambda^{\mathrm{T}}_{k,l} = \lambda_{k,l} + \bar{\bar{\lambda}}_{k,l} \qquad \mu^{\mathrm{T}}_{k,l} = \mu_{k,l} + \bar{\bar{\mu}}_{k,l} \qquad k, l = 0, 1, 2 \qquad (64)$$

Table 1 Design equations for a batch polymerization reactor based on the double moments of the bivariate (*CLDB*) distribution

Initiator

$$\frac{1}{V}\frac{\mathrm{d}(VI)}{\mathrm{d}t} = -2fk_{\mathrm{d}}I$$

Monomer

$$\frac{1}{V}\frac{\mathrm{d}(VM)}{\mathrm{d}t} = r_{\mathrm{M}} = -(k_{\mathrm{p}} + 2k_{\mathrm{fm}})\lambda^{\mathrm{T}}_{0,0}M - k_{\mathrm{fs}}S\lambda^{\mathrm{T}}_{0,0} - k_{\mathrm{I}}PR^{\bullet}M$$

Modifier

$$\frac{1}{V}\frac{\mathrm{d}(VS)}{\mathrm{d}t} = -k_{\mathrm{fs}}\lambda^{\mathrm{T}}_{0,0}S$$

Volume contraction

$$\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}t} = -r_{\mathrm{M}}MW(1/\rho_{\mathrm{m}} - 1/\rho_{\mathrm{p}})$$

Chain-length distribution moments

$$\frac{1}{V}\frac{\mathrm{d}(V\lambda_{k,l})}{\mathrm{d}t} = r_{\lambda_{k,l}} \qquad \frac{1}{V}\frac{\mathrm{d}(V\bar{\bar{\lambda}}_{k,l})}{\mathrm{d}t} = r_{\bar{\bar{\lambda}}_{k,l}} \qquad k, l = 0, 1, 2$$

$$\frac{1}{V}\frac{\mathrm{d}(V\mu_{k,l})}{\mathrm{d}t} = r_{\mu_{k,l}} \qquad \frac{1}{V}\frac{\mathrm{d}(V\bar{\bar{\mu}}_{k,l})}{\mathrm{d}t} = r_{\bar{\bar{\mu}}_{k,l}} \qquad k, l = 0, 1, 2$$

Fractional monomer conversion

$$X = (M_0V_0 - MV)/M_0V_0$$

The fundamental design equations governing the variation of the leading moments of the joint (*CLDB*) distributions of 'live' and 'dead' polymer molecules in a batch polymerization reactor are listed in *Tables 1* and *2*. *Table 1* also includes the mass balances for initiator, monomer and chain transfer agent. Notice that the corresponding moment equations for the cumulative univariate *NCLD* can be directly obtained from *Table 1* using the following relations:

$$\lambda_k = \lambda_{k,0} \qquad \mu_k = \mu_{k,0} \qquad (65)$$

From the solution of the double-moment differential equations (*Table 1*), one can estimate the instantaneous and cumulative *NACL* and *WACL*, as well as the *NADB* and the *WADB*. Since a number of physical properties such as intrinsic viscosity and melt viscosity are most sensitive to the structure of the larger molecules, the *WADB* will generally be a more meaningful measure of the effect of the molecular structure on these properties[3]. The definitions of the cumulative *NACL*, *WACL* and *NADB*, *WADB* are given by the following equations, respectively:

$$\bar{X}_{\mathrm{N}} = \sum_n \sum_b nD^{\mathrm{T}}_{n,b} \Big/ \sum_n \sum_b D^{\mathrm{T}}_{n,b} = \mu^{\mathrm{T}}_{1,0}/\mu^{\mathrm{T}}_{0,0} \qquad (66)$$

$$\bar{X}_{\mathrm{W}} = \sum_n \sum_b n^2 D^{\mathrm{T}}_{n,b} \Big/ \sum_n \sum_b nD^{\mathrm{T}}_{n,b} = \mu^{\mathrm{T}}_{2,0}/\mu^{\mathrm{T}}_{1,0} \qquad (67)$$

$$\bar{B}_{\mathrm{N}} = \sum_n \sum_b bD^{\mathrm{T}}_{n,b} \Big/ \sum_n \sum_b D^{\mathrm{T}}_{n,b} = \mu^{\mathrm{T}}_{0,1}/\mu^{\mathrm{T}}_{0,0} \qquad (68)$$

$$\bar{B}_{\mathrm{W}} = \sum_n \sum_b nbD^{\mathrm{T}}_{n,b} \Big/ \sum_n \sum_b nD^{\mathrm{T}}_{n,b} = \mu^{\mathrm{T}}_{1,1}/\mu^{\mathrm{T}}_{1,0} \qquad (69)$$

where the superscript 'T' denotes the total population of polymer chains including $\mathrm{D}_{n,b}$ and $\bar{\bar{\mathrm{D}}}_{n,b}$ molecules. Similarly, the branching density, B_{d}, will be given by:

$$B_{\mathrm{d}} = \sum_n \sum_b bD^{\mathrm{T}}_{n,b} \Big/ \sum_n \sum_b nD^{\mathrm{T}}_{n,b} = \mu^{\mathrm{T}}_{0,1}/\mu^{\mathrm{T}}_{1,0} = \bar{B}_{\mathrm{N}}/\bar{X}_{\mathrm{N}} \qquad (70)$$

Table 2 Rate functions in the moment equations of *Table 1*

$$r_{\lambda_{0,0}} = k_I PR^{\bullet}M + (k_{fs}S + k_{fp}\mu_{1,0})\lambda^{T}_{0,0} - A'''\lambda_{0,0}$$

$$r_{\lambda_{1,0}} = k_I PR^{\bullet}M + k_{fs}S\lambda^{T}_{0,0} + k_p M\lambda_{0,0} + k_{fp}\mu_{2,0}\lambda^{T}_{0,0} - \lambda_{1,0}A''' + k^{*}_{p}\lambda_{0,0}\mu^{=}_{1,0}$$

$$r_{\lambda_{0,1}} = k_{fp}\lambda^{T}_{0,0}(\mu_{1,0} + \mu_{1,1}) + k^{*}_{p}\lambda_{0,0}(\mu^{=}_{0,0} + \mu^{=}_{0,1}) - \lambda_{0,1}A'''$$

$$r_{\lambda^{=}_{0,0}} = k_{fm}\lambda^{T}_{0,0}M + k_{fp}\lambda^{T}_{0,0}\mu^{=}_{1,0} - \lambda^{=}_{0,0}A'''$$

