On the validity of the steady-state approximations in high conversion diffusion-controlled free-radical copolymerization reactions

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Chain addition polymerization reactions involve active intermediates (i.e. free radicals) whose total concentration at all times is very small. In copolymerization, in contrast to homopolymerization, one can identify two radical populations, 'P' and 'Q', ending in an M_1 or in an M_2 monomer unit, respectively. As a result, two distinct quasi-steady-state approximations (QSSAs) can be made. The first QSSA is applied to the total radical concentration and implies that the total rate of radical initiation is approximately equal to the total rate of radical termination. The second QSSA is applied to the separate radical populations P and Q and states that the rate of reaction of a P-type radical with an M_2 monomer is equal to the rate of reaction of a Q radical with an M_1 monomer. However, whether or not both approximations are applicable to a given copolymerization system is a point of concern. In the present study, the validity of the two QSSAs is examined. The conditions under which both approximations can be applied to a given copolymerization system are identified, through the application of the method of moments to several experimentally investigated free-radical copolymerization systems leading to linear and branched copolymers. It is shown that the validity of the QSSAs in free-radical copolymerization depends on the polymerization conditions, namely, the polymerization process (e.g. bulk *versus* solution) and the importance of diffusion-controlled reactions at high monomer conversions. However, the effect of both approximations on the final molecular properties is, in general, not significant.

(Keywords: free-radical copolymerization; kinetics; method of moments)

INTRODUCTION

As the application of polymers becomes more specific, so the demand to improve polymer properties increases. One way to meet this demand is to copolymerize carefully chosen monomer pairs or even multiple monomer combinations to achieve the desired end-use polymer properties. The key polymer molecular properties that directly influence the end-use characteristics of copolymers are the molecular weight distribution (MWD), the copolymer composition distribution (CCD), the degree of branching distribution (DBD) and the chain sequence distribution (CSD). Therefore there is a strong incentive to develop comprehensive kinetic models capable of predicting the development of molecular properties during the course of copolymerization.

Several mathematical models have been published dealing with free-radical copolymerization kinetics[1-29]. These models rely on the kinetic mechanism of free-radical copolymerization, which includes a number of elementary reactions. Molecular weight and compositional changes related to a free-radical copolymerization reaction system can be modelled by an infinite set of non-linear algebraic or differential-difference equations, depending on the reactor type. Early efforts to obtain analytical solutions for the rate of copolymerization, copolymer composition and instantaneous MWD made use of the long-chain hypothesis (LCH) and the quasi-steady-state approximation (QSSA) for the 'live' radical polymer chains. The LCH implies that monomers are only consumed in the propagation reactions, thus neglecting the monomer consumption due to the initiation and transfer to monomer reactions. In copolymerization, in contrast to homopolymerization, one can identify two radical populations, 'P' and 'Q', ending in an M_1 or an M_2 monomer unit, respectively. As a result, two distinct QSSAs can be made with respect to the radicals P and Q. The first QSSA is applied to the total radical concentration and implies that the total rate of radical initiation will be approximately equal to the total rate of radical termination. The second QSSA is applied to the separate radical populations P and Q and indicates that the rate of reaction of a P-type radical with an M_2 monomer is equal to the rate of reaction of a Q radical with an M_1 monomer. However, whether or not both QSSAs are applicable to a given copolymerization system is a point of concern[30-37].

In conjunction with these assumptions, a number of mathematical techniques (i.e. the moment generating function[3], z-transform[3], the continuous variable approximation[38], the Gallerkin[39] and the discrete weighted residual methods[40]) have been used for the solution of the infinite system of molecular species balance equations describing the molecular weight and compositional changes in a copolymerization reactor.

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In the present study, the method of moments is invoked in order to investigate the validity of the two QSSAs commonly used in free-radical copolymerization reactions. Copolymerizations are studied in bulk and solution, in the presence or absence of strong diffusional limitations in the termination and propagation reactions. A comparative analysis is carried out to determine the conditions under which each of the two QSSAs can be applied to a given copolymerization system. This is accomplished by the application of the method of moments to several free-radical copolymerization systems studied experimentally. Accordingly, experimental data on conversion, molecular weight averages and copolymer composition are compared to model predictions obtained with or without the use of the two approximations. Subsequently, the general rate functions describing the net production of the various macromolecular species present in a copolymerization system are derived.

POLYMERIZATION RATE FUNCTIONS

The following general mechanism is assumed to represent the general kinetics of chemically initiated free-radical chain addition copolymerizations[3–5]:

Initiation

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

$$\mathrm{PR}^{\bullet}+\mathrm{M}_j \xrightarrow{k_{\mathrm{I}_j}} \mathrm{R}^j_{2-j,j-1,0};\quad j=1,\,2 \tag{2}$$

Propagation

$$\mathrm{R}^i_{n,m,b}+\mathrm{M}_j \xrightarrow{k_{\mathrm{p}_{ij}}} \mathrm{R}^j_{n+2-j,m+j-1,b};\qquad i=1,\,2,\quad j=1,\,2 \tag{3}$$

Chain transfer to monomer

$$\mathrm{R}^i_{n,m,b}+\mathrm{M}_j \xrightarrow{k_{\mathrm{f}_{ij}}} \mathrm{R}^j_{2-j,j-1,0}+\mathrm{D}_{n,m,b};\qquad i=1,\,2,\quad j=1,\,2 \tag{4}$$

Chain transfer to modifier

$$R^i_{n,m,b}+\mathrm{S} \xrightarrow{k_{\mathrm{f}_{is}}} \mathrm{R}^i_{2-i,i-1,0}+\mathrm{D}_{n,m,b};\quad i=1,\,2 \tag{5}$$

Chain transfer to polymer

$$\mathrm{R}^i_{n,m,b}+\mathrm{D}_{r,q,x} \xrightarrow{k_{\mathrm{fp}_{ij}}} \mathrm{R}^j_{r,q,x+1}+\mathrm{D}_{n,m,b};\qquad i=1,\,2,\quad j=1,\,2 \tag{6}$$

Termination by combination

$$\mathrm{R}^i_{n,m,b}+\mathrm{R}^j_{r,q,x} \xrightarrow{k_{\mathrm{tc}_{ij}}} \mathrm{D}_{n+r,m+q,b+x};\qquad i=1,\,2,\quad j=1,\,2 \tag{7}$$

Termination by disproportionation

$$\mathrm{R}^i_{n,m,b}+\mathrm{R}^j_{r,q,x} \xrightarrow{k_{\mathrm{td}_{ij}}} \mathrm{D}_{n,m,b}+\mathrm{D}_{r,q,x};\qquad i=1,\,2,\quad j=1,\,2 \tag{8}$$

where I, $\mathrm{PR}^{\bullet}$, M_j ($j=1$, 2) and S denote the initiator, primary radicals, monomer and modifier (i.e. solvent) molecules, respectively. The particular copolymerization mechanism comprises three elementary initiation reactions, four propagation reactions, four chain transfer to monomer reactions, two chain transfer to modifier reactions, four chain transfer to polymer reactions, three termination by combination reactions and three termination by disproportionation reactions; that is, it includes a total of 23 elementary reactions. It is assumed that (i) no depropagation reactions occur and (ii) the penultimate effect is negligible.

To identify a 'live' ($\mathrm{R}^i_{n,m,b}$) or a 'dead' ($\mathrm{D}_{n,m,b}$) copolymer chain the general notation $\mathrm{G}_{n,m,b}$ is introduced. The three subscripts (n, m, b) denote a copolymer chain containing n units of monomer 1 (M_1), m units of monomer 2 (M_2) and b long chain branches (LCB), respectively. The superscript (i) refers to the ultimate monomer unit in the radical chain. It should be noted that the ultimate monomer unit in a live copolymer chain can be of either M_1 or M_2 type. As a result, two different symbols, P (for $i=1$) and Q (for $i=2$), are introduced to identify the live copolymer chains ending in an M_1 or in an M_2 monomer unit, respectively.

