Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 44 (2003) 7021–7032

polymer

www.elsevier.com/locate/polymer

Calculation of molecular weight distribution in non-linear free radical copolymerization

G.D. Verros*

Department of Informatics and Computer Technology, Technological Educational Institute (T.E.I.) of Lamia, 35100 Lamia, Greece

Received 3 April 2003; received in revised form 9 June 2003; accepted 21 August 2003

Abstract

An effective method for calculating molecular weight distribution in non-linear free radical copolymerization is proposed in this work. This method is based on the direct integration of a system of non-linear differential equations describing the conservation of 'dead' polymer and 'live' radicals in a reactor. A fairly general kinetic mechanism was employed to describe the complex kinetics of non-linear copolymerization. Assumptions made were justified by comparing calculated distributions with results obtained without making any assumption. This method may be applied to industrial free radical polymerization systems, thus leading to a more rational design of polymerization reactors.

Keywords: Free radical copolymerization; Molecular weight distribution; Mathematical modeling

1. Introduction

The production of polymers with desired end-use properties is of significant financial importance to the polymer industry. One of the most important molecular properties that control the end-use characteristics of polymers is the molecular weight distribution (MWD) as it directly affects the physical, mechanical and rheological properties of the final product.

The importance of predicting final product end-use properties as a function of process conditions in free radical polymerization has led to the development of several mathematical models, dealing with the calculation of MWD. These models can be classified to statistical models [1–7], the instantaneous MWD method [8–13], the continuous variable approximation [14–21], the method of moments [22–28], generating functions [29,30], numerical inversion of z-transforms [31] and analysis Fourier [32], deconvolution techniques [33,34], discrete weighted residuals [35–37], numerical fractionation [38–40] and the discrete population balance approach [41,42].

For copolymerization, the only applicable methods to obtain MWD are generating functions [29,30], the instantaneous MWD method [8–13] discrete weighted residuals [35–37] and the statistical approach [1–7]. The aim of our present work is to calculate the MWD in non-linear free radical copolymerization including branching reactions such as transfer to polymer. According to Liu and Amundson [43], Detar and Detar [44], Ray [45], this complex task could be achieved by directly solving the original mass conservation balances. This approach was applied to simplified reaction schemes [43,44] but only the implementation of powerful computer facilities, can allow its application to complex copolymerization kinetics.

In the following sections, the kinetic mechanism, as well as the corresponding reaction rates are briefly reviewed and the problem formulation by direct integration is given. Finally, results are discussed and conclusions are drawn.

2. Kinetic mechanism and polymerization rate functions

Copolymer chains comprise two types of repeated units. As a result, three subscripts are required in order to identify a copolymer chain having long chain branches. We denote with $R^i_{n,m,b}$ 'live' radicals and with $P_{n,m,b}$ 'dead' polymer, having n units of monomer 1 (M_1), m units of monomer 2 (M_2) and b long chain branches (LCB) per molecule,

---

* Address: P.O. Box 454, Plagiari, GR-57500 Epanomi, Greece. Tel.: +30-6972722651; fax: +30-2231022465.

E-mail address: verros@vergina.eng.auth.gr (G.D. Verros).

0032-3861/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2003.08.029

respectively. The superscript i refers to the ultimate monomer unit in the radical chain. A fairly general kinetic mechanism was used to described non-linear free radical polymerization [45,46]:

Chemical initiation:

$$\mathrm{I}\xrightarrow{k_{\mathrm{d}}}2\mathrm{PR}^*;\quad \mathrm{PR}^*+M_j\xrightarrow{k_{\mathrm{I}j}}R^j_{2-j,j-1,0};\quad j=1,2$$

Propagation:

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

Chain Transfer to Monomer:

$$R^i_{n,m,b}+M_j\xrightarrow{k_{\mathrm{tm}_{ij}}}R^j_{2-j,j-1,0}+P_{n,m,b};\quad i=1,2;\quad j=1,2$$

Chain Transfer to Modifier:

$$R^i_{n,m,b}+\mathrm{S}\xrightarrow{k_{ts_i}}R^i_{2-i,i-1,0}+P_{\mathrm{n,m,b}};\quad \mathrm{i}=1,2$$

Chain Transfer to Polymer:

$$R^i_{n,m,b}+P_{r,q,s}\xrightarrow{k_{tp_{ij}}}R^j_{r,q,s+1}+P_{\mathrm{n,m,b}};\quad \mathrm{i}=1,2;\quad \mathrm{j}=1,2$$

Termination by Combination:

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

Termination by Disproportionation:

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

Here, I is initiator, PR* stands for an initiator fragment, M represents monomer, S is modifier. It was also assumed that each polymer chain has no more than one radical, no depropagation reactions occur and the penultimate effect can be included in given rate constants. The above reaction mechanism is strictly valid at low conversion before the onset of auto-acceleration phenomenon (gel effect). Besides this limitation, the present reaction mechanism describes important industrial processes such as the ethylene copolymerization with various comonomers (vinyl acetate, acrylic acid, etc) at high pressure [47,48]. Tirrell and co-workers [49] developed a model for the gel effect in the homopolymerization case, taking into account the termination kinetic rate constants' dependence on the chain length. However, to our knowledge this model was not extended to copolymerization due to the complexity of reaction mechanism.

Based on the above kinetic mechanism a set of algebraic or differential equations, depending on the reactor type and mode of operation (steady state or dynamic) is derived in order to describe the mass conservation of the various reactants in a polymerization reactor. For a batch polymerization reactor, one can derive the following design equation: $\mathrm{d(VG)}/\mathrm{d}t = Vr_{\mathrm{G}}$. For a semi-batch polymerization reactor as well as a continuous stirred tank reactor (CSTR) operating under transient conditions the general mass balance equation takes the following form: $\mathrm{d(VG)}/\mathrm{d}t = F_{\mathrm{G,in}} - F_{\mathrm{G,out}} + Vr_{\mathrm{G}}$. Finally, for a tubular reactor operating under steady state conditions and by assuming the absence of axial and radial mixing, the design equation is: $\mathrm{d}(u_z\mathrm{G})/\mathrm{d}z = r_{\mathrm{G}}$. r_{G} denotes reaction rates of various species (initiator, monomer(s), modifier, live and dead polymer molecules), V stands for reactor volume, t is time, z represents axial coordinate and u_z is the axial velocity.

Combining the reactor design equations with the proper copolymerization rate functions will result in an extremely large system, which must be solved numerically to obtain the bivariate number chain length distribution (NCLD). In Appendix A, the respective copolymerization rate functions are given.

So far, this large system has been transformed to a low order system using the method of moments introduced by Ray [30,45], in order to calculate some characteristic averages such as the number and weight average molecular weights or the mean copolymer composition, in terms of the leading moments of the bivariate number chain length distribution.

An alternative way to write the polymerization rate functions is to introduce the total chain length $L = n + m$, instead of using symbols $R^i_{n,m}$ and $P_{n,m}$ and derive polymerization rate functions for the total number chain length distribution (TNCLD).

Let, $r_{R^i_L}$ and r_{P_L}, denote, in the case of copolymerization, the net rates of the production of live radicals and of dead polymer molecules, having a total chain length L, respectively. Based on the above kinetic mechanism, the following general rate functions can be derived:

$$\begin{aligned} r_{R^i_L} &= \Big(k_{\mathrm{I}i}\mathrm{PR}^*M_i + \sum_{j=1}^{2} k_{\mathrm{tm}ji}M_iR^j_0 + k_{\mathrm{ts}i}SR^i_0\Big)\delta(L-1) \\ &\quad + \sum_{j=1}^{2} k_{\mathrm{p}ji}M_iR^j_{L-1} - \sum_{j=1}^{2} k_{\mathrm{p}ij}M_jR^i_L - A_iR^i_L \\ &\quad + \sum_{j=1}^{2} k_{\mathrm{tp}ji}CC^{(i)}_L LP_LR^j_0 \\ r_{P_L} &= \sum_{i=1}^{2}\Big(A_i - \sum_{j=1}^{2} k_{\mathrm{tc}ij}R^i_0\Big)R^i_L - \sum_{i=1}^{2}\sum_{j=1}^{2} k_{\mathrm{tp}ji}CC^{(i)}_L LP_LR^j_0 \\ &\quad + \frac{1}{2}\sum_{i=1}^{2}\sum_{j=1}^{2} k_{\mathrm{tc}ij}\sum_{r=1}^{L-1} R^i_rR^j_{L-r} \end{aligned} \tag{1}$$

$$\begin{aligned} A_i &= \sum_{j=1}^{2}\big(k_{\mathrm{tm}ij}M_j + (k_{\mathrm{tc}ij} + k_{\mathrm{td}ij})R^j_0\big) + k_{\mathrm{ts}i}S + \sum_{j=1}^{2} k_{\mathrm{tp}ij}\sum_{n=0}^{\infty}\sum_{m=0}^{\infty} \\ &\quad \times n^{2-i}m^{i-1}P_{n,m} \end{aligned}$$

Where δ is Kronecker's delta; R^i_L, P_L represent concentration of live and dead polymers having total chain length

L, respectively. R_0^i is the total radical concentration of radicals type i and is identical to zero order moment (λ_{00}^i) of live radicals MWD. Summations $\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{2-i}m^{i-1}P_{n,m}$ are identical to the first order moments of dead polymer MWD, respectively (see Appendix A). $CC_L^{(i)} = \sum_{L=n+m} \times n^{2-i}m^{i-1}P_{n,m}/LP_L$ denotes copolymer chain composition.