$$r_{\lambda^{=}_{1,0}} = k_p M\lambda^{=}_{0,0} + k_{fm}M\lambda^{T}_{0,0} + k_{fp}\lambda^{T}_{0,0}\mu^{=}_{2,0} + k^{*}_{p}\lambda^{=}_{0,0}\mu^{=}_{1,0} - \lambda^{=}_{1,0}A'''$$

$$r_{\lambda^{=}_{0,1}} = k_{fp}\lambda^{T}_{0,0}(\mu^{=}_{1,0} + \mu^{=}_{1,1}) + k^{*}_{p}\lambda^{=}_{0,0}(\mu^{=}_{0,0} + \mu^{=}_{0,1}) - \lambda^{=}_{0,1}A'''$$

$$r_{\mu_{0,0}} = \lambda_{0,0}(A''' - k_t\lambda^{T}_{0,0}) - k_{fp}\mu_{1,0}\lambda^{T}_{0,0} + \tfrac{1}{2}k_{tc}(\lambda_{0,0})^2 + \tfrac{1}{2}k_{td}\lambda_{0,0}\lambda^{T}_{0,0}$$

$$r_{\mu^{=}_{0,0}} = \lambda^{=}_{0,0}(A''' - k_t\lambda^{T}_{0,0}) - k_{fp}\mu^{=}_{1,0}\lambda^{T}_{0,0} + \tfrac{1}{2}k_{tc}\lambda^{=}_{0,0}(\lambda^{=}_{0,0} + 2\lambda_{0,0}) - k^{*}_{p}\mu^{=}_{0,0}\lambda^{T}_{0,0} + \tfrac{1}{2}k_{td}\lambda^{T}_{0,0}(2\lambda^{=}_{0,0} + \lambda_{0,0})$$

$$r_{\mu_{1,0}} = \lambda_{1,0}(A''' - k_t\lambda^{T}_{0,0}) + k_{tc}\lambda_{0,0}\lambda_{1,0} + \tfrac{1}{2}k_{td}\lambda^{T}_{0,0}\lambda_{1,0} - k_{fp}\mu_{2,0}\lambda^{T}_{0,0}$$

$$r_{\mu^{=}_{1,0}} = \lambda^{=}_{1,0}(A''' - k_t\lambda^{T}_{0,0}) + k_{tc}(\lambda_{0,0}\lambda^{=}_{1,0} + \lambda^{=}_{0,0}\lambda_{1,0} + \lambda^{=}_{0,0}\lambda^{=}_{1,0}) - k_{fp}\mu^{=}_{2,0}\lambda^{T}_{0,0} + \tfrac{1}{2}k_{td}\lambda^{T}_{0,0}(\lambda_{1,0} + 2\lambda^{=}_{1,0}) - k^{*}_{p}\mu^{=}_{1,0}\lambda^{T}_{0,0}$$

$$r_{\mu_{0,1}} = \lambda_{0,1}(A''' - k_t\lambda^{T}_{0,0}) + k_{tc}\lambda_{0,0}\lambda_{0,1} + \tfrac{1}{2}k_{td}\lambda^{T}_{0,0}\lambda_{0,1} - k_{fp}\mu_{1,1}\lambda^{T}_{0,0}$$

$$r_{\mu^{=}_{0,1}} = \lambda^{=}_{0,1}(A''' - k_t\lambda^{T}_{0,0}) + k_{tc}(\lambda_{0,0}\lambda^{=}_{0,1} + \lambda^{=}_{0,0}\lambda_{0,1} + \lambda^{=}_{0,0}\lambda^{=}_{0,1}) - k_{fp}\mu^{=}_{1,1}\lambda^{T}_{0,0} + \tfrac{1}{2}k_{td}\lambda^{T}_{0,0}(\lambda_{0,1} + 2\lambda^{=}_{0,1}) - k^{*}_{p}\mu^{=}_{0,1}\lambda^{T}_{0,0}$$

$$r_{\mu^{T}_{1,1}} = k_p M\lambda^{T}_{0,1} + k_{fp}\lambda^{T}_{0,0}\mu^{T}_{2,0} + k_{tc}\lambda^{T}_{1,0}\lambda^{T}_{0,1} + k^{*}_{p}[\lambda^{T}_{1,0}(\mu^{=}_{0,0} + \mu^{=}_{0,1}) + \mu^{=}_{1,0}(\lambda^{T}_{0,0} + \lambda^{T}_{0,1})]$$

$$r_{\mu^{T}_{2,0}} = k_I PR^{\bullet}M + (k_{fm}M + k_{fs}S)\lambda^{T}_{0,0} + k_p M(\lambda^{T}_{0,0} + 2\lambda^{T}_{1,0}) + k_{tc}(\lambda^{T}_{1,0})^2 + 2k^{*}_{p}\mu^{=}_{1,0}\lambda^{T}_{1,0}$$

where

$$A''' = k_{fm}M + k_{fs}S + k_{fp}\mu^{T}_{1,0} + k_t\lambda^{T}_{0,0}$$

The polydispersity indices, $\bar{D}$ and $\bar{D}_B$, are defined in terms of the *NACL*, *WACL*, *NADB* and *WADB* of the cumulative joint (*CLDB*) polymer distribution:

$$\bar{D} = \bar{X}_W/\bar{X}_N \qquad \bar{D}_B = \bar{B}_W/\bar{B}_N \tag{71}$$

Finally, the number- and weight-average amount of terminal double bonds per molecule, T_N and T_W, as well as the dispersity index of the terminal double-bond distribution, are defined as[9]:

$$T_N = \mu^{=}_{0,0}/\mu^{T}_{00} \qquad T_W = \mu^{=}_{1,0}/\mu^{T}_{1,0} \qquad \bar{D}_{TDB} = T_W/T_N \tag{72}$$

PROPERTY MOMENTS METHOD

This method was originally developed by Villermaux and his coworkers[27–29] for modelling free-radical homopolymerization reactions. It is presently known as the tendency modelling method. The PMM does not consider balances on the individual species present in the reaction mixture. Instead, mass balance equations are derived for a number of selected quantities that characterize the polymer quality. These quantities are: the average concentration of 'live' radicals (whatever their size may be); the leading moments of the polymer *NCLD*; and the concentration of structural characters such as short (SCB) and long-chain branching points (LCB) and terminal double bonds (TDB) irrespective of the macromolecules carrying them. To derive the conservation equations with respect to these quantities, one must identify the various rate functions through which a conserved quantity is consumed and/or produced. One of the most important features of the PMM is the direct determination of the rate functions for the leading moments of the instantaneous *NCLD* of polymer molecules.

The derivation of the model equations comprises the following steps:

(1) Inventory of processes whereby new chains are started from an initiation centre. Calculation of the corresponding rate functions and the associated moments of the 'live' polymer *NCLD*.