Let $r_{\mathrm{R}^i_{n,m,b}}$, $r_{\mathrm{D}_{n,m,b}}$ be the corresponding net rates of production of live radicals and dead copolymer chains. 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 copolymer chains. Based on the above kinetic mechanism of free-radical copolymerization, the following general rate functions can be derived[3–5]:

$$\begin{aligned} r_{\mathrm{R}^i_{n,m,b}} = {} & \left(k_{\mathrm{I}_i}\mathrm{PR}^{\bullet}\mathrm{M}_i+\sum_{j=1}^{2} k_{\mathrm{f}_{ji}}\mathrm{M}_i\mathrm{R}^j_{0,0}+k_{\mathrm{f}_{is}}\mathrm{SR}^i_{0,0}\right) \\ & \times\delta(n+i-2,\,m+1-i,b) \\ & +\sum_{j=1}^{2} k_{\mathrm{p}_{ji}}\mathrm{M}_i\mathrm{R}^j_{n+i-2,m+1-i,b}-\sum_{j=1}^{2} k_{\mathrm{p}_{ij}}\mathrm{M}_j\mathrm{R}^i_{n,m,b} \\ & -\mathrm{A}_i\mathrm{R}^i_{n,m,b}+\sum_{j=1}^{2} k_{\mathrm{fp}_{ji}}\mathrm{R}^j_{0,0}(n+m)\mathrm{D}_{n,m,b-1};\quad i=1,\,2 \end{aligned} \tag{9}$$

$$\begin{aligned} r_{\mathrm{D}_{n,m,b}} = {} & \sum_{i=1}^{2}\left(A_i-\sum_{j=1}^{2} k_{\mathrm{tc}_{ij}}\mathrm{R}^j_{0,0}\right)\mathrm{R}^i_{n,m,b} \\ & -(n+m)\mathrm{D}_{n,m,b}\sum_{i=1}^{2}\sum_{j=1}^{2} k_{\mathrm{fp}_{ij}}\mathrm{R}^i_{0,0} \\ & +\frac{1}{2}\sum_{i=1}^{2}\sum_{j=1}^{2} k_{\mathrm{tc}_{ij}}\sum_{r=1}^{n-1}\sum_{q=1}^{m-1}\sum_{x=0}^{b}\mathrm{R}^i_{r,q,x}\mathrm{R}^j_{n-r,m-q,b-x} \end{aligned} \tag{10}$$

where

$$\begin{aligned} \mathrm{A}_i = {} & \sum_{j=1}^{2}(k_{\mathrm{f}_{ij}}\mathrm{M}_j+k_{\mathrm{t}_{ij}}\mathrm{R}^j_{0,0})+k_{\mathrm{f}_{is}}\mathrm{S} \\ & +\sum_{j=1}^{2} k_{\mathrm{fp}_{ij}}\sum_{r=0}^{\infty}\sum_{q=0}^{\infty}\sum_{x=0}^{\infty}(r+q)\mathrm{D}_{r,q,x} \end{aligned} \tag{11}$$

R^i_{00} denotes the total concentration of total live macroradicals of type P (for $i=1$) and Q (for $i=2$), respectively, and is given by the expression:

$$\mathrm{R}^i_{00}=\sum_{n=0}^{N_\infty}\sum_{m=0}^{M_\infty}\sum_{b=0}^{B_\infty}\mathrm{R}^i_{n,m,b} \tag{12}$$

$\delta(n,\,m,\,b)$ is Kronecker's delta and is given by:

$$\delta(n,\,m,\,b)\equiv\delta(n)\delta(m)\delta(b);\quad \delta(i)\equiv\begin{cases}1 & \text{for}\ i=0\\ 0 & \text{for}\ i\neq 0\end{cases} \tag{13}$$

For a batch copolymerization reactor, one can derive the following general balance equation for the $G_{n,m,b}$ copolymer chains:

$$\frac{1}{V}\frac{\mathrm{d}(VG_{n,m,b})}{\mathrm{d}t}=r_{G_{n,m,b}};$$

$$n=1,\ldots,N_\infty,\ m=1,\ldots,M_\infty,\ b=1,\ldots,B_\infty \quad (14)$$

Application of the design equation (14) to the various molecular 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, CCD and DBD. In order 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 that can be easily solved[3-5].

THE METHOD OF MOMENTS

The method of moments is one of the most frequently employed mathematical techniques; it is based on the statistical representation of the MWD, chain length distribution (CLD) or any other distribution of interest (e.g. CCD, DBD) in terms of the leading moments of the respective differential distribution[3].

Contrary to homopolymers, copolymer chains will comprise two types of repeat units. One commonly used notation for identification of a copolymer chain considers only the number of M_1 (n) and M_2 (m) monomer units in the copolymer chain ($G_{n,m}$). Consequently, bivariate distributions are introduced to describe the molecular and compositional developments in a copolymerization system. Accordingly, one can define the corresponding moments of the bivariate chain length–copolymer composition (CLCC) distributions associated with the live and dead copolymer chains:

$$\lambda^i_{k,l}=\sum_{n=1}^{N_\infty}\sum_{m=1}^{M_\infty} n^k m^l R^i_{n,m};\quad R^1_{n,m}\equiv P_{n,m} \text{ and } R^2_{n,m}\equiv Q_{n,m} \quad (15)$$

$$\mu_{k,l}=\sum_{n=1}^{N_\infty}\sum_{m=1}^{M_\infty} n^k m^l D_{n,m} \quad (16)$$

The corresponding reaction rates for the moments $\lambda^i_{k,l}$ and $\mu_{k,l}$ can be obtained from equations (9) and (10) by multiplying each term by $n^k m^l$ and summing the resulting expressions over the total variations of n and m. The final expressions for the moment rate equations are[6]:

$$\begin{aligned} r_{\lambda^i_{k,l}}=&\left(k_{\mathrm{I}_i}\mathrm{PR}^\bullet\mathrm{M}_i+\sum_{j=1}^{2}k_{\mathrm{f}_{ji}}\mathrm{M}_i\lambda^j_{0,0}+k_{\mathrm{f}_{is}}\mathrm{S}\lambda^i_{0,0}\right)\delta(l)\\ &+\sum_{j=1}^{2}k_{\mathrm{p}_{ji}}\mathrm{M}_i\left[(2-i)\sum_r\binom{k}{r}\lambda^j_{r,l}+(i-1)\sum_r\binom{r}{l}\lambda^j_{k,r}\right]\\ &-\sum_{j=1}^{2}k_{\mathrm{p}_{ij}}\mathrm{M}_j\lambda^i_{k,l}-\left(A'_i+\sum_{j=1}^{2}k_{\mathrm{tc}_{ij}}\lambda^j_{0,0}\right)\lambda^i_{k,l} \end{aligned} \quad (17)$$

$$r_{\mu_{k,l}}=\sum_{j=1}^{2}A'_j\lambda^j_{k,l}+\frac{1}{2}\sum_{r=1}^{2}\sum_{q=1}^{2}k_{\mathrm{tc}_{rq}}\sum_i^k\sum_j^l\binom{k}{i}\binom{l}{j}\lambda^r_{i,j}\lambda^q_{k-i,l-j} \quad (18)$$

with

$$A'_i=\sum_{j=1}^{2}k_{\mathrm{f}_{ij}}\mathrm{M}_j+k_{\mathrm{f}_{is}}\mathrm{S}+\sum_{j=1}^{2}k_{\mathrm{td}_{ij}}\lambda^j_{0,0} \quad (19)$$

Based on the above definitions of the moment rate functions, the differential equations governing the molecular and compositional developments in a batch copolymerization reactor can be derived easily (see *Table 1*). In this table, mass balances for initiator, monomers and chain transfer agent are also included. The use of double moments allows the calculation of the individual distributions of monomers M_1 and M_2 in the copolymer chain. The cumulative number average ($\bar{X}_{N_i}$) and weight average ($\bar{X}_{W_i}$) chain length for the i monomer can be calculated in terms of the leading moments of the dead CLCC distribution:

$$\bar{X}_{N_1}=\mu_{1,0}/\mu_{0,0};\quad \bar{X}_{N_2}=\mu_{0,1}/\mu_{0,0} \quad (20)$$

$$\bar{X}_{W_1}=(W_1\mu_{2,0}+W_2\mu_{1,1})/(W_1\mu_{1,0}+W_2\mu_{0,1}) \quad (21)$$

$$\bar{X}_{W_2}=(W_1\mu_{1,1}+W_2\mu_{0,2})/(W_1\mu_{1,0}+W_2\mu_{0,1}) \quad (22)$$

where W_i denotes the molecular weight of the i monomer. Accordingly, the cumulative total number average ($\bar{X}_N$) and weight average ($\bar{X}_W$) chain lengths of the dead CLCC distribution are defined as:

$$\bar{X}_N=\sum_{i=1}^{2}\bar{X}_{N_i}=(\mu_{1,0}+\mu_{0,1})/\mu_{0,0} \quad (23)$$

$$\bar{X}_W=\sum_{i=1}^{2}\bar{X}_{W_i}=(W_1\mu_{2,0}+(W_1+W_2)\mu_{1,1}+W_2\mu_{0,2})/(W_1\mu_{1,0}+W_2\mu_{0,1}) \quad (24)$$

Similarly, the cumulative number and weight average copolymer compositions are defined as:

$$\bar{C}_{N_1}=\mu_{1,0}/(\mu_{1,0}+\mu_{0,1}) \quad (25)$$

Table 1 Design equations for a batch copolymerization reactor based on the double moments of the bivariate CLCC or TCLDB distribution