The above system (Eq. (1)) can be transformed using several mathematical techniques to a low order partial differential equations system. This low order system could be solved analytically or numerically to obtain polymer MWD. The aim of our present work is to calculate polymer MWD by direct integration of the large system of ordinary summation-difference equations describing macromolecular mass conservation in polymerization reactors (Eq. (1)). This is examined in detail in Section 3.

3. Problem formulation

The first step for solving the problem by direct integration is to choose the correct integration scheme. The equations of the model include the low molecular weight species mass balances such as initiator(s), monomer(s), modifier(s), primary radicals, coupled with energy and momentum conservation equations and the moment distribution equations as well as the macromolecular (live and dead polymer) equations. The former type of equation is usually stiff but the latter not stiff which renders a simultaneous integration of the equation system ineffective. Therefore we have chosen the following two level algorithm.

The first level includes integration of monomer(s), initiator(s) and modifier(s) primary radical and moments' stiff equations using multi-step predictor–corrector methods, such as Gear's method. The definition of stiff differential equations as well as a detailed description of single step and predictor–corrector algorithms are given elsewhere [50]. The second level includes integration of live and dead polymer mass balances using a single step method. Explicit methods such as forward Euler are preferred in cases that physical parameters (kinetic rate constants, physical properties etc.) depend on calculated distribution or on chain length distribution. Implicit methods such as backward Euler require additional computations but offer improved stability properties. In our present work the backward Euler integration scheme has been chosen.

To implement the dual integration scheme we divide time (batch reactor, semi-batch reactor or dynamic CSTR) or reactor length (PFR) in sub-intervals. In each subinterval low molecular weight species mass balances and moments equations were solved using Gear's method. The calculated values were used in the second level where integration by backward Euler of macromolecular species balances takes place.

Model equations (Eq. (1)) could be solved numerically to obtain the total weight molecular weight distribution (TWMWD) in non-linear copolymerization. However, it is impractical to calculate this distribution by solving the original dead polymer and live radical mass balances without making any kinetic assumption.

In order to increase computational efficiency and decrease the required time for execution four well established assumptions were implemented: (a) the uniform copolymer composition assumption, (b) the long chain hypothesis (c) the quasi steady state (QSSA) approximation for live copolymer radicals and (d) the continuous variable approximation (CVA).

In order to calculate MWD we have to calculate the copolymer composition distribution $CC_L^{(i)}$ (see Eq. (1)) from the entire bivariate number chain length distribution (NCLD) and solve an extremely large system ($\sim 10^9$ equations) that is impractical. Following Stockmayer [3] we simply assume that the composition $CC_L^{(i)}$ follows uniform distribution and therefore its value is equal to its mean value $\overline{CC^{(i)}}$. This assumption was shown by Stockmayer [3], Ray [45], Hamielec and co-workers [10], to be valid for linear copolymer chains having total length (L) above 100. According to Ray [45], this assumption can be viewed as a consequence of long chain hypothesis (LCH) which assumes that the initiation rate of a polymer chain is much slower than the corresponding propagation rates. In other words, monomer is consumed mainly by propagation reactions and polymer chains are quite long.

To reduce execution time for the solution of the problem we have to resort to the quasi-steady approximation (QSSA). Hamielec and co-workers [51–53] successfully implemented this assumption to calculate MWD by instantaneous MWD method in linear copolymerization with diffusion controlled termination reactions. According to the QSSA the rate of variation with time (or axial length in PFR) of live radical concentration, is relatively small, compared to the other terms of Eq. (1). Consequently, the first term of reactor design equation drops for live radical mass balances and these equations are transformed to a highly coupled algebraic system, ($r_{R_L^i} = 0$) which is solved numerically in order to calculate live radical MWD.

The continuous variable approximation (CVA) was implemented to decrease the number of equations of the algebraic live radical mass balance system. The CVA introduced by Bamford and Jenkins [14], Zeman and Amundson [15,16] was utilized in many works [17–21] dealing with the calculation of MWD in free radical homopolymerization. By applying the CVA the discrete system is transformed to a continuous variable system by expanding the concentration of live radicals having total chain length L, in Taylor expansion truncated after the second term:

$$R_{L-1}^i = R_L^i - \left.\frac{\partial R^i}{\partial x}\right|_{x=L} + \frac{1}{2}\left.\frac{\partial^2 R^i}{\partial x^2}\right|_{x=L} \qquad i = 1,2 \qquad (2)$$

The derivatives in the above expression can be directly calculated by using a finite difference scheme significantly reducing the number of equations to be solved:

$$\left.\frac{\partial R^i}{\partial x}\right|_{x=L} = \frac{(R^i_L - R^i_{L-\eta\mathrm{step}})}{\eta\mathrm{step}};\ \left.\frac{\partial^2 R^i}{\partial x^2}\right|_{x=L} = \frac{(R^i_L - 2R^i_{L-\eta\mathrm{step}} + R^i_{L-2\eta\mathrm{step}})}{\eta^2_{\mathrm{step}}}; \qquad (3)$$

$i = 1, 2$

Where ηstep is the chain length step used in the discretization.

Implementation of the CVA reduces the number of mass balances of live radicals to be solved and transforms them to an ordinary differential equations system with respect to chain length that can be directly solved using the finite difference scheme of Eq. (2).

An additional difficulty in solving directly polymerization rate functions arises from the calculation of summations appearing in the termination by combination reaction rates (Eq. (1)). These summations transformed to integrals by the CVA were evaluated using 7-point Newton–Cotes integration rule.

By using the above assumptions one can directly calculate dead polymer TWMWD by solving the corresponding mass balances (Eq. (1)). The detailed approach is given in Appendix B.

It should be noted here, that the TWMWD could be obtained by direct integration of the original macromolecular balances (Eq. (1)) without invoking QSSA or CVA ('theoretical solution'). The validity of these assumptions for non-linear copolymerization, is re-examined in this work, by comparing the calculated distribution with the theoretical solution. Both solutions (with and without assumptions) follow the same integration scheme. The only difference is the computational efficiency of the solution.

Moreover, the uniform copolymer composition assumption was justified, for the first time to our knowledge, in non-linear copolymerization by comparing the mean molecular weights of the calculated distribution with the corresponding ones obtained by the method of moments. Additionally, in Appendix A, a review of the moments of bivariate number chain length distribution (NCLD) and the definition of the mean molecular weights as well as copolymer composition is given. Detailed equations for the leading moments reaction rates of bivariate NCLD are given by Ray and co-workers [30,45,54].

Please, note that in the present method only the zero order moments of live radical distribution and the first order moments of dead polymer distribution are required to calculate the entire MWD.

4. Results and discussion

For our simulation studies an isothermal batch reactor of 1lt was considered. Model parameters are given in Table 1. At low conversion, the rate of termination of the macroradical coils is governed by segmental diffusion of the coils ends. The increasing polymer concentration lowers the thermodynamic quality of the solvent, shrinking the macroradical coils and thereby increasing the segmental concentration gradient across them. [51–53] According to O'Driscoll and co-workers [55], this results in a reduction in the rate of polymerization during the initial steps of polymerization that can be modeled by the following equation:

$$\frac{k_{\mathrm{t}ij}}{k_{\mathrm{t}0,ij}} = \frac{k_{\mathrm{tseg},ij}}{k_{\mathrm{t}0,ij}} = 1 + \Delta_{ij}[\mathrm{c}] \qquad i,j = 1,2 \qquad (4)$$

where $k_{\mathrm{t}ij}$ are the termination rate constants (either by combination or by disproportionation), $k_{\mathrm{t}0,ij}$ denotes termination kinetic rate constants at zero polymer concentration, $k_{\mathrm{tseg},ij}$ are the segmental-diffusion-controlled termination rate constants, [c] is the polymer concentration in g/l and Δ_{ij} is a parameter dependent on macroradical molecular weight and solvent quality. Following Hamielec and co-workers [51–53] we set Δ_{ij} equal to 2.5×10^{-3} l/g for all termination reactions.