(2) Use of the mixing theorem to calculate the average moments of the total 'live' radical population.

(3) Inventory of processes whereby termination of 'live' polymer chains results in the production of 'dead' macromolecules. Derivation of the corresponding rate functions and the associated moments of the *NCLD* of the instantaneously formed 'dead' polymer molecules.

(4) Use of the mixing theorem to calculate the average moments of the instantaneously formed 'dead' polymer population.

(5) Derivation of the overall production rates for the quantities of interest.

Derivation of the leading moments of the 'live' and 'dead' polymer NCLD

In this section, the moments of the *NCLD* of the 'live' radical population are derived based on the following kinetic mechanism:

Initiation

$$I \xrightarrow{k_d} 2P \tag{73}$$

Propagation

$$P + M \xrightarrow{k_p} P \tag{74}$$

Chain transfer to monomer

$$P + M \xrightarrow{k_{fm}} D + P + TDB \tag{75}$$

Chain transfer to modifier

$$P + S \xrightarrow{k_{fs}} D + P \tag{76}$$

Chain transfer to polymer

$$P + D \xrightarrow{k_{fp}} P + D + LCB \tag{77}$$

Reaction of a terminal double bond

$$\mathrm{P} + \mathrm{D} + \mathrm{TDB} \xrightarrow{k_p^*} \mathrm{P} + \mathrm{LCB} \tag{78}$$

Termination by combination

$$\mathrm{P} + \mathrm{P} \xrightarrow{k_{tc}} \mathrm{D} \tag{79}$$

Termination by disproportionation

$$\mathrm{P} + \mathrm{P} \xrightarrow{k_{td}} \mathrm{D} + \mathrm{D} + \mathrm{TDB} \tag{80}$$

Assuming that the quasi-steady-state approximation holds, one can easily show that the total concentration of the 'live' radicals will be given by[2]:

$$\lambda_0 = \sum_n P_n = (2fk_dI/k_t)^{1/2} \tag{81}$$

Following the general developments of the PMM, we define the normalized moments of the 'live' radical *NCLD*:

$$\lambda'_k = \lambda_k/\lambda_0 \tag{82}$$

A quantity that is very important in the calculation of the leading moments of the 'live' radical *NCLD* is that of the average kinetic chain length. According to Flory[11] it is defined as:

$$\begin{aligned} L &= (\text{rate of chain propagation})/(\text{rates of chain initiation}) \\ &= k_pM\lambda_0/(2fk_dI + k_{fm}M\lambda_0 + k_{fs}S\lambda_0 + k_{fp}\lambda_0\mu_1 \\ &\qquad + k_p^*\lambda_0\mu_0^{=}) \end{aligned} \tag{83}$$

Notice that, in equation (83), λ_k and μ_k refer to the moments of the combined (i.e. polymer chains with and without a terminal double bond) 'live' and 'dead' polymer populations, respectively.

Subsequently, all reactions related to the initiation of new polymer chains are identified. These reactions together with their corresponding rate functions and the associated moments of the *NCLD* are shown in *Table 3*. For the particular kinetic scheme considered in this study, chain initiation occurs by three different mechanisms. The first mechanism considers the initiation of linear polymer chains starting from a small radical (i.e. initiation, chain transfer to monomer and chain transfer to modifier reactions). One can easily show that the moments of the *NCLD* of growing linear polymer chains will obey the Schulz–Flory distribution and will be given by:

$$(\lambda'_1)_j = L \qquad (\lambda'_2)_j = 2L^2 \tag{84}$$

Table 3 Processes initiating new chains

Reaction	Rate functions, r_i	Moments of the *NCLD*	
		First moment	Second moment
Initiation	$2fk_dI$	L	$2L^2$
Transfer to monomer	$k_{fm}\lambda_0M$	L	$2L^2$
Transfer to modifier	$k_{fs}\lambda_0S$	L	$2L^2$
Transfer to polymer	$k_{fp}\lambda_0\mu_1$	$L+\mu_2/\mu_1$	$2L^2 + 2L\mu_2/\mu_1 + \mu_3/\mu_1$
Propagation of a TDB	$k_p^*\lambda_0\mu_0^{=}$	$L + \lambda'_1 + \mu_1/\mu_0$	$2L^2 + 2L(\mu_1/\mu_0 + \lambda'_1)$ $+ \mu_2/\mu_0 + \lambda'_2 + 2\lambda'_1\mu_1/\mu_0$

Table 4 Processes producing macromolecules

Reaction	Rate functions, r_i	Moments of the *INCLD*	
		First moment, $(\mu'_1)_i$	Second moment, $(\mu'_2)_i$
Termination by combination	$\frac{1}{2}k_{tc}\lambda_0^2$	$2\lambda'_1$	$2\lambda'_2+2(\lambda'_1)^2$
Termination by disproportionation	$k_{td}\lambda_0^2$	λ'_1	λ'_2
Transfer to monomer	$k_{fm}\lambda_0M$	λ'_1	λ'_2
Transfer to modifier	$k_{fs}\lambda_0S$	λ'_1	λ'_2
Transfer to polymer	$k_{fp}\lambda_0\mu_1$	λ'_1	λ'_2
	$-k_{fp}\lambda_0\mu_1$	μ_2/μ_1	μ_3/μ_1
Propagation on TDB	$-k_p^*\lambda_0\mu_0^{=}$	μ_1/μ_0	μ_2/μ_0

where the subscript j denotes the particular initiation process.

The second chain initiation mechanism is related to chain transfer to polymer reaction. The moments of the corresponding *NCLD* of the 'live' branched polymer chains will be[29]:

$$(\lambda'_1)_j = L + \mu_2/\mu_1 \qquad (\lambda'_2)_j = 2L^2 + 2L(\mu_2/\mu_1) + \mu_3/\mu_1 \tag{85}$$

The third initiation mechanism considers the propagation to a terminal double bond reaction. The moments of the associated *NCLD* of the 'live' polymer chains are expressed as[29]:

$$\begin{aligned} (\lambda'_1)_j &= L + \lambda'_1 + \mu_1/\mu_0 \\ (\lambda'_2)_j &= 2L^2 + 2L(\mu_1/\mu_0 + \lambda'_1) + \mu_2/\mu_0 + \lambda'_2 \\ &\quad + 2\lambda'_1\mu_1/\mu_0 \end{aligned} \tag{86}$$