Initiator

$$\frac{1}{V}\frac{\mathrm{d}(V\mathrm{I})}{\mathrm{d}t}=-k_\mathrm{d}\mathrm{I}$$

Monomers

$$\frac{1}{V}\frac{\mathrm{d}(V\mathrm{M}_1)}{\mathrm{d}t}=r_{\mathrm{M}_1}=-[(k_{\mathrm{p}_{11}}+k_{\mathrm{f}_{11}})\lambda^\mathrm{P}_{0,0}+(k_{\mathrm{p}_{21}}+k_{\mathrm{f}_{21}})\lambda^\mathrm{Q}_{0,0}]\mathrm{M}_1-\mathrm{k}_{\mathrm{I}_1}\mathrm{PR}^\bullet\mathrm{M}_1$$

$$\frac{1}{V}\frac{\mathrm{d}(V\mathrm{M}_2)}{\mathrm{d}t}=r_{\mathrm{M}_2}=-[(k_{\mathrm{p}_{12}}+k_{\mathrm{f}_{12}})\lambda^\mathrm{P}_{0,0}+(k_{\mathrm{p}_{22}}+k_{\mathrm{f}_{22}})\lambda^\mathrm{Q}_{0,0}]\mathrm{M}_2-\mathrm{k}_{\mathrm{I}_2}\mathrm{PR}^\bullet\mathrm{M}_2$$

Modifier

$$\frac{1}{V}\frac{\mathrm{d}(V\mathrm{S})}{\mathrm{d}t}=-(k_{\mathrm{f}_{1S}}\lambda^\mathrm{P}_{0,0}+k_{\mathrm{f}_{2S}}\lambda^\mathrm{Q}_{0,0})\mathrm{S}$$

Volume contraction

$$\frac{1}{V}\frac{\mathrm{d}(V)}{\mathrm{d}t}=-[r_{\mathrm{M}_1}(\mathrm{M}W_1)(1/\rho_1-1/\rho_\mathrm{p})+r_{\mathrm{M}_2}(\mathrm{M}W_2)(1/\rho_2-1/\rho_\mathrm{p})]$$

Chain length distribution moments

$$\frac{1}{V}\frac{\mathrm{d}(V\lambda^i_{k,l})}{\mathrm{d}t}=r_{\lambda^i_{k,l}};\quad i=\mathrm{P,Q};\quad \frac{1}{V}\frac{\mathrm{d}(V\mu_{k,l})}{\mathrm{d}t}=r_{\mu_{k,l}}$$

Fractional monomer conversion

$$x=[V_0(\mathrm{M}_{10}+\mathrm{M}_{20})-V(\mathrm{M}_1+\mathrm{M}_2)]/[V_0(\mathrm{M}_{10}+\mathrm{M}_{20})]$$

$$\bar{C}_{\mathrm{W}_1}=(W_1\mu_{2,0}+W_2\mu_{1,1})/(W_1\mu_{2,0}+(W_1+W_2)\mu_{1,1}+W_2\mu_{0,2}) \tag{26}$$

In many model developments, it is often sufficient to consider the univariate total chain length distribution (TCLD) defined in terms of the total degree of polymerization $(n+m)$. Notice that the moments of the TCLD can be obtained directly in terms of the corresponding bivariate CLCC distribution for the live and dead copolymer chains:

$$\lambda^i_\kappa=\sum_{n=1}^{N_\infty}\sum_{m=1}^{M_\infty}(n+m)^\kappa \mathrm{R}^i_{n,m};\quad \text{where } \mathrm{R}^1_{n,m}\equiv \mathrm{P}_{n,m} \text{ and } \mathrm{R}^2_{n,m}\equiv \mathrm{Q}_{n,m} \tag{27}$$

$$\mu_\kappa=\sum_{n=1}^{N_\infty}\sum_{m=1}^{M_\infty}(n+m)^\kappa \mathrm{D}_{n,m} \tag{28}$$

The reaction rates for the corresponding moments λ^i_κ and μ_κ can be obtained from equations (9) and (10) by multiplying each term by $(n+m)^k$ and summing the resulting expressions over the total variation of $(n+m)$. The final expressions for the moment rate functions are[6]:

$$\begin{aligned}r_{\lambda^i_k}={}&k_{\mathrm{I}_i}\mathrm{PR}^{\bullet}\mathrm{M}_i+\sum_{j=1}^{2}k_{\mathrm{f}_{ji}}\mathrm{M}_i\lambda^j_0+k_{\mathrm{f}_{is}}\mathrm{S}\lambda^i_0+\sum_{j=1}^{2}k_{\mathrm{p}_{ji}}\mathrm{M}_i\sum_r^k\binom{k}{r}\lambda^j_r\\&-\sum_{j=1}^{2}k_{\mathrm{p}_{ij}}\mathrm{M}_j\lambda^i_k-\left(A''_i+\sum_{j=1}^{2}k_{\mathrm{tc}_{ij}}\lambda^j_0\right)\lambda^i_k+\mu_{k+1}\sum_{j=1}^{2}k_{\mathrm{fp}_{ji}}\lambda^j_0\end{aligned} \tag{29}$$

$$\begin{aligned}r_{\mu_k}={}&\sum_{j=1}^{2}A''_j\lambda^j_k+\frac{1}{2}\sum_{r=1}^{2}\sum_{q=1}^{2}k_{\mathrm{tc}_{rq}}\sum_i^k\binom{k}{i}\lambda^r_i\lambda^q_{k-i}\\&-\mu_{k+1}\sum_{i=1}^{2}\sum_{j=1}^{2}k_{\mathrm{fp}_{ij}}\lambda^i_0\end{aligned} \tag{30}$$

where

$$A''_i=\sum_{j=1}^{2}k_{\mathrm{f}_{ij}}\mathrm{M}_j+k_{\mathrm{f}_{is}}\mathrm{S}+\sum_{j=1}^{2}k_{\mathrm{td}_{ij}}\lambda^j_0+\sum_{j=1}^{2}k_{\mathrm{fp}_{ij}}\mu_1 \tag{31}$$

Consequently, the cumulative number average $(\bar{X}_\mathrm{N})$ and weight average $(\bar{X}_\mathrm{W})$ chain length will be given by the following equations:

$$\bar{X}_\mathrm{N}=(\mu_1+\lambda^\mathrm{P}_1+\lambda^\mathrm{Q}_1)/(\mu_0+\lambda^\mathrm{P}_0+\lambda^\mathrm{Q}_0)\cong\mu_1/\mu_0 \tag{32}$$

$$\bar{X}_\mathrm{W}=(\mu_2+\lambda^\mathrm{P}_2+\lambda^\mathrm{Q}_2)/(\mu_1+\lambda^\mathrm{P}_1+\lambda^\mathrm{Q}_1)\cong\mu_2/\mu_1 \tag{33}$$

The polydispersity index is defined as the ratio of the weight average to the number average chain length $(\bar{X}_\mathrm{W}/\bar{X}_\mathrm{N})$.

For branched copolymers, a bivariate distribution, $\mathrm{G}_{x,b}$, defined in terms of the total chain length $(x=n+m)$ and the number of branch points per polymer molecule, b, is usually introduced to characterize the total chain length and branching frequency distribution in the copolymer chains. Accordingly, the moments of the total chain length–degree of branching (TCLDB) distributions for the live and dead copolymer chains are expressed as:

$$\lambda^i_{k,l}=\sum_{n=1}^{N_\infty}\sum_{m=1}^{M_\infty}\sum_{b=1}^{B_\infty}(n+m)^k b^l \mathrm{R}^i_{n,m,b};\quad \mathrm{R}^1_{n,m,b}\equiv\mathrm{P}_{n,m,b},\ \mathrm{R}^2_{n,m,b}\equiv\mathrm{Q}_{n,m,b} \tag{34}$$

$$\mu_{k,l}=\sum_{n=1}^{N_\infty}\sum_{m=1}^{M_\infty}\sum_{b=1}^{B_\infty}(n+m)^k b^l \mathrm{D}_{n,m,b} \tag{35}$$