As the reaction proceeds and the polymer concentration increases, there is a transition from segmental- to translational-diffusion control. This transition corresponds to the onset of the gel effect and is associated with a critical total

Table 1
Physical constant for copolymerization numerical experiment

A. *Kinetic rate constants*		
Reaction	Value	Units
Initiation, k_{d} (efficiency: 0.5)	2.2×10^{-4}	s^{-1}
Chain initiation, $k_{\mathrm{i}1}$	$(k_{\mathrm{p}11} + k_{\mathrm{p}21})$	$\mathrm{l\,mol^{-1}\,s^{-1}}$
Chain initiation, $k_{\mathrm{i}2}$	$(k_{\mathrm{p}22} + k_{\mathrm{p}12})$	$\mathrm{l\,mol^{-1}\,s^{-1}}$
Propagation, $k_{\mathrm{p}11}$	1971.0	$\mathrm{l\,mol^{-1}\,s^{-1}}$
Propagation, $k_{\mathrm{p}12}$	9900.0	$\mathrm{l\,mol^{-1}\,s^{-1}}$
Propagation, $k_{\mathrm{p}21}$	900.0	$\mathrm{l\,mol^{-1}\,s^{-1}}$
Propagation, $k_{\mathrm{p}22}$	2971.0	$\mathrm{l\,mol^{-1}\,s^{-1}}$
Transfer to monomer, $k_{\mathrm{tm}11}$	$k_{\mathrm{p}11} \times 10^{-3}$	$\mathrm{l\,mol^{-1}\,s^{-1}}$
Transfer to monomer, $k_{\mathrm{tm}12}$	$k_{\mathrm{p}11} \times 210^{-3}$	$\mathrm{l\,mol^{-1}\,s^{-1}}$
Transfer to monomer, $k_{\mathrm{tm}21}$	$k_{\mathrm{p}11} \times 410^{-3}$	$\mathrm{l\,mol^{-1}\,s^{-1}}$
Transfer to monomer, $k_{\mathrm{tm}22}$	$k_{\mathrm{p}11} \times 1.10^{-3}$	$\mathrm{l\,mol^{-1}\,s^{-1}}$
Transfer to polymer, $k_{\mathrm{tp}11}$	$k_{\mathrm{p}11} \times 5.510^{-3}$	$\mathrm{l\,mol^{-1}\,s^{-1}}$
Transfer to polymer, $k_{\mathrm{tp}12}$	$k_{\mathrm{p}11} \times 5.510^{-3}$	$\mathrm{l\,mol^{-1}\,s^{-1}}$
Transfer to polymer, $k_{\mathrm{tp}21}$	$k_{\mathrm{p}11} \times 5.510^{-3}$	$\mathrm{l\,mol^{-1}\,s^{-1}}$
Transfer to polymer, $k_{\mathrm{tp}22}$	$k_{\mathrm{p}11} \times 5.10^{-2}$	$\mathrm{l\,mol^{-1}\,s^{-1}}$
Termination by combination, $k_{\mathrm{tc}0,11}$	1.55×10^{9}	$\mathrm{l\,mol^{-1}\,s^{-1}}$
Termination by combination, $k_{\mathrm{tc}0,12}$	$(k_{\mathrm{tc}11} \times k_{\mathrm{tc}22})0.5$	$\mathrm{l\,mol^{-1}\,s^{-1}}$
Termination by Combination, $\mathrm{k}_{\mathrm{tc}0,22}$	2.55×10^{9}	$\mathrm{l\,mol^{-1}\,s^{-1}}$
B. *Initial concentrations* (mol/l)		
Initiator	0.05	
Monomer 1	13.82	
Monomer 2	10.82	

conversion X_{crit}.[51–53]. Total conversion X, is defined as:

$$X = \frac{\sum_{i=1,2} C_{m0,i} y_{mi}}{\sum_{i=1,2} C_{m0,i}}$$

where $C_{m0,i}$ is the ith monomer initial concentration and y_{mi} is the ith monomer fractional conversion as calculated by the respective monomer balance.

Without any loss of generality we assume a X_{crit} value of 0.2 for copolymerization with kinetic rate constants given in Table 1.

To enlarge the effect of uniform copolymer composition on calculated MWD, high values of transfer to polymer kinetic rate constants are selected. Molecular weight of monomer 1 was 86 g/g mol and the respective value for monomer 2 was 158 g/g mol.

The computational efficiency of the method was shown by selecting relatively small values of the integration parameters. The step for the integration of dead polymer equations with respect to time (t_{step}) was 10 s; chain length step (ηstep) was 1, resulting in a highly coupled non-linear system of 1.2×10^5 differential equations. With these parameters, total real time for execution in a personal computer operating at 2.7 GHz was about 2 min for the solution with assumptions as opposed to 3 h to find a solution without employing QSSA and CVA (theoretical solution). Source codes written in FORTRAN 77 are available by directly contacting the author of this work.

Fig. 1 shows monomers conversion and mole fraction copolymer composition as a function of polymerization time.

Figs. 2 and 3 illustrate the effect of chain length step (ηstep) and time step ($t$step) on the calculated MWD. Fig. 2 completely justifies continuous variable approximation because a remarkable increase in chain length step (ηstep) has little effect on the calculated distribution. Fig. 3 shows that a significant increase in time step integration introduce negligible errors in calculations.

In Figs. 4–7 we compare, average molecular weights as calculated independently from the method of moments with present model calculations to validate the assumption of uniform copolymer composition implemented in model development. Please, note that in the calculations of average molecular weights using the method of moments (see Appendix A), the assumption of uniform copolymer composition was not made.

It should be noted here, that as the chain transfer to monomer kinetic rate constants increase (Case IV) more polymer chains with low molecular weight are produced leading to a decrease in number average molecular weight. In Case IV, the uniform copolymer composition assumption is not expected to be valid because most polymer chains produced, have small chain length. However, an excellent agreement for Case IV of average molecular weights as calculated using the method of moments with calculated values by using the present method is illustrated in Figs. 6 and 7. This agreement is attributed to the fact, that as the transfer to monomer kinetic rate constants increase the contribution in molecular weight development of transfer to polymer reactions decrease. Therefore, the error due to uniform copolymer assumption becomes negligible. The excellent agreement illustrated in all cases (Figs. 4–7) completely justifies the uniform copolymer composition assumption. It should be noted here that the critical conversion X_{crit} considered in all simulations, corresponds to the maximum molecular weights (Table 1,Case I). In fact, as the transfer to polymer kinetic rate constants decrease (Cases II and III) or as the transfer to monomer kinetic rate constants increase (Case IV) molecular weights decrease,

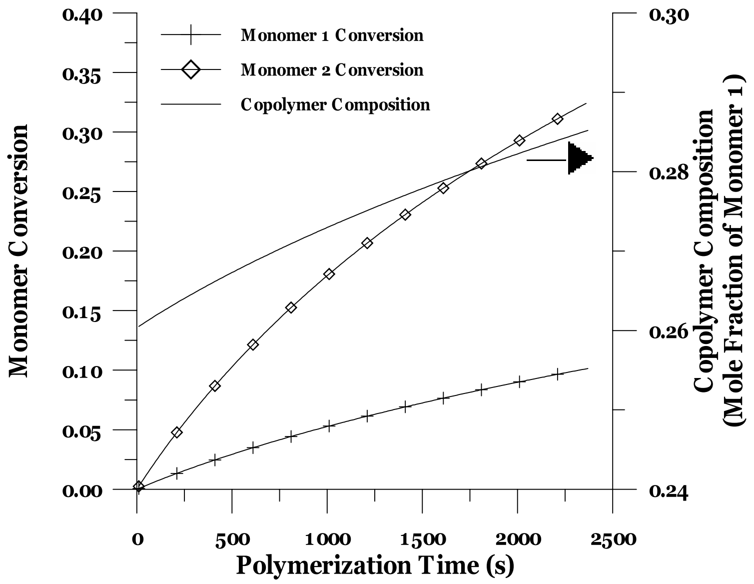

Fig. 1. Monomer conversions and copolymer composition as a function of polymerization time.