From the application of the mixing theorem, one can calculate the average moments of the total growing radical population (i.e. all chain initiation processes):

$$\lambda'_k \sum_j r_j = \sum_j (\lambda'_k)_j r_j \tag{87}$$

where r_j denotes the net production rate of polymer chains by the 'j' process. These rates are reported in *Table 3*. From the results of *Table 3* and the use of the mixing theorem, equation (87), we obtain the following expressions for the average moments of the cumulative *NCLD* of all growing polymer chains:

$$\lambda'_1 = \frac{k_pM\lambda_0 + k_{fp}\lambda_0\mu_2 + k_p^*\lambda_0\mu_0^{=}\mu_1/\mu_0}{2fk_dI + k_{fm}M\lambda_0 + k_{fs}S\lambda_0 + k_{fp}\lambda_0\mu_1} \tag{88}$$

$$\lambda'_2 = \frac{2k_pM\lambda_1 + k_{fp}\lambda_0\mu_3 + k_p^*\lambda_0\mu_0^{=}(\mu_2/\mu_0 + 2\lambda'_1\mu_1/\mu_0)}{2fk_dI + k_{fm}M\lambda_0 + k_{fs}S\lambda_0 + k_{fp}\lambda_0\mu_1} \tag{89}$$

Subsequently, all processes related to the production of 'dead' polymerization chains are identified together with their corresponding rate functions and the associated moments of the instantaneous 'dead' polymer *NCLD*. These results appear in *Table 4*. It can be easily seen that the moments of the instantaneous *NCLD* of 'dead' polymer molecules produced by termination, disproportionation as well as by chain transfer to monomer and to modifier reactions are identical to the moments of the deactivated 'live' radicals.

From the application of the mixing theorem, one can calculate the moments of the total population of 'dead' polymer molecules, (μ_k), produced via all termination reactions[27]:

$$\begin{aligned} r_{\mu_k} &= \mu'_k \sum_i r_i = \sum_i (\mu'_k)_i r_i \qquad k = 1, 2 \\ r_{\mu_0} &= \sum_i r_i \end{aligned} \tag{90}$$

From equation (90) and the results of *Table 4*, the net production rates for the moments of 'dead' macromolecules are written:

$$r_{\mu_0} = 2fk_dI + k_{fm}M\lambda_0 + k_{fs}S\lambda_0 - k_p^*\lambda_0\mu_0^{=} \tag{91}$$

$$r_{\mu_1} = k_pM\lambda_0 \tag{92}$$

$$r_{\mu_2} = 2\lambda_1(k_pM + k_p^*\mu_0^{=}\mu_1/\mu_0) + k_{tc}\lambda_1^2 \tag{93}$$

Finally, the net consumption rates for the initiator, monomer and modifier will be:

$$r_I = -2fk_dI \tag{94}$$

$$r_M = -k_pM\lambda_0 \tag{95}$$

$$r_S = -k_{fs}S\lambda_0 \tag{96}$$

According to the property moments method, rate equations for structural characters of the polymer chains are directly derived. Based on the general kinetic scheme considered in this study (equations (73)–(80)) one can identify two structural parameters of the polymer chains related to the number of long-chain branches (LCB) and the number of terminal double bonds (TDB). The respective net production rates for LCB and TDB per polymer molecule will be given by:

$$r_{LCB} = k_{fp}\lambda_0\mu_1 + k_p^*\lambda_0\mu_0^{=} \tag{97}$$

$$r_{TDB} = r_{\mu_0^{=}} = k_{fm}\lambda_0M - k_p^*\lambda_0\mu_0^{=} + k_{td}\lambda_0^2 \tag{98}$$

RESULTS AND DISCUSSION

In this section, the main features of the three kinetic modelling methods (IPM, MM and PMM), as well as the conditions that each method should satisfy for its application to a given polymerization system, are identified. This is achieved by application of the three methods to polymerization systems for which experimental results on conversion and molecular weight are available. The polymerizations examined in the present study include the bulk polymerization of methyl methacrylate (MMA), the solution polymerization of vinyl acetate (VAC) and the bulk thermal polymerization of *p*-methylstyrene.

The bulk polymerization of MMA

This polymerization was selected as a representative example of the production of linear polymers and the appearance of strong diffusional limitations in the propagation and termination rate constants. The bulk polymerization of MMA has been experimentally studied by several investigators[5,30]. The values of the kinetic rate constants as well as the diffusion model describing the diffusional limitations in k_p and k_t are presented in *Table 5*.

Table 5 Kinetic and diffusion-controlled rate constants for the bulk polymerization of MMA[31,32]

$k_d = 6.32 \times 10^{16} \exp(-30\,660/RT)$ for AIBN	$[\mathrm{min}^{-1}]$
$f = 0.58$ for AIBN	
$k_{p0} = 2.95 \times 10^7 \exp(-4350/RT)$	$[\mathrm{l\ mol^{-1}\ min^{-1}}]$
$k_{fm} = k_p \times 9.48 \times 10^3 \exp(-13\,880/RT)$	
$k_{t0} = 5.88 \times 10^9 \exp(-701/RT)$	$[\mathrm{l\ mol^{-1}\ min^{-1}}]$
$k_{tc}/k_{td} = 3.956 \times 10^{-4} \exp(4090/RT)$	
$\rho_m = 0.968 - 1.225 \times 10^{-3}(T - 273.15)$	$[\mathrm{g\ ml^{-1}}]$
$\rho_p = 1.2$	$[\mathrm{g\ ml^{-1}}]$
$MW = 100.13$	

$$k_t = k_{t0}\frac{C}{C + \theta_t k_{t0}\lambda_0}$$

$$k_p = k_{p0}\frac{C}{C + \theta_p k_{p0}\lambda_0}$$

$$\log_{10} C = \frac{1 - \varphi_p}{A + B(1 - \varphi_p)}$$

$A = 0.168 - 8.21 \times 10^6(T - 273.15 - 114)^2$

$B = 0.03$

$\theta_p = 5.481 \times 10^{-16} \exp(13\,982/T)$

$\theta_t = 1.1353 \times 10^{-22}/[\mathrm{I}]_0 \exp(17\,420/T)$

$\varphi_p = X(1 - \varepsilon)/(1 - \varepsilon X)$

T in K

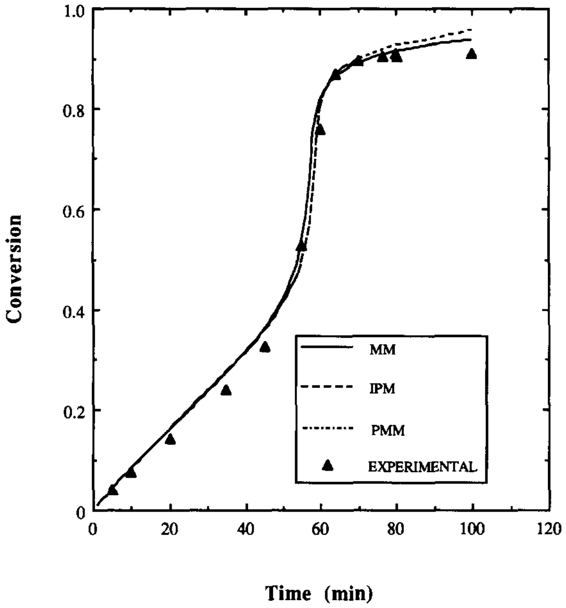

Figure 1 Predicted conversion values *versus* time for the bulk polymerization of MMA at $T = 70°\mathrm{C}$, $[\mathrm{I}]_0 = 0.0258\ \mathrm{mol\ l^{-1}}$ (▲, experimental data[30])