The corresponding reaction rates for the moments $\lambda^i_{k,l}$ and $\mu_{k,l}$ can be obtained from equations (9) and (10) by multiplying each term by $(n+m)^k b^l$ and summing the resulting expressions over the total variation of n, m and b. The final moment rate equations take the following form:

$$\begin{aligned}r_{\lambda^i_{k,l}}={}&\left(k_{\mathrm{I}_i}\mathrm{PR}^{\bullet}\mathrm{M}_i+\sum_{j=1}^{2}k_{\mathrm{f}_{ji}}\mathrm{M}_i\lambda^j_{0,0}+k_{\mathrm{f}_{is}}\mathrm{S}\lambda^i_{0,0}\right)\delta(l)\\&+\sum_{j=1}^{2}k_{\mathrm{p}_{ji}}\mathrm{M}_i\sum_r^k\binom{k}{r}\lambda^j_{r,l}-\sum_{j=1}^{2}k_{\mathrm{p}_{ij}}\mathrm{M}_j\lambda^i_{k,l}\\&-\left(A'''_j+\sum_{j=1}^{2}k_{\mathrm{tc}_{ij}}\lambda^j_{0,0}\right)\lambda^i_{k,l}+\sum_{r=1}^{2}k_{\mathrm{fp}_{ri}}\lambda^r_{0,0}\sum_j^l\binom{l}{j}\mu_{k+1,j}\end{aligned} \tag{36}$$

$$\begin{aligned}r_{\mu_{k,l}}={}&\sum_{j=1}^{2}A'''_j\lambda^j_{k,l}+\frac{1}{2}\sum_{r=1}^{2}\sum_{q=1}^{2}k_{\mathrm{tc}_{rq}}\sum_i^k\sum_j^l\binom{k}{i}\binom{l}{j}\lambda^r_{i,j}\lambda^q_{k-i,l-j}\\&-\mu_{k+1,l}\sum_{i=1}^{2}\sum_{j=1}^{2}k_{\mathrm{fp}_{ij}}\lambda^i_{0,0}\end{aligned} \tag{37}$$

where $A'''_i=A''_i$ and $B'''_i=B''_i$, with $\lambda^i_0=\lambda^i_{0,0}$, $\mu_1=\mu_{1,0}$.

The differential equations governing the variation of the leading moments of the joint (TCLDB) distributions for the live and dead copolymer molecules in a batch reactor are summarized in *Tables 1* and *2*. From the solution of the double moment differential equations, one can obtain estimates of the cumulative total number average chain length $(\bar{X}_\mathrm{N})$, the cumulative total weight

Table 2 Moment rate functions of the bivariate TCLDB distribution

$$\begin{aligned}r_{\lambda^\mathrm{P}_{0,0}}={}&k_{\mathrm{I}_1}\mathrm{PR}^{\bullet}\mathrm{M}_1+(k_{\mathrm{p}_{21}}\mathrm{M}_1+k_{\mathrm{f}_{21}}\mathrm{M}_1+k_{\mathrm{fp}_{21}}\mu_{1,0})\lambda^\mathrm{Q}_{0,0}\\&-(k_{\mathrm{p}_{12}}\mathrm{M}_2+k_{\mathrm{f}_{12}}\mathrm{M}_2+k_{\mathrm{fp}_{12}}\mu_{1,0})\lambda^\mathrm{P}_{0,0}-(k_{\mathrm{t}_{11}}\lambda^\mathrm{P}_{0,0}+k_{\mathrm{t}_{12}}\lambda^\mathrm{Q}_{0,0})\lambda^\mathrm{P}_{0,0}\\
r_{\lambda^\mathrm{P}_{1,0}}={}&k_{\mathrm{I}_1}\mathrm{PR}^{\bullet}\mathrm{M}_1+[(k_{\mathrm{p}_{11}}+k_{\mathrm{f}_{11}})\lambda^\mathrm{P}_{0,0}+(k_{\mathrm{p}_{21}}+k_{\mathrm{f}_{21}})\lambda^\mathrm{Q}_{0,0}]\mathrm{M}_1\\&-k_{\mathrm{p}_{12}}\lambda^\mathrm{P}_{1,0}\mathrm{M}_2+k_{\mathrm{p}_{21}}\lambda^\mathrm{Q}_{1,0}\mathrm{M}_1+k_{\mathrm{f}_{1\mathrm{S}}}\mathrm{S}\lambda^\mathrm{P}_{0,0}-\lambda^\mathrm{P}_{1,0}(A'+k_{\mathrm{tc}_{11}}\lambda^\mathrm{P}_{0,0}+k_{\mathrm{tc}_{12}}\lambda^\mathrm{Q}_{0,0})\\&+\mu_{2,0}(k_{\mathrm{fp}_{11}}\lambda^\mathrm{P}_{0,0}+k_{\mathrm{fp}_{21}}\lambda^\mathrm{Q}_{0,0})-\mu_{1,0}\lambda^\mathrm{P}_{1,0}(k_{\mathrm{fp}_{11}}+k_{\mathrm{fp}_{12}})\\
r_{\lambda^\mathrm{P}_{0,1}}={}&k_{\mathrm{p}_{21}}\lambda^\mathrm{Q}_{0,1}\mathrm{M}_1-k_{\mathrm{p}_{12}}\lambda^\mathrm{P}_{0,1}\mathrm{M}_2-\lambda^\mathrm{P}_{0,1}(A'+k_{\mathrm{tc}_{11}}\lambda^\mathrm{P}_{0,0}+k_{\mathrm{tc}_{12}}\lambda^\mathrm{Q}_{0,0})\\&+(\mu_{1,0}+\mu_{1,1})(k_{\mathrm{fp}_{11}}\lambda^\mathrm{P}_{0,0}+k_{\mathrm{fp}_{21}}\lambda^\mathrm{Q}_{0,0})-\mu_{1,0}\lambda^\mathrm{P}_{0,1}(k_{\mathrm{fp}_{11}}+k_{\mathrm{fp}_{12}})\\
r_{\lambda^\mathrm{Q}_{0,0}}={}&k_{\mathrm{I}_2}\mathrm{PR}^{\bullet}\mathrm{M}_2-(k_{\mathrm{p}_{21}}\mathrm{M}_1+k_{\mathrm{f}_{21}}\mathrm{M}_1+k_{\mathrm{fp}_{21}}\mu_{1,0})\lambda^\mathrm{Q}_{0,0}\\&+(k_{\mathrm{p}_{12}}\mathrm{M}_2+k_{\mathrm{f}_{12}}\mathrm{M}_2+k_{\mathrm{fp}_{12}}\mu_{1,0})\lambda^\mathrm{P}_{0,0}-(k_{\mathrm{t}_{12}}\lambda^\mathrm{P}_{0,0}+k_{\mathrm{t}_{22}}\lambda^\mathrm{Q}_{0,0})\lambda^\mathrm{Q}_{0,0}\\
r_{\lambda^\mathrm{Q}_{1,0}}={}&k_{\mathrm{I}2}\mathrm{PR}^{\bullet}\mathrm{M}_2+[(k_{\mathrm{p}_{12}}+k_{\mathrm{f}_{12}})\lambda^\mathrm{P}_{0,0}+(k_{\mathrm{p}_{22}}+k_{\mathrm{f}_{22}})\lambda^\mathrm{Q}_{0,0}]\mathrm{M}_2\\&+k_{\mathrm{p}_{12}}\lambda^\mathrm{P}_{1,0}\mathrm{M}_2-k_{\mathrm{p}_{21}}\lambda^\mathrm{Q}_{1,0}\mathrm{M}_1+k_{\mathrm{f}_{2\mathrm{S}}}\mathrm{S}\lambda^\mathrm{Q}_{0,0}-\lambda^\mathrm{Q}_{1,0}(B'+k_{\mathrm{tc}_{12}}\lambda^\mathrm{P}_{0,0}+k_{\mathrm{tc}_{22}}\lambda^\mathrm{Q}_{0,0})\\&+\mu_{2,0}(k_{\mathrm{fp}_{12}}\lambda^\mathrm{P}_{0,0}+k_{\mathrm{fp}_{22}}\lambda^\mathrm{Q}_{0,0})-\mu_{1,0}\lambda^\mathrm{Q}_{1,0}(k_{\mathrm{fp}_{21}}+k_{\mathrm{fp}_{22}})\\
r_{\lambda^\mathrm{Q}_{0,1}}={}&k_{\mathrm{p}_{12}}\lambda^\mathrm{P}_{0,1}\mathrm{M}_2-k_{\mathrm{p}_{21}}\lambda^\mathrm{Q}_{0,1}\mathrm{M}_1-\lambda^\mathrm{Q}_{0,1}(B'+k_{\mathrm{tc}_{12}}\lambda^\mathrm{P}_{0,0}+k_{\mathrm{tc}_{22}}\lambda^\mathrm{Q}_{0,0})\\&+(\mu_{1,0}+\mu_{1,1})(k_{\mathrm{fp}_{12}}\lambda^\mathrm{P}_{0,0}+k_{\mathrm{fp}_{22}}\lambda^\mathrm{Q}_{0,0})-\mu_{1,0}\lambda^\mathrm{Q}_{0,1}(k_{\mathrm{fp}_{21}}+k_{\mathrm{fp}_{22}})\\
r_{\mu_{0,0}}={}&\lambda^\mathrm{P}_{0,0}A'+\lambda^\mathrm{Q}_{0,0}B'+1/2k_{\mathrm{tc}_{11}}(\lambda^\mathrm{P}_{0,0})^2+k_{\mathrm{tc}_{12}}\lambda^\mathrm{P}_{0,0}\lambda^\mathrm{Q}_{0,0}+1/2k_{\mathrm{tc}_{22}}(\lambda^\mathrm{Q}_{0,0})^2\\
r_{\mu_{1,0}}={}&\lambda^\mathrm{P}_{1,0}A'+\lambda^\mathrm{Q}_{1,0}B'+k_{\mathrm{tc}_{11}}\lambda^\mathrm{P}_{0,0}\lambda^\mathrm{P}_{1,0}+k_{\mathrm{tc}_{22}}\lambda^\mathrm{Q}_{0,0}\lambda^\mathrm{Q}_{1,0}\\&+k_{\mathrm{tc}_{12}}(\lambda^\mathrm{P}_{0,0}\lambda^\mathrm{Q}_{1,0}+\lambda^\mathrm{P}_{1,0}\lambda^\mathrm{Q}_{0,0})\\&+(k_{\mathrm{fp}_{11}}+k_{\mathrm{fp}_{12}})(\mu_{1,0}\lambda^\mathrm{P}_{1,0}-\mu_{2,0}\lambda^\mathrm{P}_{0,0})+(k_{\mathrm{fp}_{21}}+k_{\mathrm{fp}_{22}})(\mu_{1,0}\lambda^\mathrm{Q}_{1,0}-\mu_{2,0}\lambda^\mathrm{Q}_{0,0})\\
r_{\mu_{0,1}}={}&\lambda^\mathrm{P}_{0,1}A'+\lambda^\mathrm{Q}_{0,1}B'+k_{\mathrm{tc}_{11}}\lambda^\mathrm{P}_{0,0}\lambda^\mathrm{P}_{0,1}+k_{\mathrm{tc}_{22}}\lambda^\mathrm{Q}_{0,0}\lambda^\mathrm{Q}_{0,1}\\&+k_{tc_{12}}(\lambda^\mathrm{P}_{0,0}\lambda^\mathrm{Q}_{0,1}+\lambda^\mathrm{P}_{0,1}\lambda^\mathrm{Q}_{0,0})\\&+(k_{\mathrm{fp}_{11}}+k_{\mathrm{fp}_{12}})(\mu_{1,0}\lambda^\mathrm{P}_{0,1}-\mu_{1,1}\lambda^\mathrm{P}_{0,0})+(k_{\mathrm{fp}_{21}}+k_{\mathrm{fp}_{22}})(\mu_{1,0}\lambda^\mathrm{Q}_{0,1}-\mu_{1,1}\lambda^\mathrm{Q}_{0,0})\\
r_{\mu_{1,1}}={}&\lambda^\mathrm{P}_{0,1}(k_{\mathrm{p}_{11}}\mathrm{M}_1+k_{\mathrm{p}_{12}}\mathrm{M}_2+k_{\mathrm{tc}_{11}}\lambda^\mathrm{P}_{1,0}+k_{\mathrm{tc}_{12}}\lambda^\mathrm{Q}_{1,0})\\&+\lambda^\mathrm{Q}_{0,1}(k_{\mathrm{p}_{21}}\mathrm{M}_1+k_{\mathrm{p}_{22}}\mathrm{M}_2+k_{\mathrm{tc}_{12}}\lambda^\mathrm{P}_{1,0}+k_{\mathrm{tc}_{22}}\lambda^\mathrm{Q}_{1,0})\\&+[(k_{\mathrm{fp}_{11}}+k_{\mathrm{fp}_{12}})\lambda^\mathrm{P}_{0,0}+(k_{\mathrm{fp}_{21}}+k_{\mathrm{fp}_{22}})\lambda^\mathrm{Q}_{0,0}]\mu_{2,0}\\
r_{\mu_{2,0}}={}&(\lambda^\mathrm{P}_{0,0}+2\lambda^\mathrm{P}_{1,0})(k_{\mathrm{p}_{11}}\mathrm{M}_1+k_{\mathrm{p}_{12}}\mathrm{M}_2)+(\lambda^\mathrm{Q}_{0,0}+2\lambda^\mathrm{Q}_{1,0})(k_{\mathrm{p}_{21}}\mathrm{M}_1+k_{\mathrm{p}_{22}}\mathrm{M}_2)\\&+\lambda^\mathrm{P}_{0,0}(k_{\mathrm{f}_{11}}\mathrm{M}_1+k_{\mathrm{f}_{12}}\mathrm{M}_2)+\lambda^\mathrm{Q}_{0,0}(k_{\mathrm{f}_{21}}\mathrm{M}_1+k_{\mathrm{f}_{22}}\mathrm{M}_2)+2fk_\mathrm{d}\mathrm{I}\\&+k_{\mathrm{tc}_{11}}(\lambda^\mathrm{P}_{1,0})^2+2k_{\mathrm{tc}_{12}}\lambda^\mathrm{Q}_{1,0}\lambda^\mathrm{P}_{1,0}+k_{\mathrm{tc}_{22}}(\lambda^\mathrm{Q}_{1,0})^2+\mathrm{S}(k_{\mathrm{f}_{1\mathrm{S}}}\lambda^\mathrm{P}_{0,0}+k_{\mathrm{f}_{2\mathrm{S}}}\lambda^\mathrm{Q}_{0,0})\end{aligned}$$