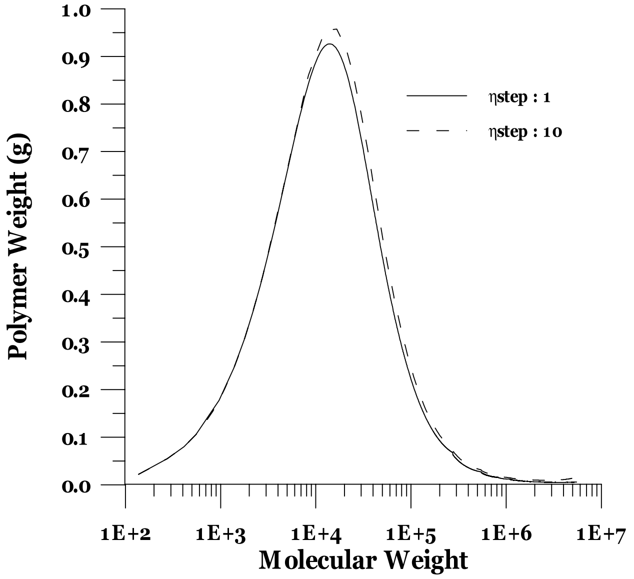

Fig. 2. Total weight molecular weight distribution as a function of chain length step (ηstep). Polymerization time 2400 s. Kinetic rate constants as in Table 1. $t_{\mathrm{step}} = 10$ s.

the onset of the gel effect is delayed, its magnitude is reduced and therefore higher values of X_{crit} are expected.

Figs. 8 and 9 depict TWMWD after 2400 s of polymerization, as a function of chain transfer to polymer and chain transfer to monomer kinetic rate constants. In Fig. 8, theoretical solution and calculated distributions coincide, justifying QSSA. It was also shown that as the transfer to polymer kinetic rate constants increase, calculated maximum of MWDs corresponding to NAMW decreases, while there is an accumulation of polymer chains at high molecular weight, leading to an increase of WAMW and broader distributions.

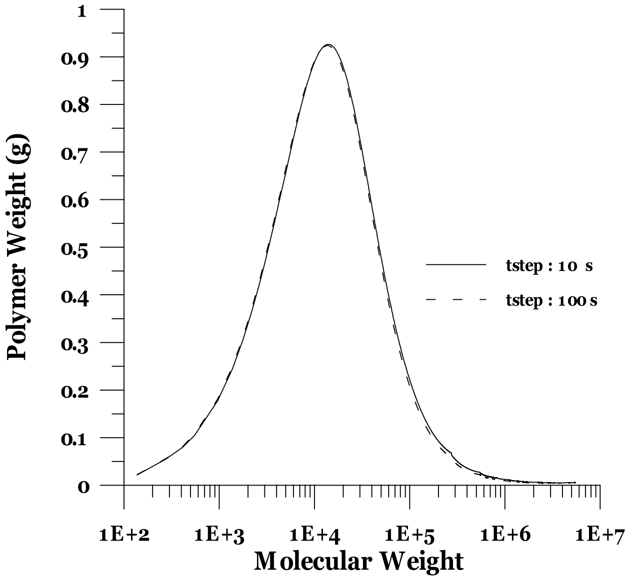

Fig. 3. Total weight molecular weight distribution as a function of time step ($t$step). Polymerization time 2400 s. Kinetic rate constants as in Table 1. ηstep = 1.

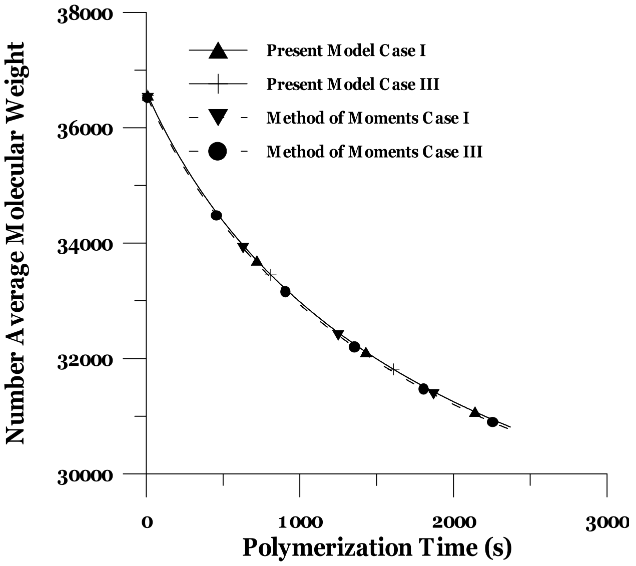

Fig. 4. Comparison of calculated number average molecular weights with obtained by the method of moments. Kinetic rate constants: Case I as in Table 1. Case II $k'_{\mathrm{tp}ij} = 0.5 \times k_{\mathrm{tp}ij}$. Case III $k''_{\mathrm{tp}ij} = 0.1 \times k_{\mathrm{tp}ij}$. $n_{\mathrm{step}} = 1$; $t_{\mathrm{step}} = 10$ s.

In Fig. 9, the effect of chain transfer to monomer kinetic rate constants on calculated distribution is shown. The increase of chain transfer to monomer kinetic rate constant leads to narrower distributions with increased maximum values.

In Fig. 10 TWMWD is depicted as a function of polymerization time. As time proceeds, polymer weight near the tail of the distribution increases, due to the acceleration of the chain transfer to polymer reaction rate, caused by an increase in conversion and resulting in a significant increase in WAMW (Fig. 5). However, the

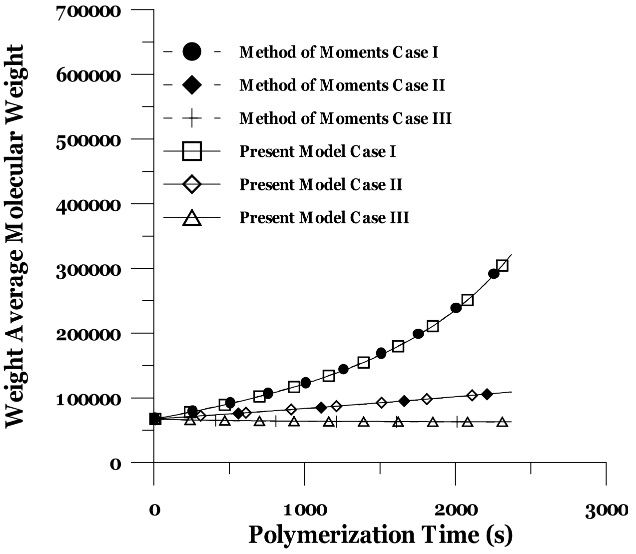

Fig. 5. Comparison of calculated weight average molecular weights with obtained by the method of moments. Kinetic rate constants: Case I as in Table 1. Case II $k'_{\mathrm{tp}ij} = 0.5 \times k_{\mathrm{tp}ij}$. Case III $k''_{\mathrm{tp}ij} = 0.1 \times k_{\mathrm{tp}ij}$. $n_{\mathrm{step}} = 1$; $t_{\mathrm{step}} = 10$ s.

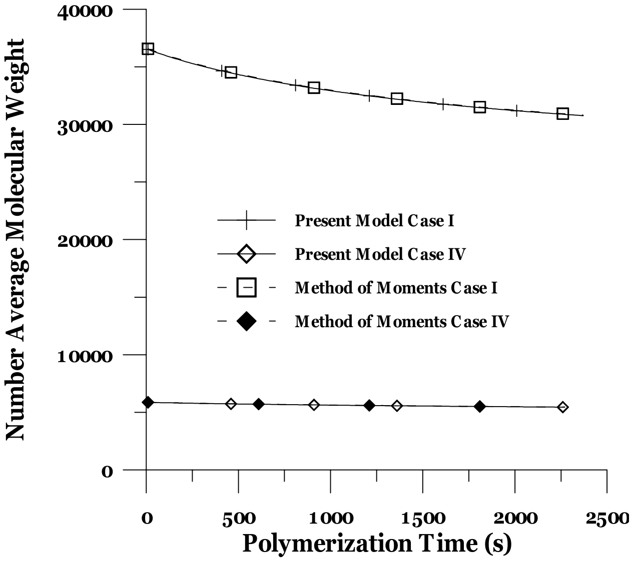

Fig. 6. Comparison of calculated number average molecular weights with obtained by the method of moments. Kinetic rate constants: Case I as in Table 1. Case IV $k'_{tmij} = 10 \times k_{tmij}$. $n_{\text{step}} = 1$; $t_{\text{step}} = 10$ s.

position of the distribution peak is almost unaffected, resulting in an almost constant NAMW (Fig. 4).

To further validate reaction mechanism and modeling assumptions, the proposed method for the calculation of TWMWD is applied to p-methylstyrene (p-Mst)/acrylonitrile (AN) bulk copolymerization in a batch reactor. This copolymerization was studied experimentally and theoretical by Hamielec and co-workers [53] and is a typical example of chemical initiated non-linear copolymerization. The kinetic rate constants used in their model are given in Table 2. The segmental diffusion was modeled by O'Driscoll and co-workers model [55] (Eq. (4)). According to Hamielec and co-workers [53] the Δ_{ij} is equal to 2.5×10^{-3} l/g for all termination reactions. Simulations in our present work were run until the onset of the gel effect which is associated with a total critical conversion X_{crit}. Values of X_{crit} as a function of process conditions are given in the original work of Hamielec and co-workers [53]. Polymerization temperature was equal to 80 °C. The following numerical parameters were used in all simulations: $t$step was 10 s; chain length step (ηstep) was 1, resulting in a highly coupled non-linear system of 1.2×10^5 differential equations.