Since this system leads to the production of linear polymer chains, all three kinetic models will be valid and applicable to the description of MMA polymerization. Conversion and molecular-weight simulation results obtained by the three models are plotted in *Figures 1* and *2* and compared to experimental data reported by Balke and Hamielec[30]. From the results of *Figures 1* and *2*, it can be seen that no significant differences exist between the predictions of the three models. It should be pointed out that both IPM and PMM make use of the QSSA. On the other hand, the MM does not necessarily call upon the application of QSSA.

When the polymerization is governed by diffusional phenomena, the termination rate constant and, at very high conversions, the propagation rate constant as well as the initiator efficiency can decrease by several orders

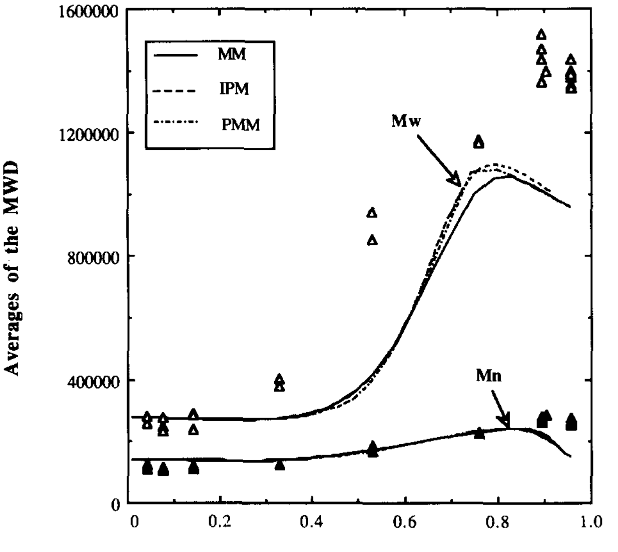

Figure 2 Predicted averages of the *MWD* (M_n and M_w) for the bulk polymerization of MMA; experimental conditions as in *Figure 1* (▲, △, experimental data[30])

of magnitude. This causes an accumulation of 'live' radicals in the reacting mixture. Hence, the QSSA, which assumes that the net rate of radical termination is approximately equal to the rate of radical initiation, will not be strictly valid. However, the present simulation results show that, although the QSSA will not be satisfied at high conversions, conversion and molecular-weight predictions obtained by the three methods will not vary significantly. This is due to the fact that the polymer mass produced at high conversions represents only a small fraction of the total polymer produced. Asa result, any inaccuracies in the prediction of instantaneous M_n and M_w values during the late stage of polymerization will not significantly alter the cumulative values of M_n and M_w. It can be seen that all three models fail to predict the experimental values of $\bar{M}_w$ in the conversion range of 20–60%. This behaviour is explained in a recent publication by Zhu and Hamielec[33]. According to these investigators, one can satisfactorily predict the experimental variation in $\bar{M}_w$ by considering two termination rate constants (i.e. k_{tn} and k_{tw}), one depending on the number-average and the other on the weight-average chain length of the terminating polymer molecules.

The solution polymerization of VAC

This polymerization was selected as a representative example of the production of branched polymers in the presence of weak diffusional limitations in k_p and k_t. It was experimentally studied by Graessly and coworkers[34,35] and theoretically by Hamer and Ray[7,13], Reichert and coworkers[6,14] and Graessly *et al.*[3,15,35–40]. The values of the kinetic rate constants as well as the diffusion model describing the diffusional limitations in k_p and k_t are presented in *Table 6*.

Since this system leads to the production of branched polymer chains, the IPM cannot be applied to this polymerization. The M_N and M_W values calculated by the MM and PMM are depicted in *Figure 3*. The discrete points represent the experimental measurements reported by Graessly *et al.*[34,35]. As can be seen, the PMM slightly underestimates the *WAMW* and *NAMW*. The *NADB* and *WADB* calculated by the MM and PMM are plotted in *Figure 4*. It is obvious that no significant differences exist in the calculation of *NADB* by the two methods. This is due to the fact that equation (97) of PMM, which describes the net rate of production of long-chain branches, can be directly derived from equation (99) assuming that the QSSA is valid. According to the results of *Table 2*, the net production rate of LCB will be given by:

$$r_{\mu^{\mathrm{T}}_{0,1}} = k_{\mathrm{fp}}\lambda^{\mathrm{T}}_{0,0}\mu^{\mathrm{T}}_{1,0} + k^{*}_{\mathrm{p}}\lambda^{\mathrm{T}}_{0,0}\mu^{=}_{0,0} \tag{99}$$

Assuming that $\lambda_0 = \lambda^{\mathrm{T}}_{0,0}$, $\mu_1 = \mu^{\mathrm{T}}_{1,0}$, $\mu^{=}_0 = \mu^{=}_{0,0}$, then one obtains:

$$r_{\mathrm{LCB}} = r_{\mu^{\mathrm{T}}_{0,1}} \tag{100}$$

Table 6 Kinetic and diffusion-controlled rate constants for the solution polymerization of VAC[7,13]

$k_d = 4.5 \times 10^{14} \exp(-30\,000/RT)$ for AIBN $[\mathrm{s^{-1}}]$
$f = 0.50$ for AIBN
$k_p = 7 \times 10^{7} \exp(-6300/RT)$ $[\mathrm{l\,mol^{-1}\,s^{-1}}]$
$k_{fm} = k_p \times 1.42 \times 10^{-2} \exp(-2700/RT)$
$k_{fs} = k_p \times 1.04 \times 10^{-5}$
$k_{tc0} = 2.7 \times 10^{10} \exp(-2800/RT)$ $[\mathrm{l\,mol^{-1}\,s^{-1}}]$
$k_t = k_{t0} \exp[-(g_1 - g_2 T)X_T]$
$g_1 = 32.2$
$g_2 = 0.08$ $[\mathrm{K^{-1}}]$

$$X_T = \frac{x_1}{1 + f_s + f_I}$$

$$x_1 = \frac{\rho_{\mathrm{MSI_0}} - \rho_{\mathrm{MSI}}}{\rho_{\mathrm{MSI_0}}}$$