where

$$A'=k_{\mathrm{f}_{11}}\mathrm{M}_1+k_{\mathrm{f}_{12}}\mathrm{M}_2+k_{\mathrm{f}_{1\mathrm{S}}}\mathrm{S}+k_{\mathrm{td}_{11}}\lambda^\mathrm{P}_{0,0}+k_{\mathrm{td}_{12}}\lambda^\mathrm{Q}_{0,0}$$

$$B'=k_{\mathrm{f}_{21}}\mathrm{M}_1+k_{\mathrm{f}_{22}}\mathrm{M}_2+k_{\mathrm{f}_{2\mathrm{S}}}\mathrm{S}+k_{\mathrm{td}_{12}}\lambda^\mathrm{P}_{0,0}+k_{\mathrm{td}22}\lambda^\mathrm{Q}_{0,0}$$

average chain length ($\bar{X}_W$), the number average degree of branching ($\bar{B}_N$) and the weight average degree of branching ($\bar{B}_W$). These molecular averages are defined as:

$$\bar{X}_N=\mu_{1,0}/\mu_{0,0} \qquad \bar{X}_W \cong \mu_{2,0}/\mu_{1,0} \tag{38}$$

$$\bar{B}_N=\mu_{0,1}/\mu_{0,0} \qquad \bar{B}_W \cong \mu_{1,1}/\mu_{1,0} \tag{39}$$

The branching density, $\bar{B}_d$, will be given by the ratio $\bar{B}_N/\bar{X}_N$.

ON THE VALIDITY OF THE STEADY-STATE APPROXIMATIONS

Chain addition polymerization reactions involve active intermediates (i.e. free radicals) whose total concentration at all times is very small. As a result, the QSSAs for these intermediates are commonly used. Assuming a negligible change of the volume of the reaction medium, one can derive the following equation governing the rate of change of the total radical population in a batch reactor:

$$\mathrm{d}(\mathrm{P}_{n,m,b}+\mathrm{Q}_{n,m,b})/\mathrm{d}t=R_i-R_t \tag{40}$$

Assuming that the first QSSA for the total radical concentration is valid, equation (40) can be replaced by a corresponding algebraic equation:

$$R_i \cong R_t \tag{41}$$

Equation (41) implies that the rate of radical initiation (R_i) will be approximately equal to the rate of radical termination (R_t). Notice that equation (41) does not imply that the total live radical concentration remains constant with time; it merely asserts that the concentration of intermediates, even though it is time dependent, may be closely approximated by an algebraic equation (41), as long as the derivative $\mathrm{d}(\mathrm{P}_{n,m,b}+\mathrm{Q}_{n,m,b})/\mathrm{d}t$ is small with respect to the remaining terms in equation (40).

If, in addition to approximation (41), one can assume that the QSSA can also be applied to the separate radical populations P and Q, then one can show that the reaction rate of a P radical with an M_2 monomer will be approximately equal to the reaction rate of a Q radical with an M_1 monomer[41]:

$$k_{\mathrm{p}_{12}}\mathrm{P}_{n,m,b}\mathrm{M}_2=k_{\mathrm{p}_{21}}\mathrm{Q}_{n,m,b}\mathrm{M}_1 \tag{42}$$

This means that the number of $\mathrm{M}_1\mathrm{M}_2$ sequences in a polymer chain will be equal to the number of $\mathrm{M}_2\mathrm{M}_1$ sequences ± 1. For long copolymer chains (e.g. chains with a degree of polymerization of 1000), the error introduced by equation (42) will be in the order of $\pm 0.1\%$. On the other hand, when the polymer chain length is very short (e.g. 10, as might be the case in solution copolymerizations), the error introduced by this approximation will be of the order of $\pm 10\%$.