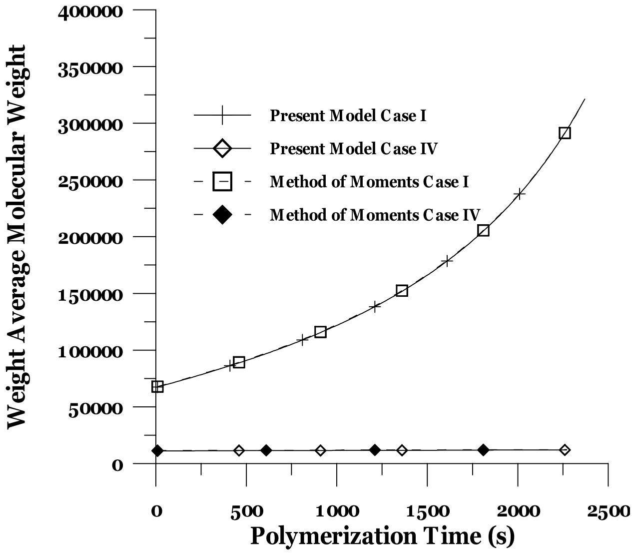

Fig. 7. Comparison of calculated weight average molecular weights with obtained by the method of moments. Kinetic rate constants: Case I as in Table 1. Case IV $k'_{\text{tm}ij} = 10 \times k_{\text{tm}ij}$. $n_{\text{step}} = 1$; $t_{\text{step}} = 10$ s.

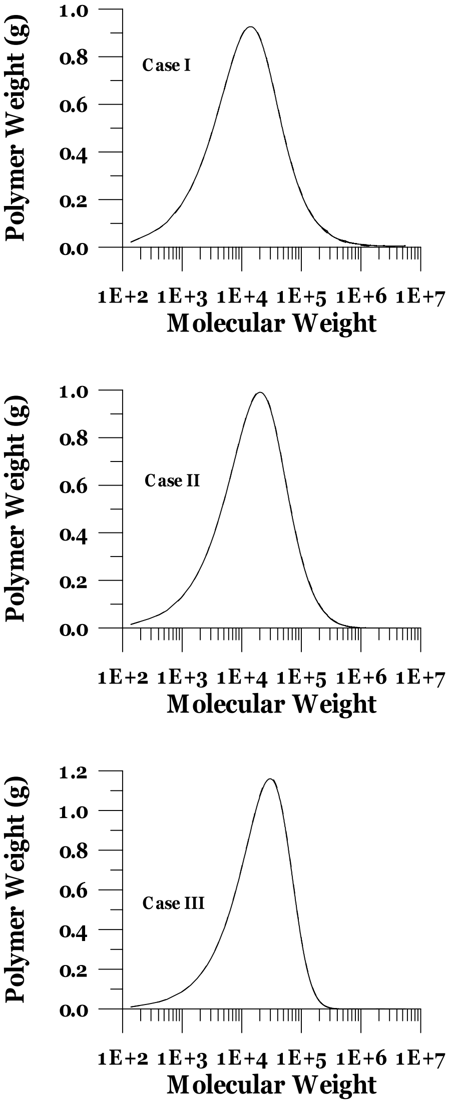

Fig. 8. Total weight molecular weight distribution at polymerization time 2400s' as a function of transfer to polymer kinetic rate constants. Continuous lines: model predictions. Broken lines: theoretical solution. Kinetic rate constants: Case I as in Table 1. Case II $k'_{\text{tp}ij} = 0.5 \times k_{\text{tp}ij}$. Case III $k''_{\text{tp}ij} = 0.1 \times k_{\text{tp}ij}$. $n_{\text{step}} = 1$; $t_{\text{step}} = 10$ s.

Following Hamielec and co-workers [53], in Figs. 11 and 12 total conversion for different initial initiator (AIBN) concentration and initial p-Mst mole fraction (F_0) is compared with experimental data [53].

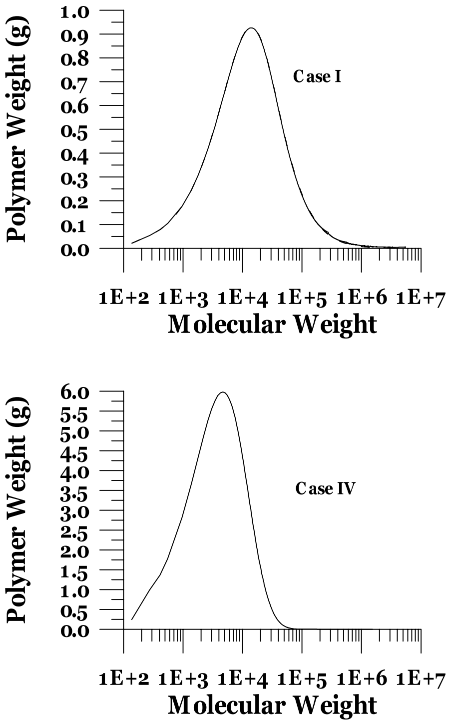

Fig. 9. Total weight molecular weight distribution at polymerization time 2400s' as a function of transfer to monomer kinetic rate constants. Kinetic rate constants: Case I as in Table 1. Case IV $k'_{\mathrm{tm}ij} = 10 \times k_{\mathrm{tm}ij}$. $n_{\mathrm{step}} = 1$; $t_{\mathrm{step}} = 10$ s.

In Figs. 13 and 14 p-Mst residual mole fraction is plotted as a function of total conversion for different initial initiator (AIBN) concentration and initial p-Mst mole fraction (F_0). The good agreement depicted between experimental data and model predictions shown in Figs. 11–13 validates the reaction mechanism assumptions such as the inclusion of the penultimate effect in given rate constants at low conversion.

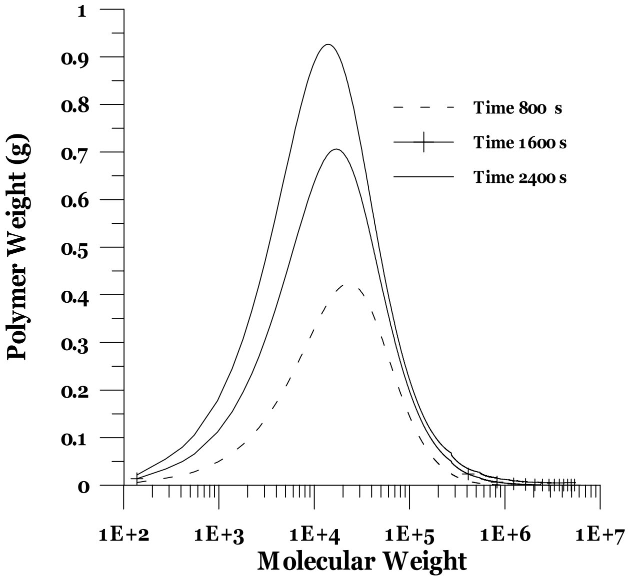

Fig. 10. Total weight molecular weight distribution as a function of polymerization time. Kinetic rate constants as in Table 1. $n_{\mathrm{step}} = 1$; $t_{\mathrm{step}} = 10$ s.

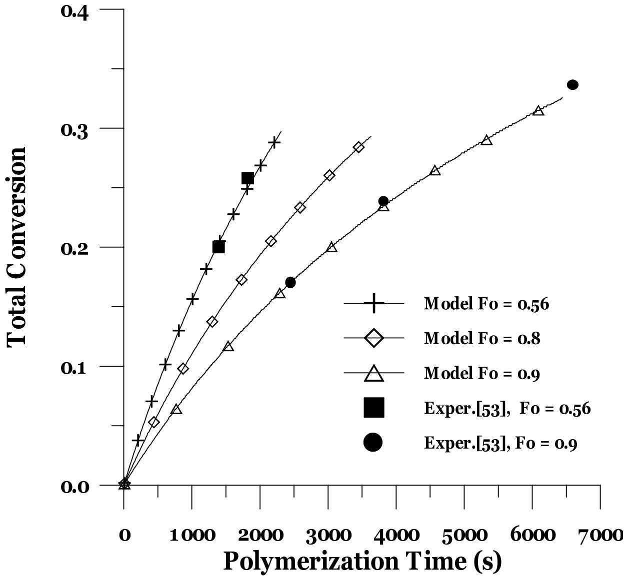

Fig. 11. Total conversion as a function of polymerization time for p-Mst/AN copolymerization. Polymerization temperature 80 °C. Initial initiator concentration 0.01 M.