$k_{fp0} = k_p \times 7 \times 10^{-3} \exp(-2700/RT)$
$k_{fp} = k_{fp0} \exp(-0.282M/S)$
$k^{*}_{p} = k_p \times 0.66$
$\rho_m = (MW)_m/(0.053\,46 + 1.33 \times 10^{-4}T)$ $[\mathrm{g\,l^{-1}}]$
$\rho_p = (MW)_m/(0.056\,08 + 5.41 \times 10^{-5}T)$ $[\mathrm{g\,l^{-1}}]$
$\rho_s = 779$ $[\mathrm{g\,l^{-1}}]$
$(MW)_m = 86.09$
$(MW)_s = 74$
T in K

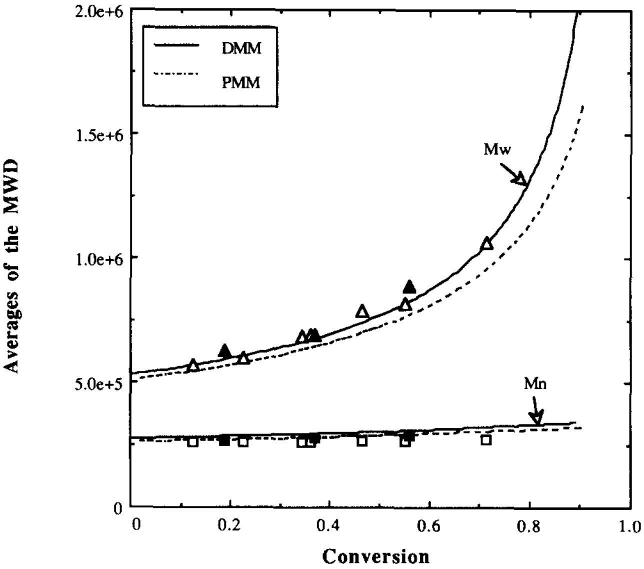

Figure 3 Predicted averages of the *MWD* (M_n and M_w) for the solution polymerization of VAC at $T = 60°\mathrm{C}$, $[\mathrm{I}]_0 = 0.0016\ \mathrm{mol\,l^{-1}}$, solvent/monomer ratio = 2 (experimental data: open symbols[34], filled symbols[35])

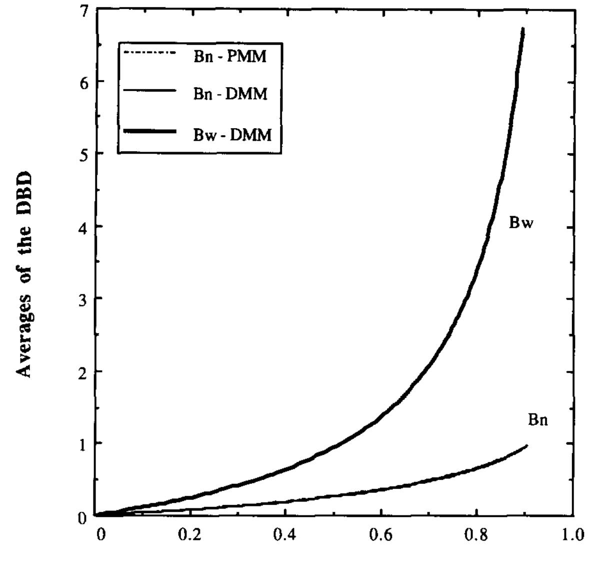

Figure 4 Averages of the *DBD* (B_n and B_w) for the solution polymerization of VAC; experimental conditions as in *Figure 3*

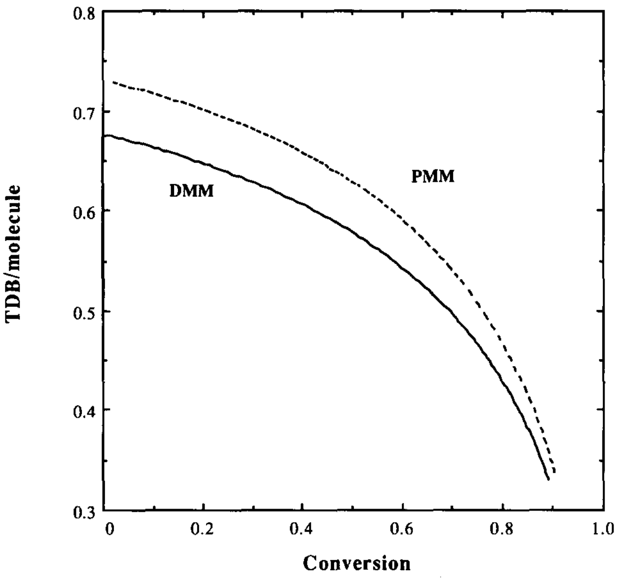

Figure 5 Number of terminal double bonds per polymer molecule for the solution polymerization of VAC; experimental conditions as in *Figure 3*

It is important to point out that only the double moments method (DMM) allows the calculation of the *WADB* from the moments of the joint (*CLDB*) distribution.

The number of terminal double bonds per polymer molecule calculated by the MM and PMM is plotted in *Figure 5*. The observed difference between the two methods is due to the fact that, contrary to the PMM, which assumes the formation of *one* TDB per termination reaction (equation (80)), the MM assumes that only part of the terminated polymer chains will contain a TDB. In fact, the kinetic equations (22)–(24) imply a production of 0.5, 0.5 and 0 TDB per molecule, respectively. According to the MM, the net rate of formation of TDB assuming that the QSSA is valid will be equal to:

$$r_{\mu_{0,0}^{=}} = k_{\mathrm{fm}}\lambda_{0,0}^{\mathrm{T}}M - k_{\mathrm{p}}^{*}\lambda_{0,0}^{\mathrm{T}}\mu_{0,0}^{=} + \tfrac{1}{2}k_{\mathrm{td}}\lambda_{0,0}^{\mathrm{T}}\lambda_{0,0} - \tfrac{1}{2}k_{\mathrm{tc}}(\lambda_{0,0}^{=})^2 \qquad (101)$$

Equation (101) differs from equation (58) in the last termination term, which explains the observed underestimation of the number of TDB by the MM.

The dispersity index of the TDB distribution is plotted in *Figure 6*. In the PMM, the dispersity index is assumed to be unity. On the other hand, the DMM shows that the dispersity index of the TDB distribution will vary with conversion.