RESULTS AND DISCUSSION

The validity of the two QSSAs is subsequently examined in relation to the solution copolymerization of methylmethacrylate–styrene (MMA–St), and the bulk copolymerization of *p*-methylstyrene–acrylonitrile (pmSt–ACN).

Solution copolymerization of MMA–St

This system was selected as a representative example of the production of linear copolymers. The solution copolymerization of MMA–St has been studied experimentally by Pittman-Bedjer[42]; the values of the kinetic rate constants are given in ref. 42.

Since the selected copolymerization takes place in a dilute solution, diffusion-controlled reactions will not be important[43–46]. In *Figure 1*, the net radical initiation rate, R_i, is plotted against the total radical termination rate, R_t, during the course of the copolymerization. The results of this figure confirm the validity of equation (40) and its application to this copolymerization system.

In *Figure 2*, the term $k_{\mathrm{p}_{12}}\lambda_0^{\mathrm{P}}\mathrm{M}_2$ is plotted against the term $k_{\mathrm{p}_{21}}\lambda_0^{\mathrm{Q}}\mathrm{M}_1$. It can be seen that the values of the two terms are almost identical up to a conversion of about 90%, but they differ at higher conversions. This is due to the fact that at high conversions the average chain length decreases (i.e. it becomes less than 20), therefore

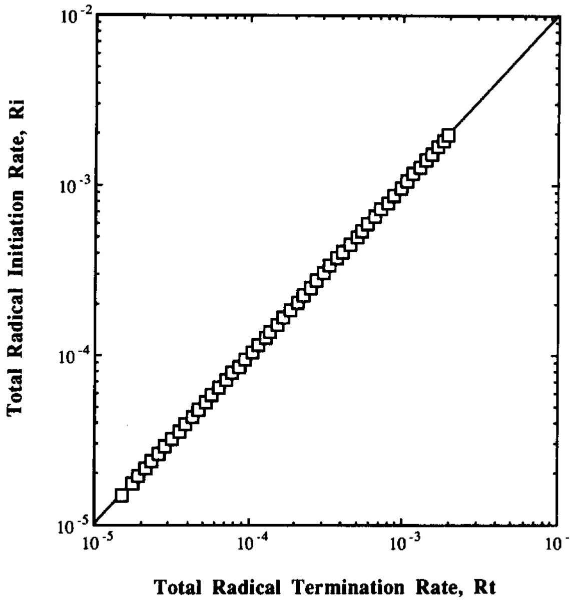

Figure 1 Rate of radical initiation (R_i) *versus* rate of radical termination (R_t) for the solution copolymerization of MMA–St at 80°C, $[\mathrm{I}]_0=0.2\ \mathrm{g\ mol\ l^{-1}}, f_{10}=0.75$

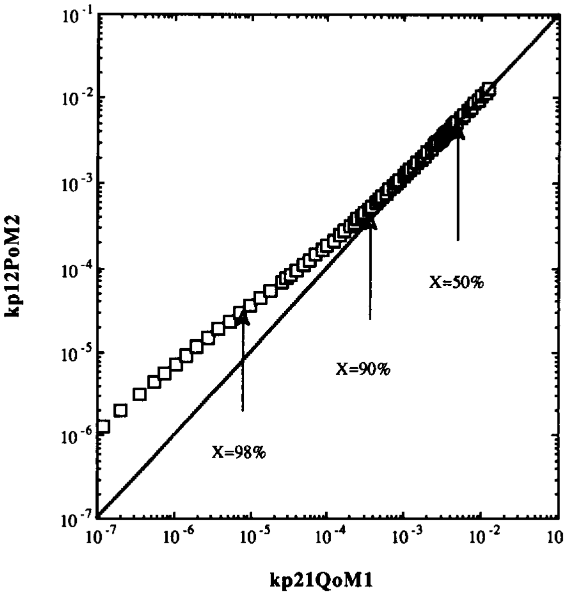

Figure 2 Verification of the second QSSA applicable to the separate radical populations P and Q. Solution copolymerization of MMA–St (experimental conditions as in *Figure 1*)

the application of the second QSSA to the two separate populations of P and Q radicals will not hold true.

Conversion and molecular weight simulation results obtained with or without the application of the two approximations are shown in *Figures 3* and *4*. It is apparent that no significant differences exist between the two numerical solutions, which means that in dilute solution copolymerizations both approximations will be valid.

The bulk copolymerization of p*-methylstyrene–acrylonitrile*

This system was selected as a representative example of the production of branched copolymers and the appearance of diffusion-controlled phenomena in the copolymerization kinetics. It was experimentally studied by Yaraskavitch *et al.*[47,48]. The values of the kinetic rate constants, as well as the relationships describing the diffusional limitations in k_t and k_p, can be found in refs 47 and 48.

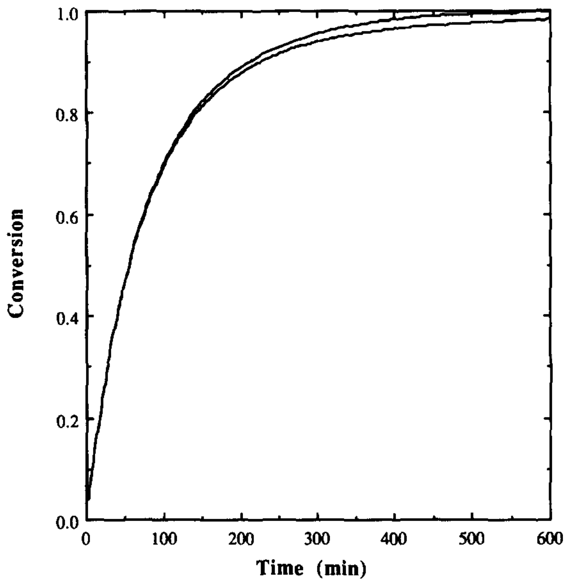

Figure 3 Conversion–time histories calculated by the 'exact' and 'approximate' model. Solution copolymerization of MMA–St at 80°C, $[I]_0 = 0.2\ \mathrm{g\,mol\,l^{-1}}$, $f_{10} = 0.75$

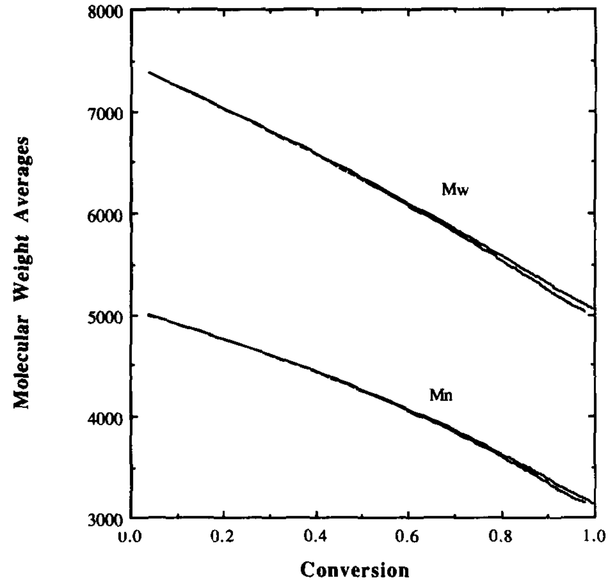

Figure 4 Exact and approximate average molecular weights for the solution copolymerization of MMA–St (experimental conditions as in *Figure 3*)

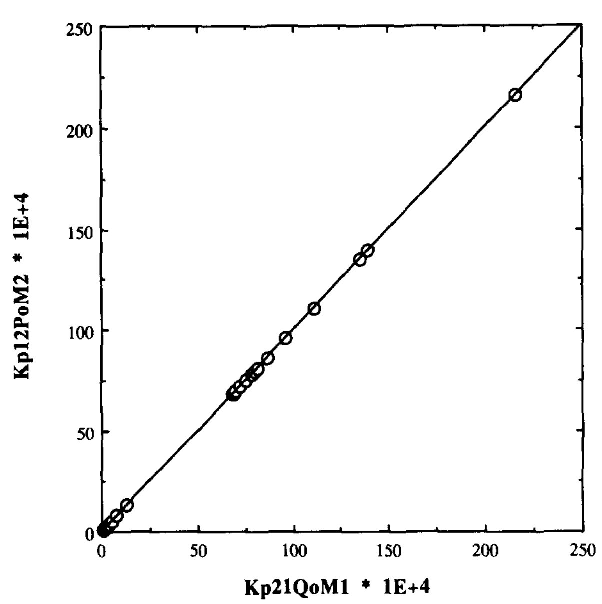

Figure 5 Verification of the second QSSA applicable to the separate radical populations P and Q. Bulk copolymerization of pMSt–ACN at 60°C, $[I]_0 = 0.01\ \mathrm{g\,mol\,l^{-1}}$, $f_{10} = 0.56$