In Figs. 15 and 16 average molecular weights for different initial initiator (AIBN) concentration and initial p-Mst mole fraction are compared with present model calculations as well as with experimental data obtained by Hamielec and co-workers [53] by using size exclusion chromatography (SEC) and low-angle laser light scattering photometry (LALLSP). The excellent agreement between present model average molecular weight calculations and the ones obtained using the method of moments validates the present method.

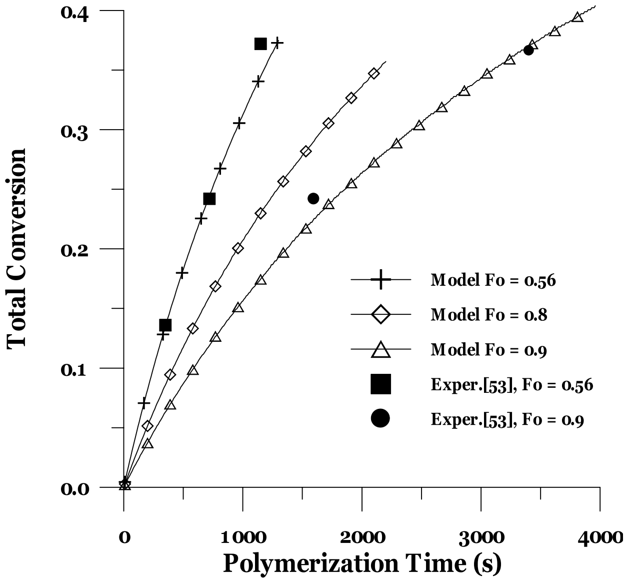

Fig. 12. Total conversion as a function of polymerization time for p-Mst/AN copolymerization. Polymerization temperature 80 °C. Initial initiator concentration 0.05 M.

Table 2
Kinetic rate constants for PMS-AN copolymerization [53,56]

Kinetic rate constants	Value	Units
Initiation AIBN, k_d (efficiency: 1)	$1.05 \times 10^{15} \exp(-15500/T)$	s^{-1}
Chain initiation, k_{i1}	$(k_{p11} + k_{p21})$	$l\ mol^{-1}\ s^{-1}$
Chain initiation, k_{i2}	$(k_{p22} + k_{p12})$	$l\ mol^{-1}\ s^{-1}$
Propagation, k_{p11}	$1.05 \times 10^{7} \exp(-3557/T)$	$l\ mol^{-1}\ s^{-1}$
Reactivity ratio, $r_1 = k_{p11}/k_{p12}$	0.26 ± 0.02	–
Reactivity ratio, $r_2 = k_{p22}/k_{p21}$	0.066 ± 0.029	–
Propagation, k_{p22}	$1.047 \times 10^{8} \exp(-3663/T)$	$l\ mol^{-1}\ s^{-1}$
Transfer to polymer, k_{tp11}	$1.1 \times 10^{-4} k_{p11}$	$l\ mol^{-1}\ s^{-1}$
Transfer to polymer, k_{tp12}	$1.1 \times 10^{-4} k_{p11}$	$l\ mol^{-1}\ s^{-1}$
Termination by combination, $k_{tc0,11}$	$(1.31 \pm 0.13) \times 10^{8}$	$l\ mol^{-1}\ s^{-1}$
Termination by combination, $k_{tc0,12}$	$(1.31 \pm 0.13) \times 10^{8}$	$l\ mol^{-1}\ s^{-1}$
Termination by combination, $k_{tc0,22}$	$(1.31 \pm 0.13) \times 10^{8}$	$l\ mol^{-1}\ s^{-1}$

Finally, in Fig. 17 TWMWD, as calculated using the present method, is depicted as a function of total conversion. Maximum value of the distribution is almost constant, resulting in an almost constant NAMW (Fig. 15) and narrower distributions are obtained at higher total conversions corresponding to a decrease in WAMW (Fig. 15).

5. Conclusions

In the present work we developed a simple and effective method for calculating MWD of non-linear copolymers produced by free radical polymerization. This method is based on direct integration using single step methods of a large non-linear system of differential equations describing the conservation of macromolecular species in the reactor. Application of the quasi steady state approximation and the continuous variable approximation as well as uniform copolymer composition assumption reduce computational load and execution time, without introducing significant error in results.

This method has general value and can be applied in other free radical polymerization systems to calculate MWD, thus leading to a more rational design of polymerization reactors.

Acknowledgements

The author is thankful to Dr NA Malamataris, Department of Mechanical Engineering, T.E.I. of W. Macedonia, for useful discussions and conscientious proofreading. Mrs K Somerscales is acknowledged for her help in the English language. The reviewers are acknowledged for their

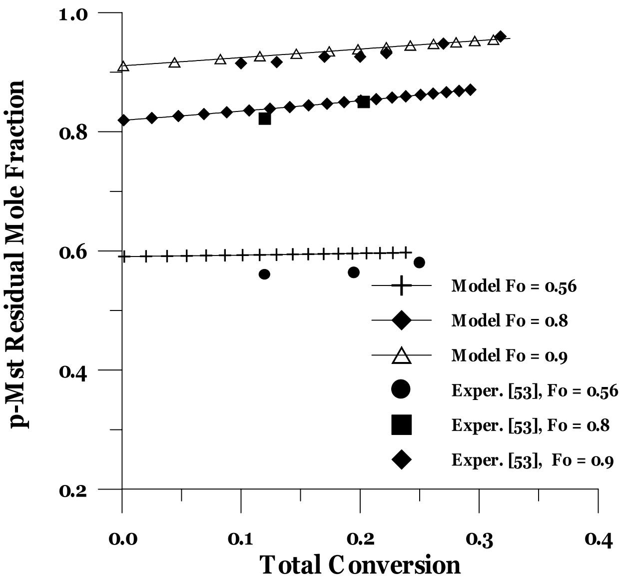

Fig. 13. *p*-Mst residual mole fraction as a function of total conversion for *p*-Mst/AN copolymerization. Polymerization temperature 80 °C. Initial initiator concentration 0.01 M.

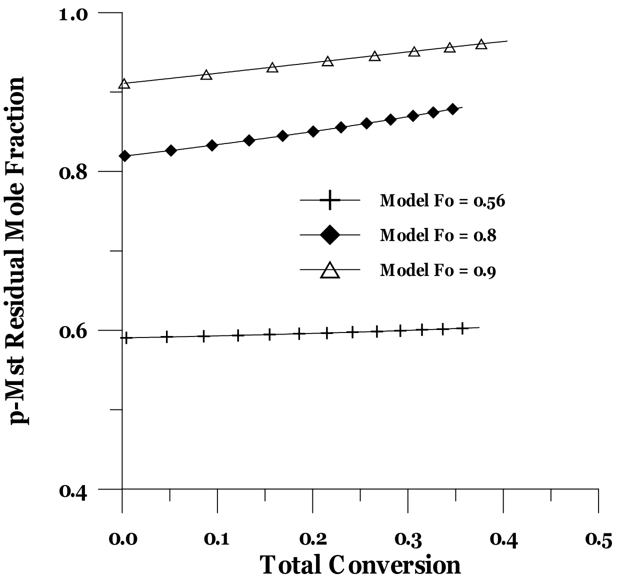

Fig. 14. *p*-Mst residual mole fraction as a function of total conversion for *p*-Mst/AN copolymerization. Polymerization temperature 80 °C. Initial initiator concentration 0.05 M.

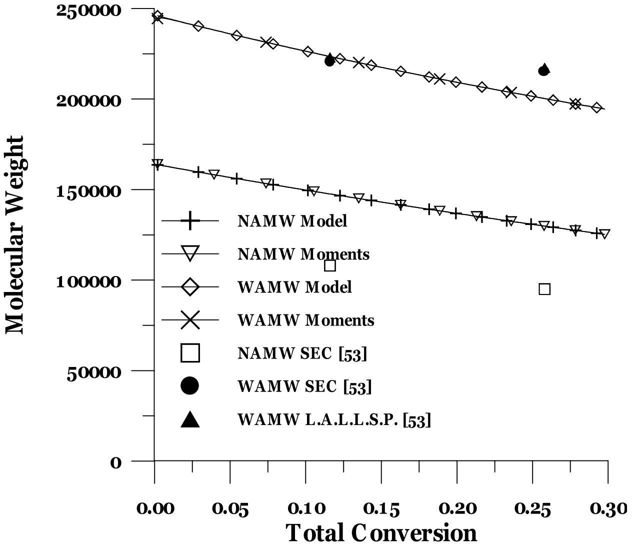

Fig. 15. Comparison of calculated average molecular weights for *p*-Mst/AN copolymerization with experimental data [53] and ones obtained using the method of moments $F_o = 0.56$. Polymerization temperature 80 °C. Initial initiator concentration 0.01 M.

constructive comments and their help in improving this work.