The bulk thermal polymerization of p-methylstyrene

This system was selected as a representative example of the production of branched polymers at high temperatures, in the presence of weak diffusional limitations in k_t and k_p. The polymerization has been experimentally studied by Chiantore and Hamielec[24]. The values of the kinetic rate constants, as well as the diffusion model describing the dependence of k_t and k_p on conversion, are given in *Table 7*.

Since this system leads to branched polymer chains, only the MM and the PMM can be applied. For this polymerization, it has been reported[24] that the terminal double-bond reaction is negligible. Conversion and molecular-weight results obtained by the two methods (i.e. MM and PMM) are plotted in *Figures 7* and *8* and compared to experimental data (discrete points) of Chiantore and Hamielec[24]. As can be seen, no significant

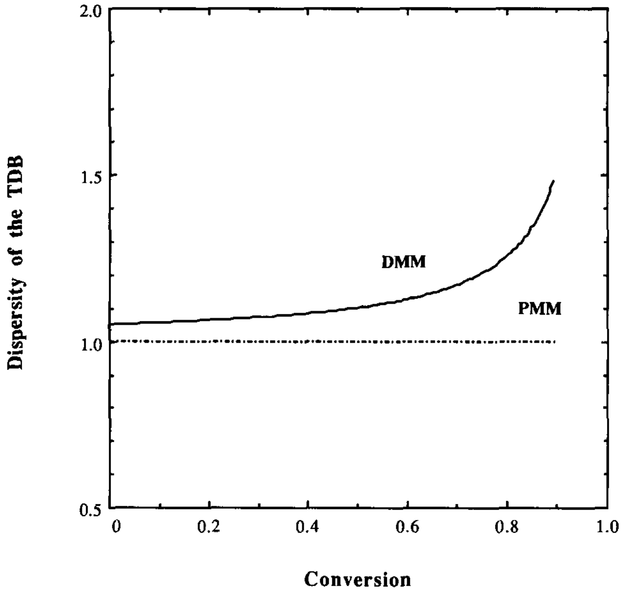

Figure 6 Dispersity of the TDB distribution for the solution polymerization of VAC; experimental conditions as in *Figure 3*

Table 7 Kinetic and diffusion-controlled rate constants for the thermal polymerization of *p*-MSt[24]

$R_i = k_i M^3$	
$k_i = 1.13 \times 10^4 \exp(-24\,560/RT)$	$[\mathrm{l^2\,mol^{-2}\,s^{-1}}]$
$k_p = 6.306 \times 10^8 \exp(-7068/RT)$	$[\mathrm{l\,mol^{-1}\,s^{-1}}]$
$k_{fs} = -k_p[1.1 \times 10^{-3} + 2.56 \times 10^{-6}(T - 393.12)]$ $\log_{10}[(473.12 - T)/202.5]$	
$k_{tc0} = 1.41 \times 10^{11} \exp(-1976/RT)$	$[\mathrm{l\,mol^{-1}\,s^{-1}}]$
$k_{tc} = k_{tc0} \exp[-2(A_1X + A_2X^2 + A_3X^3)]$	
$A_1 = 0.405 - 5.05 \times 10^{-3}T$	
$A_2 = 16.65 - 1.76 \times 10^{-2}T$	
$A_3 = -8.98 + 7.85 \times 10^{-3}T$	
$k_{fp} = k_p \times 1.1 \times 10^{-4}$	
T in K	

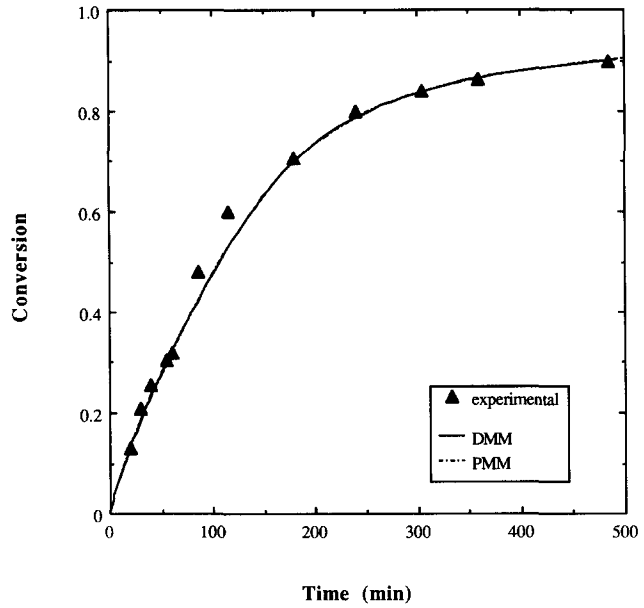

Figure 7 Predicted conversion profile *versus* time for the bulk thermal polymerization of *p*-methylstyrene at $T = 140°C$ (▲, experimental data[24])

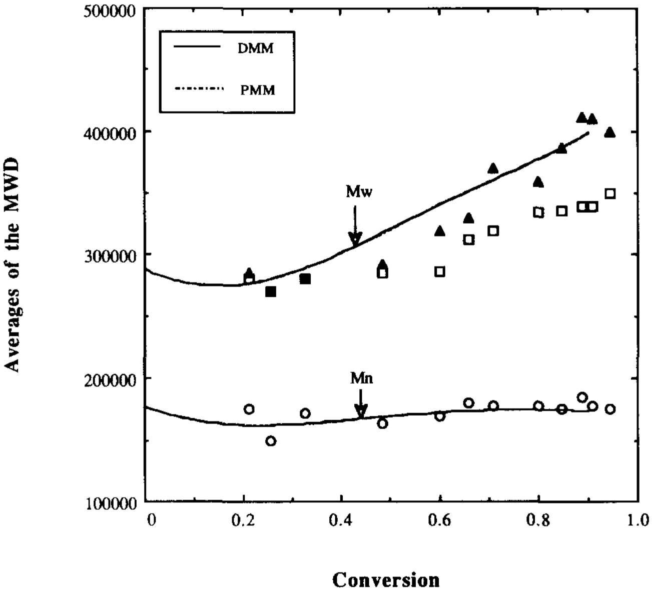

Figure 8 Averages of the *MWD* (M_n and M_w) for the bulk thermal polymerization of *p*-methylstyrene at $T = 140°C$ (experimental data[24]: ▲, M_w from l.a.l.l.s.p.; □, M_w from s.e.c.; ○, M_n from s.e.c.)

differences exist in the calculation of conversion, and *NAMW* and *WAMW* values by the two methods. The *NADB* calculated by the MM and PMM is plotted in *Figure 9*. No difference exists between the two methods. In the same figure, the *WADB* calculated by the DMM is also plotted. Finally, in *Figure 10*, the number of terminal double bonds is depicted with respect to monomer conversion.