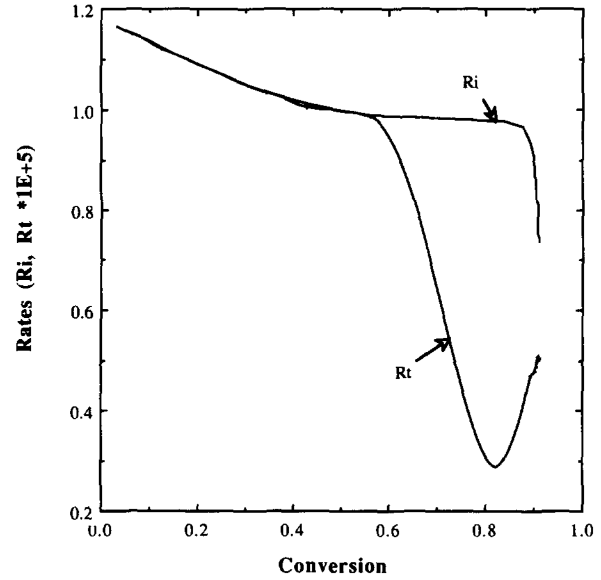

Figure 6 Variation of R_i and R_t with respect to monomer conversion for the bulk copolymerization of pMSt–ACN (experimental conditions as in *Figure 5*)

The validity of the second QSSA for the separate populations of P and Q radicals is illustrated in *Figure 5*. It can be seen that no significant differences exist between the values of the two terms $k_{p_{12}}\lambda_0^P M_1$ and $k_{p_{21}}\lambda_0^Q M_1$, since the average chain length for this system[47] is about 3000. Thus, the error introduced by the second QSSA will be less than ±0.033%. On the other hand, the appearance of diffusion-controlled phenomena results in a significant reduction of the termination rate constants, which causes a decrease of the termination rate (R_t). In *Figure 6*, the total radical initiation rate, R_i, is plotted with respect to the variation of the total radical termination rate, R_t. It is apparent that after a certain conversion (~60%), the two rates show a significant deviation. This means that at high conversions, the QSSA for the total radical population will not be strictly valid and its application will result in an overestimation of the total radical population.

Simulation results obtained with or without the application of the two QSSAs are shown in *Figures 7* and *8*. Discrete points in these figures indicate the experimental results of Yaraskavitch[47]. It is interesting to note that no significant differences exist between the calculated values of conversion and number average molecular weights obtained with or without the use of two approximations. However, the application of the QSSA results in a slight overestimation of weight average molecular weight compared to the values obtained by the exact solution. From *Figure 8* it can also be seen that the polydispersity index increases as the monomer conversion increases.

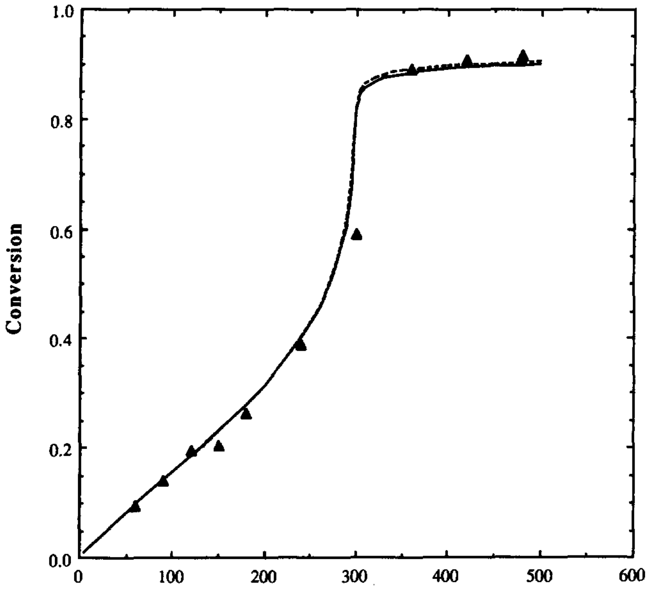

Figure 7 Conversion–time histories calculated by the 'exact' (——) and 'approximate' (---) model. Bulk copolymerization of pMSt–ACN at 60°C, $[I]_0=0.01\,g\,mol\,l^{-1}$, $f_{10}=0.56$. ▲, Experimental data[47]: $k_{fp}=1.2k_p$

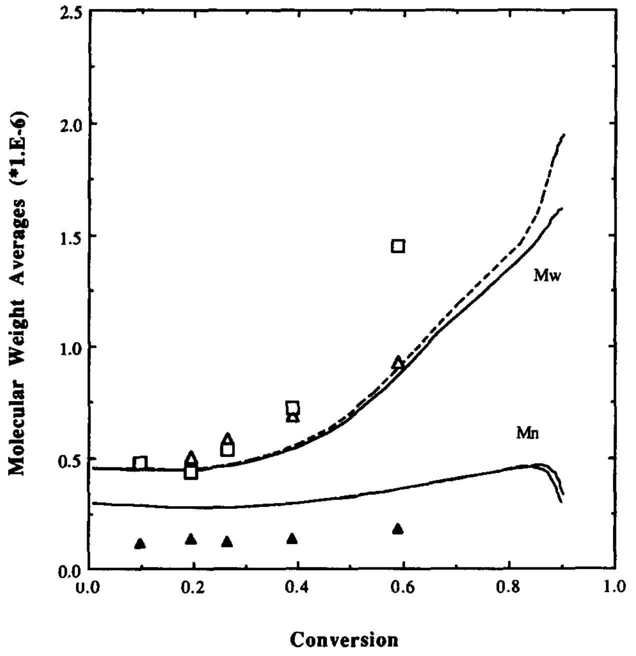

Figure 8 Average molecular weights for the bulk copolymerization of pMSt–ACN (experimental conditions as in *Figure 7*). Experimental data[47]: ▲, M_n and △, M_w (size exclusion chromatography); □, M_w (low angle laser light scattering). ——, 'Exact' and ---, 'approximate' model

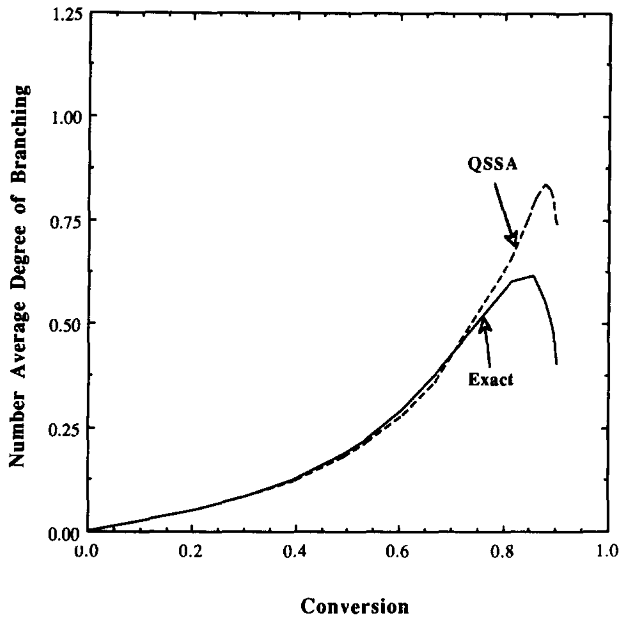

Figure 9 Number average degree of branching for the pMSt–ACN bulk copolymerization (experimental conditions as in *Figure 7*)

Finally, in *Figure 9* the number average degree of branching obtained by the solution of the exact as well as the approximate model (e.g. application of the QSSA) is plotted with respect to conversion. It can be seen that the two models yield the same values for $\bar{B}_N$ up to a conversion of about 70%. However, at higher conversions a significant difference appears in the calculated values of $\bar{B}_N$.

CONCLUSIONS

In the present investigation, the validity of the QSSAs commonly applied in high conversion free-radical copolymerization reactions was examined by a direct comparison of model results obtained with or without the use of the two approximations. Molecular and compositional changes occurring during copolymerizations in a batch reactor were modelled using the method of moments.