Appendix A

Let $R^i_{n,m}$ and $P_{n,m}$ denote the concentrations of live and dead polymer, having n units of monomer 1 and m units of monomer 2, respectively. Based on the previously described copolymerization mechanism one can directly derive the following polymerization rate functions for the bivariate number chain length distribution (NCLD):

$$r_{R^i_{n,m}} = \left(k_{\mathrm{I}i}\mathrm{PR}^*M_i + \sum_{j=1}^{2} k_{\mathrm{tm}ji}M_iR_0^j + k_{\mathrm{ts}i}SR_0^i\right)\delta(n+i-2, m+1-i) + \sum_{j=1}^{2} k_{\mathrm{p}ji}M_iR^j_{n+i-2,m+1-i} - \sum_{j=1}^{2} k_{\mathrm{p}ij}M_jR^i_{n,m} - A_iR^i_{n,m} + \sum_{j=1}^{2} k_{\mathrm{tp}ji}n^{2-i}m^{i-1}P_{n,m}R_0^j$$

$$r_{P_{n,m}} = \sum_{i=1}^{2}\left(A_i - \sum_{j=1}^{2} k_{\mathrm{tc}ij}R_0^i\right)R^i_{n,m} - \sum_{i=1}^{2}\sum_{j=1}^{2} \times k_{\mathrm{tp}ji}n^{2-i}m^{i-1}P_{n,m}R_0^j + \frac{1}{2}\sum_{i=1}^{2}\sum_{j=1}^{2} k_{\mathrm{tc}ij}\sum_{r=1}^{n-1}\sum_{q=1}^{m-1} \times R^i_{r,q}R^j_{n-r,m-q} \qquad \text{(A1)}$$

$$A_i = \sum_{j=1}^{2}(k_{\mathrm{tm}ij}M_j + (k_{\mathrm{tc}ij} + k_{\mathrm{td}ij})R_0^j) + k_{\mathrm{ts}i}S + \sum_{j=1}^{2} k_{\mathrm{tp}ij}\sum_{n=0}^{\infty}\sum_{m=0}^{\infty} \times n^{2-i}m^{i-1}P_{n,m}$$

Where $\delta(a,b) = \delta(a)\delta(b)$, δ is Kronecker's delta. $R_0^i = \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} R^i_{n,m}$ is the total radical concentration of radicals type i.According to Ray and co-workers [30,45] the leading moments of the bivariate NCLD associated with live and dead polymer chains are defined as:

$$\lambda_{kl}^{(i)} = \sum_{m=1}^{\infty}\sum_{n=1}^{\infty} n^km^lR^i_{n,m}; \quad \mu_{kl} = \sum_{m=1}^{\infty}\sum_{n=1}^{\infty} n^km^lP_{n,m} \qquad \text{(A2)}$$

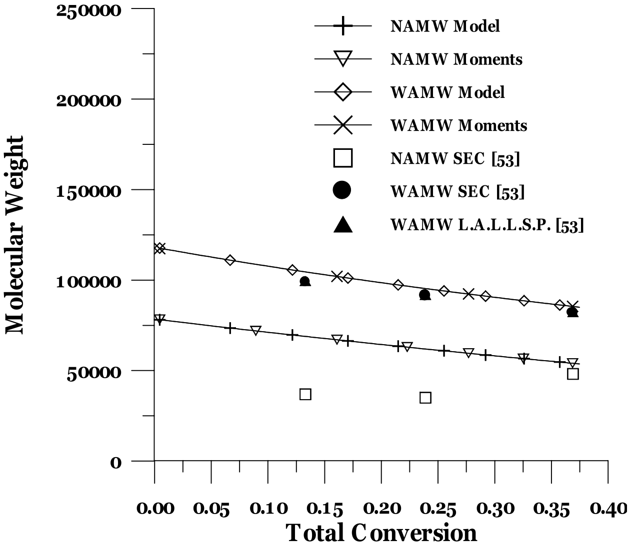

Fig. 16. Comparison of calculated average molecular weights for *p*-Mst/AN copolymerization with experimental data [53] and ones obtained using the method of moments $F_o = 0.56$. Polymerization temperature 80 °C. Initial initiator concentration 0.05 M.

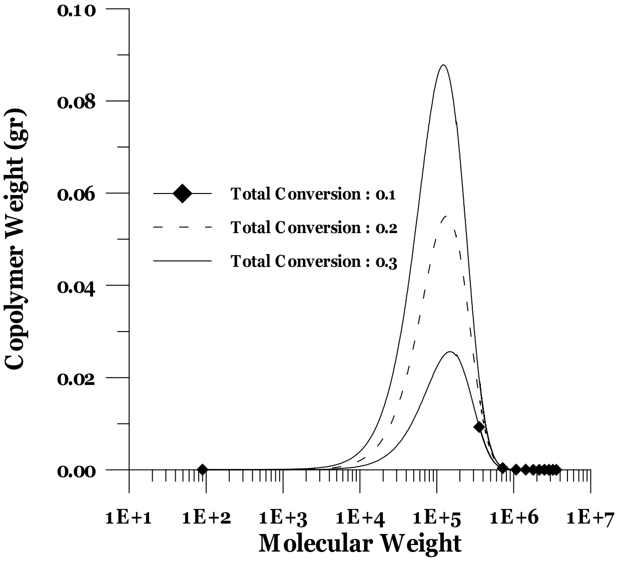

Fig. 17. Total weight molecular weight distribution for *p*-MS/AN copolymerization as a function of total conversion $F_o = 0.56$. Polymerization temperature 80 °C. Initial initiator concentration 0.01 M $n_{\mathrm{step}} = 1$; $t_{\mathrm{step}} = 10$ s.

The corresponding reaction rates for the moments can be obtained from Eq. (A1) by multiplying each term by $n^k m^l$ and summing over the total variation of n and m. The final equations for the moment rate functions are:

$$\begin{aligned}
r_{\lambda^i_{kl}} &= \left(k_{\mathrm{I}i}\mathrm{PR}^* M_i + \sum_{j=1}^{2} k_{\mathrm{tm}ji} M_i \lambda^j_{00} + k_{\mathrm{ts}i} S \lambda^i_{00}\right)\delta(k)\delta(l) \\
&\quad + \sum_{j=1}^{2} k_{\mathrm{p}ji} M_i \left((2-i)\sum_{r=0}^{k}\binom{k}{r}\lambda^j_{rl} + (i-1)\sum_{r=0}^{l} \right. \\
&\quad \left. \times \binom{l}{r}\lambda^j_{kr}\right) - \sum_{j=1}^{2} k_{\mathrm{p}ij} M_j \lambda^i_{kl} - A_i \lambda^i_{kl} + \sum_{r=1}^{2} \\
&\quad \times k_{\mathrm{tpr}i}\lambda^r_{00}\sum_{j}^{l}\binom{l}{j}\mu_{k+1,j} + (2-i)\sum_{r=1}^{2} \\
&\quad \times k_{\mathrm{tp}ri}\mu_{k+1,l}\lambda^r_{00} + (i-1)\sum_{r=1}^{2} k_{\mathrm{tp}ri}\mu_{k,l+1}\lambda^r_{00} \qquad \text{(A3)}
\end{aligned}$$

$$\begin{aligned}
r_{\mu_{kl}} &= \sum_{i=1}^{2}\left(A_i - \sum_{j=1}^{2} k_{\mathrm{tc}ij}\lambda^j_{00}\right)\lambda^i_{kl} - \sum_{q=1}^{2}\sum_{r=1}^{2} k_{\mathrm{tp}rq}[(2-q)\mu_{k+1,l} \\
&\quad + (q-1)\mu_{k,l+1}]\lambda^r_{00} + \frac{1}{2}\sum_{r=1}^{2}\sum_{q=1}^{2} k_{\mathrm{tc}rq}\sum_{i}^{k}\sum_{j}^{l}\binom{k}{i} \\
&\quad \times \binom{l}{j}\lambda^r_{i,j}\lambda^q_{k-i,l-j}
\end{aligned}$$

Combining the above reaction rates with the reactor design equation results in a low order stiff system that is solved numerically. The number average molecular weight (NAMW) and the weight average molecular weight (WAMW) as well as the copolymer composition, expressed as mean mole fraction $\overline{CC^{(i)}}$ of i monomer in copolymer are given as a function of the leading moments:

$$\begin{aligned}
\mathrm{NAMW} &= \frac{(\mathrm{MW}_1\mu_{10} + \mathrm{MW}_2\mu_{01})}{\mu_{00}}; \quad \mathrm{WAMW} \\
&= \frac{\mathrm{MW}_1(\mu_{20}+\mu_{11}) + \mathrm{MW}_2(\mu_{02}+\mu_{11})}{\mu_{10}+\mu_{01}} \qquad \text{(A4)}
\end{aligned}$$

$$\overline{CC^{(1)}} = \frac{\mu_{10}}{(\mu_{10}+\mu_{01})}; \quad \overline{CC^{(2)}} = 1 - \overline{CC^{(1)}}$$

Where MW_i is the ith monomer molecular weight.