CONCLUSIONS

In the present investigation, three commonly used kinetic modelling methods – namely, the instantaneous property method, the method of moments and the property moments method – are derived using a unified mathematical framework. The main differences and similarities of the three kinetic modelling methods are also discussed. This is achieved through the application of the three modelling methods to several free-radical polymerizations for which experimental data are available.

It appears that the method of moments is the most general one and can be applied to both linear and branched polymerizations either in the presence or in the absence of strong diffusional limitations in the termination and propagation rate constants. For linear polymerizations, in the absence of diffusion-controlled phenomena, the IPM appears to be superior to the other two methods, owing to its simpler mathematical formulation and its ability to provide information on the complete *NCLD*.

However, for polymerizations leading to branched

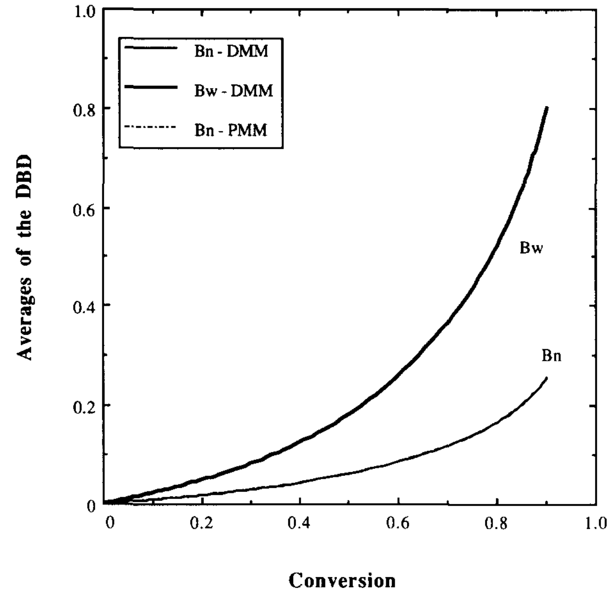

Figure 9 Averages of the *DBD* (B_n and B_w) for the bulk thermal polymerization of *p*-methylstyrene at $T = 140°C$

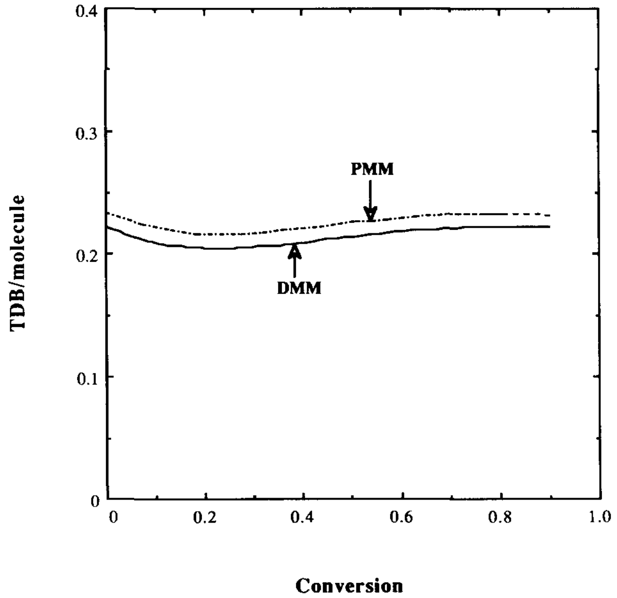

Figure 10 Number of terminal double bonds per polymer molecule for the bulk thermal polymerization of *p*-methylstyrene at $T = 140°C$

molecules, only the MM and the PMM can be applied. In the absence of diffusion-controlled phenomena, the use of the PMM offers some advantages over the method of moments, owing to its simpler mathematical derivation. However, in the presence of diffusion-controlled polymerizations leading to the formation of both linear and branched polymers, the method of moments should be chosen for modelling molecular and structural developments, since it does not require the use of QSSA and LCH. Furthermore, it is the only method that can provide information on *WADB* and, in general, can account for complex kinetics in a more systematic way.

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NOMENCLATURE

B_d	branching density
B_N	number-average degree of branching
B_W	weight-average degree of branching
CLD	chain-length distribution
CLDB	chain length–degree of branching [distribution]
D	polydispersity
DB	degree of branching
DBD	degree-of-branching distribution
DMM	double moments method
$\mathrm{D}_{n,b}$; $D_{n,b}$	'dead' polymer having *n* monomer units and *b* number of branches; its concentration
f	initiator efficiency
$\mathrm{G}_{n,b}$; $G_{n,b}$	general description of a macromolecule having *n* monomer units and *b* number of branches; its concentration
I; *I*	initiator; its concentration
INCLD	instantaneous number chain-length distribution
k_d	initiator decomposition rate constant
k_{fm}	chain transfer to monomer rate constant
k_{fp}	chain transfer to polymer rate constant
k_{fs}	chain transfer to modifier (solvent, agent) rate constant
k_p	propagation rate constant
k_t	$= k_{tc} + k_{td}$
k_{tc}	termination by combination rate constant
k_{td}	termination by disproportionation rate constant
k_p^*	terminal double-bond reaction rate constant
L	average kinetic chain length of 'live' radicals
LCB	long-chain branch
M; *M*	monomer; its concentration
M_N	number-average molecular weight
M_W	weight-average molecular weight
NACL	number-average chain length
NADB	number-average degree of branching
NAMW	number-average molecular weight
NCLD	number chain-length distribution
PMM	property moments method
$\mathrm{P}_{n,b}$; $P_{n,b}$	'live' radical having *n* monomer units and *b* number of branches; its concentration
$\mathrm{PR}^\bullet$; $PR^\bullet$	primary radical from the fragmentation of the initiator; its concentration
S; *S*	modifier (solvent agent); its concentration
SMM	single moments method

T	temperature
t	time
TCL	total chain length
TDB	terminal double bond
T_N	number-average degree of terminal double bonds
T_W	weight-average degree of terminal double bonds
V	reactor volume
$w(i, x)$	chain-length distribution
$WACL$	weight-average chain length
$WADB$	weight-average degree of branching
$WAMW$	weight-average molecular weight
X	fractional monomer conversion

Greek symbols

$\delta(X)$	Kronecker delta
$\lambda_{k,l}$	'live' radical moments
$\mu_{k,l}$	'dead' polymer moments
ρ_m, ρ_p	density of monomer and polymer, respectively
τ, β	dimensionless parameters used in the instantaneous property method
φ_p	volume fraction of polymer

Subscripts

b	number of long-chain branches in a polymer chain
n	number of monomer units in the polymer chain
0	initial conditions

Superscripts

$\bar{}$	cumulative
r	radical
T	total (sum of all species with and without a terminal double bond)
$=$	terminal double bond incorporated into a macromolecule