It was shown that the second QSSA, applicable to the separate radical populations P and Q, will not be valid for free-radical copolymerizations leading to the production of very short polymer chains, which is usually the case in dilute solution copolymerizations. Despite this, errors in the calculated values of conversion and final copolymer properties were not significant. In the presence of diffusion-controlled reactions, for both linear and branched copolymerizations, the QSSA for the total radical concentration will not be valid at high conversions. However, it was found that its application did not significantly affect the calculated values of conversion and number average molecular weight, although a slight overestimation of the weight average molecular weight was observed.

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REFERENCES

1 Mayo, F. R. and Walling, C. *Chem. Rev.* 1950, **46**, 191

2 Bamford, C. H., Barb, W. G., Jenkins, A. D. and Onyon, D. F. 'Kinetics of Vinyl Polymerization by Radical Mechanisms', Butterworths, London, 1958

3 Ray, W. H. *J. Macrom. Sci., Rev. Macrom. Chem.* 1972, **C8**, 1

4 Biesenberger, J. A. and Sebastian, D. H. 'Principles of Polymerization Engineering', Wiley-Interscience, New York, 1983

5 Tirrell, M., Galvan, R. and Laurence, R. L. in 'Chemical Reaction and Reactor Engineering' (Eds J. J. Carberry and A. Varma), Marcel Dekker, New York, 1987

6 Arriola, D. J. and Ray, W. H. AIChE Annual Meeting, New York, 1987

7 Hamielec, A. E., MacGregor, J. F. and Penlidis, A. *Makromol. Chem., Macromol. Symp.* 1987, **10/11**, 521

8 Sharma, D. K. and Soane, D. S. *Macromolecules* 1988, **21**, 700

9 Storti, G., Morbidelli, M. and Carra, S. in 'Computer Application in Applied Polymer Science II' (Ed. T. Provder), *Am. Chem. Soc. Symp. Ser.* **404**, American Chemical Society, Washington, DC, 1989, Ch. 30

10 Tobita, H. and Hamielec, A. E. in 'Computer Application in Applied Polymer Science II' (Ed. T. Provder), *Am. Chem. Soc. Symp. Ser.* **404**, American Chemical Society, Washington, DC, 1989, Ch. 21

11 Tobita, H. and Hamielec, A. E. *Makromol. Chem., Macromol. Symp.* 1988, **20/21**, 501

12 Tobita, H. and Hamielec, A. E. *Macromolecules* 1989, **22**, 3098

13 Congalidis, J. P., Richards, J. R. and Ray, W. H. *AIChE J.* 1989, **35** (6), 891

14 Dubé, M. A., Rilling, K. and Penlidis, A. *J. Appl. Polym. Sci.* 1991, **43**, 2137

15 Tobita, H. and Hamielec, A. E. *Polymer* 1991, **32**, 2641

16 Braun, D. and Czerwinsky, W. K. in 'Chemistry and Physics of Macromolecules' (Eds E. W. Fischer, R. C. Schulz and H. Sillescu), VCH, Weinheim, 1991, Ch. 6

17 Achilias, D. S. and Kiparissides, C. *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.* 1992, **C32** (2), 183

18 Atiqullah, M., Hassan, M. M. and Beg, S. A. *J. Appl. Polym. Sci.* 1992, **46**, 879

19 Urretabizkaia, A., Arzamendi, G. and Asua, J. M. *Chem. Eng. Sci.* 1992, **47** (9–11), 2579

20 Zabisky, R. C. M., Chan, W.-M., Gloor, P. E. and Hamielec, A. E. *Polymer* 1992, **33**, 2243

21 Butala, D. N., Liang, W. R. and Choi, K. Y. *J. Appl. Polym. Sci.* 1992, **44**, 1759

22 Yoon, W. J. and Choi, K. Y. *J. Appl. Polym. Sci.* 1992, **46**, 1353

23 Yoon, W. J. and Choi, K. Y. *Polymer* 1992, **33**, 4582

24 Storti, G., Polotti, G., Canu, P. and Morbidelli, M. *J. Polym. Sci., Part A: Polym. Chem.* 1992, **30**, 751

25 Tobita, H. and Hamielec, A. E. *Polymer* 1992, **33**, 3647

26 Tobita, H. *Macromolecules* 1992, **25**, 2671

27 Tobita, H. *Macromolecules* 1993, **26**, 836

28 Fontenot, K. and Schork, F. J. *Polym. React. Eng.* 1992–1993, **1**(2), 289

29 Engelmann, U. and Schmidt-Naake, G. *Makromol. Chem., Theory Simul.* 1993, **2**, 275

30 Stockmayer, W. H. *J. Chem. Phys.* 1944, **12**, 143

31 Hamielec, A. E., Hodgins, J. W. and Tebbens, K. *AIChE J.* 1967, **13**(6), 1087

32 Ray, W. H. *Can. J. Chem. Eng.* 1969, **47**, 503

33 Biesenberger, J. A. and Capinpin, R. J. *J. Appl. Polym. Sci.* 1972, **16**, 695

34 Dionisio, J. M. and O'Driscoll, K. F. *J. Polym. Sci., Polym. Phys. Edn* 1980, **18**, 241

35 Chiu, W. Y., Carratt, G. M. and Soong, D. S. *Macromolecules* 1983, **16**, 348

36 Coyle, D. J., Tulig, T. J. and Tirrell, M. *Ind. Eng. Chem. Fundam.* 1985, **24**, 343

37 Venkateshwaran, G. and Kumar, A. *J. Appl. Polym. Sci.* 1992, **45**, 187

38 Chaimberg, M. and Cohen, Y. *Ind. Eng. Chem., Res.* 1990, **29**, 1152

39 Budde, U. and Wulkow, M. *Chem. Eng. Sci.* 1991, **46** (2), 497

40 Canu, P. and Ray, W. H. *Comput. Chem. Eng.* 1991, **15** (8), 549

41 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, 1953

42 Pittman-Bedjer, T. P. PhD thesis, University of Minnesota, 1982

43 Mita, I. and Horie, K. *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.* 1987, **C27**(1), 91

44 Zhu, S., Tian, Y., Hamielec, A. E. and Eaton, D. R. *Polymer* 1990, **31**, 154

45 Zhu, S. and Hamielec, A. E. *Macromolecules* 1989, **22**, 3093

46 Achilias, D. S. and Kiparissides, C. *Macromolecules* 1992, **25**, 3739

47 Yaraskavitch, I. M. MSc thesis, McMaster University, Hamilton, 1986

48 Yaraskavitch, I. M., Brash, J. L. and Hamielec, A. E. *Polymer* 1987, **28**, 489

NOMENCLATURE

$\bar{B}_{\mathrm{d}}$	Branching density
$\bar{B}_{\mathrm{N}}$	Number average degree of branching
$\bar{B}_{\mathrm{W}}$	Weight average degree of branching
f	Initiator efficiency
$\mathrm{G}_{n,m,b}$	Polymer chains having n M_1 monomer units, m M_2 monomer units and b branches
I	Initiator
k_{d}	Initiator decomposition rate constant
$k_{\mathrm{f}_{ij}}$	Kinetic rate constant for the transfer of a radical of type i to a monomer of type j
$k_{\mathrm{f}_{is}}$	Kinetic rate constant for the transfer of a radical of type i to a modifier molecule
$k_{\mathrm{fp}_{ij}}$	Kinetic rate constant for the transfer of a radical of type i to a polymer molecule and resulting in a radical of type j
k_{I_j}	Kinetic rate constant for the initiation of a primary radical with a monomer of type j
$k_{p_{ij}}$	Propagation rate constant of a radical of type i with a monomer of type j
$k_{\mathrm{tc}_{ij}}$	Termination by combination rate constant for a radical of type i with a radical of type j
$k_{\mathrm{td}_{ij}}$	Termination by disproportionation rate constant for a radical of type i with a radical of type j
$k_{\mathrm{t}_{ij}}$	$k_{\mathrm{tc}_{ij}}+k_{\mathrm{td}_{ij}}$
M	Monomer
$\mathrm{PR}^{\bullet}$	Primary radical resulting from the fragmentation of the initiator
$r_{\mathrm{G}_{n,m,b}}$	Net rate of production of copolymer chains
R_{i}	Rate of radical initiation
R_{t}	Rate of radical termination
S	Concentration of the modifier
t	Time
V	Reactor volume
W_i	Molecular weight of the i monomer
x	Total monomer conversion
$\bar{X}_{\mathrm{N}}$	Number average chain length
$\bar{X}_{\mathrm{W}}$	Weight average chain length
$\delta(\chi)$	Kronecker's delta
$\lambda^{i}_{k,l}$	Moments of the live radical chains
$\mu_{k,l}$	Moments of the dead polymer chains
ρ_i, ρ_{P}	Monomer i ($i=1, 2$) and polymer density, respectively

Superscripts

i	Type of the terminal unit in a radical chain
P	Radical terminating in M_1 monomer
Q	Radical terminating in M_2 monomer