Appendix B

By applying QSSA live radicals mass balances (Eq. 1) become time invariant equations ($r_{R^i_L} = 0$). These equations by introducing the expanded live radical concentration in a Taylor series (Eqs. (2) and (3)), are written in the following form:

$$\begin{aligned}
&\left(k_{\mathrm{I}i}\mathrm{PR}^* M_i + \sum_{j=1}^{2} k_{\mathrm{tm}ji} M_i R^j_0 + k_{\mathrm{ts}i} S R^i_0\right)\delta(L-1) \\
&\quad + \sum_{j=1}^{2} k_{\mathrm{p}ji} M_i R^j_L - \sum_{j=1}^{2} k_{\mathrm{p}ji} M_i \frac{(R^j_L - R^j_{L-\eta\mathrm{step}})}{\eta\mathrm{step}} \\
&\quad + \frac{1}{2}\sum_{j=1}^{2} k_{\mathrm{p}ji} M_i \frac{(R^j_L - 2R^j_{L-\eta\mathrm{step}} + R^j_{L-2\eta\mathrm{step}})}{\eta\mathrm{step}^2} \\
&\quad - \sum_{j=1}^{2} k_{\mathrm{p}ij} M_j R^i_L - A_i R^i_L + \sum_{j=1}^{2} k_{\mathrm{tp}ji} CC^{(i)}_L L P_L R^j_0 = 0 \\
&i = 1,2 \qquad \text{(B1)}
\end{aligned}$$

Using single step methods such as backward Euler one can solve dead polymer conservation mass balances (for simplicity only BR case is shown):

$$P^t_L = P^{t-t\mathrm{step}}_L + r^{t\mathrm{step}}_{P_L} \qquad \text{(B2)}$$

or equivalently

$$P^t_L = \frac{P^{t-t\mathrm{step}}_L + \left(\sum_{i=1}^{2}\left(A_i - \sum_{j=1}^{2} k_{\mathrm{tc}ij} R^j_0\right)R^i_L + \frac{1}{2}\sum_{i=1}^{2}\sum_{j=1}^{2} k_{\mathrm{tc}ij}\sum_{r=1}^{L-1} R^i_r R^j_{L-r}\right)t\mathrm{step}}{\left(1 + t\mathrm{step}\sum_{i=1}^{2}\sum_{j=1}^{2} k_{\mathrm{tp}ji} CC^{(i)}_L L R^j_0\right)} \qquad \text{(B3)}$$

$$\begin{aligned}
A_i &= \sum_{j=1}^{2}(k_{\mathrm{tm}ij}M_j + (k_{\mathrm{tc}ij} + k_{\mathrm{td}ij})R^j_0) + k_{\mathrm{ts}i}S + \sum_{j=1}^{2} k_{\mathrm{tp}ij}\sum_{n=0}^{\infty}\sum_{m=0}^{\infty} \\
&\quad \times n^{2-i} m^{i-1} P_{n,m}
\end{aligned}$$

Where P^t_L denotes dead polymer concentrations having total chain length L, at time t; $t$step is the respective integration step.r_{P_L} represents dead polymer rate functions (see Eq. (1)) calculated at time t.

By applying uniform copolymer composition assumption ($CC^{(i)}_L = \overline{CC^{(i)}}$) and introducing Eq. (B3) in (B1) an algebraic system is derived. One can directly solve this algebraic system to obtain live polymer MWD. Once this distribution is calculated, dead polymer distribution is directly calculated from Eq. (B3).

References

[1] Flory PJ. Principles of polymer chemistry. Ithaca: Cornell University Press; 1953.

[2] Simha R, Branson H. J Chem Phys 1944;12:253.

[3] Stockmayer WH. J Chem Phys 1945;13:199.

[4] Tobita H. Macromolecules 1993;26:836.
[5] Tobita H. Polymer 1994;35:3023.
[6] Tobita H. Polymer 1994;35:3032.
[7] Tobita H. Macromolecules 1996;29:693.
[8] Stockmayer WH. J Am Chem Soc 1945;13:199.
[9] Hamielec AE, Hodgins JW, Tebbens K. AIChE J 1967;13:1087.
[10] Hamielec AE, MacGregor JF, Penlidis A. Makromol Chem Macromol Symp 1987;10/11:521.
[11] Tobita H, Hamielec AE. Macromolecules 1989;22:3098.
[12] Xie T, Hamielec AE. Macromol Theor Simul 1993;2:455.
[13] Fiorentino S, Ghielmi A, Storti G, Morbidelli M. Ind Engng Chem Res 1997;36:1283.
[14] Bamford CH, Jenkins AD. Trans Faraday Soc 1960;56:907.
[15] Zeman R, Amundson NR. Chem Engng Sci 1965;20:331.
[16] Zeman R, Amundson NR. Chem Engng Sci 1965;20:637.
[17] Coyle DJ, Tulig TJ, Tirell M. Ind Engng Chem Fundam 1985;24:343.
[18] Ellis MF, Taylor TW, Gonzalez V, Jensen KF. AIChE J 1988;34(8):1341.
[19] Bailagou PE, Soong DS. Chem Engng Sci 1985;40(1):87.
[20] Gonzalez-Romero VM, Rodriguez BE. Chem Engng Commun 1987;59:185.
[21] Chaimberg M, Cohen Y. Ind Engng Chem Res 1990;29:1152.
[22] Nagasubramanian K, Graessley WW. Chem Engng Sci 1970;25:1549.
[23] Blavier L, Villermeaux J. Chem Engng Sci 1984;39:101.
[24] Tobita H, Ito K. Polym React Engng 1992/1993;1(3):407.
[25] Crowley TJ, Choi KY. Ind Engng Chem Res 1997;36:1419.
[26] Pladis P, Kiparissides C. Chem Engng Sci 1998;53:3315.
[27] Yoon WJ, Ryu JH, Cheong C, Choi KY. Macromol Theory Simul 1998;7:327.
[28] Iedema PD, Hoefsloot HCJ. Macromol Theory Simul 2002;11:410.
[29] Ray WH. Macromolecules 1971;4:162.
[30] Ray WH, Douglas TL, Godsalve EW. Macromolecules 1971;4:166.
[31] Mills PL. Comput Chem Engng 1986;10(4):399.
[32] Nordhus H, Moen O, Singstad P. J Macromol Sci-Pure Appl Chem 1997;A34:1017.
[33] Soares JBP, Hamielec AE. Polymer 1995;36:2257.
[34] Maschio G, Scali C. Macromol Chem Phys 1999;200:1708.
[35] Budde U, Wulkow M. Chem Engng Sci 1991;46(2):497.
[36] Canu P, Ray WH. Comput Chem Engng 1991;15(8):549.
[37] Wulkow M. Macromol Theory Simul 1996;5:393.
[38] Teymour F, Campbell JD. Macromolecules 1994;27:2460.
[39] Batte A, Ghielmi A, Storti G, Morbidelli M. Macromol Theory Simul 1999;8:498.
[40] Papavasiliou G, Birol I, Teymour F. Macromol Theory Simul 2002;11:533.
[41] Kumar S, Ramkrishna D. Chem Engng Sci 1997;52:4659.
[42] Batte A, Storti G, Morbidelli M. Macromol Theory Simul 2002;11:37.
[43] Liu SL, Amundson NR. Rubber Chem Technol 1961;34:995.
[44] Detar DF, Detar CE. J Phys Chem 1966;70:3842.
[45] Ray WH. J Macromol Sci Rev Macromol Chem 1972;C8:1.
[46] Biesenberger JA, Sebastian DH. Principles of polymerization engineering. New York: Wiley; 1987.
[47] Verros G, Papadakis M, Kiparissides C. Polym React Engng 1993;1(3):427.
[48] Kiparissides C, Verros G, MacGregor JF. JMS-Rev Macromol Chem Phys 1993;C33(3):437.
[49] Tulig TJ, Tirrell M. Macromolecules 1981;14:1501.
[50] Parker TS, Chua LO. Practical numerical algorithms for chaotic systems. New York: Springer; 1989.
[51] Jones KM, Bhattacharya D, Brash JL, Hamielec AE. Polymer 1986;27:602.
[52] Bhattacharya D, Hamielec AE. Polymer 1986;27:611.
[53] Yaraskavitch IM, Brash JL, Hamielec AE. Polymer 1987;28:489.
[54] Arriola DJ. Ph.D. Thesis, University of Wisconsin (USA) 1989.
[55] Mahabadi HK. O'Driscoll K.F. Macromolecules 1977;10:55.
[56] Chiantore O, Hamielec AE. Polymer 1985;26:608.