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# Modelling the polymerisation of methyl methacrylate (MMA) in a partially stirred reactor

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#### Abstract

A stochastic particle model has been developed to describe the idealised free radical polymerisation of methyl methacrylate (MMA) in imperfectly mixed batch and plug flow reactors. Using the method of moments, the model allows efficient computation of the number and weight average degrees of polymerisation, higher moments, monomer conversion and (based on the Schulz-Flory distribution) the degree of polymerisation distributions, as a function of time and mixing. The model was validated against PREDICI<sup>TM</sup> for the homogeneous case. For non-homogeneous cases it was shown that, for some typical initial conditions, the rate of mixing has several effects at low monomer conversions, corresponding to low residence times. At large residence times, the influence of mixing disappears and the reactions converge to the homogeneous case.

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## 1 Introduction

Acrylate polymerisation reactions are the basis for the formation of many large scale industrial products (e.g. adhesive dispersions or acrylic glasses). The characteristic feature of acrylate polymerisations is that the rate of reaction may be of the same order of magnitude as mixing times within polymerisation reactors. Thus, the mixing times within an acrylate polymerisation reactor may have a profound influence on the temporal evolution of the product quality, characterised by the degree of polymerisation distribution [14].

In 1989 the U.S. production of acrylic monomers was ca 450,000t, split between Rohm and Hass, Hoechst Celanese, BASF and Union Carbide, representing about 45% of worldwide production. Most of the remainder was produced in Western Europe (ca 35%) and Japan (ca 15%). Essentially all of this was converted to acrylic polymers and copolymers [8].

The main limiting factor in the production of acrylic polymers is the large quantity of heat released during reaction and the increase in viscosity with monomer conversion. Thus for safety reasons, it is desired that the content of unconverted monomer in the reactor is minimised at any given time. Most industrial acrylic polymerisations are therefore performed in stirred semi-batch reactors, where cold monomer is dropped into a hot mixture of initiator and polymer. Occasionally some acrylic polymerisations are performed in CSTRs. Again, the main problem and safety issue is that of heat transfer out of the reactor to avoid thermal runaway.

Typically, new polymer products, characterised by their degree of polymerisation distribution, are identified on a laboratory scale. A modern protocol to optimise the production of new products would be to build a kinetic model of the system in CiT's PREDICI<sup>TM</sup> or AspenTech's POLYMERS PLUS<sup>TM</sup>. The model would then be used to simulate the polymerisation and optimise the production process with respect to variables such as the reactor temperature and the rate of addition of monomer. Such models normally assume that the reaction mixture is homogeneous however, and the degree of micro-mixing is not considered at all. Thus scale-up problems may be encountered and the new conditions may not work as expected, producing the wrong product (i.e. the wrong degree of polymerisation distribution), since the extent of mixing in a process is strongly coupled to the scale of the process. This is highly unsatisfactory. What is required is a model that can combine the above effects with a mixing model, which in turn can be coupled to the physical size and

configuration of the reactor and stirring mechanism.

Various approaches for modelling different polymerisation reactions have been developed. Early models in the literature to describe the kinetic behaviour of free radical polymerisations and the resulting degree of polymerisation distributions are based on the complicated kinetic scheme of free radical polymerisation, involving different numbers of basic kinetic steps. The volume contraction effect was often ignored and non-conventional kinetic phenomena like the gel effect were included in very different ways. These models were mostly used to calculate the conversion-time history only.

More recent models have used a variety of numerical techniques to predict the degree of polymerisation distributions based on simplified kinetic mechanisms. Budde and Wulkow [4] demonstrated the use of the discrete Galerkin method to solve homogeneous systems for an approximation of the degree of polymerisation distribution. based on the shape of the Schulz-Flory distribution, for a methyl methacrylate (MMA) polymerisation reaction, including volume contraction and the gel effect. Wulkow [18] eventually developed the software package PREDICI<sup>TM</sup> based on this method. Hutchinson [6] presented a simplified model for the polymerisation kinetics with cross linking for a MMA and ethylene glycol dimethacrylate system. The kinetic model was solved deterministically as a homogeneous system, using the method of moments to describe the degree of polymerisation distribution at different temperatures. Kim and Laurence [7] investigated the influence of mixing on MMA solution polymerisation using a model based on two CSTRs in parallel, where the model was specified in terms of an exchange ratio and a volume ratio. They were able to trace steady solution branches of monomer conversion and temperature against residence time. They showed the existence of multiple steady state solutions, but could not predict the dynamics of the system. Tosun [14] derived a mathematical model of mixing in a semi-batch polymerisation reactor using the segregated mixing model developed by Villermaux [17]. Villermaux [16] also introduced the interaction-by-exchange-with-the-mean (IEM) model which is often used to model non-ideal mixing.

These heuristic models can be derived (see Kraft [9]) from the more general concept of the composition probability density function (PDF) transport equation as described by Pope [12]. Tsai and Fox [15] used the joint composition PDF coupled to a CFD (Computational Fluid Dynamics) simulation to model the effect of turbulent mixing on a tubular low-density polyethylene reactor. This approach is computationally very expensive. If statistical homogeneity is assumed, the PDF transport equation reduces to the stochastic reactor model: partially stirred plug flow reactor (PaSPFR). The stochastic model is much faster to solve numerically, but still retains the description of mixing and chemical reaction.

The purpose of this paper is to use the PaSPFR model as a polymerisation reactor model to study the principal interaction between the polymerisation kinetics and the influence of local mixing on the polymerisation process. We focus on the polymerisation of methyl methacrylate (MMA). The reaction is suitably fast to allow the study of the effect of mixing. Thus the MMA system may be regarded as a model for all acrylate polymerisations. Further, it has been the subject of much previous investigation and is well documented in the literature [6, 7, 13, 4]. The PaSPFR model is solved by constructing a stochastic particle model to describe the polymerisation of MMA under different mixing conditions, characterised using the IEM model. A simplified kinetic mechanism, consistent with those in the literature [6, 13, 4], is used to describe the polymerisation, with isothermal kinetic data being taken from Budde [3]. Temperature gradients, volume contraction, the gel effect and the influence of viscosity on mixing time are noted as being important, but are disregarded so far in order to keep the model as simple as possible for this first theoretical study. The direct solution of the large stiff system of ordinary differential equations (ODEs) generated by the models of free radical polymerisation is not possible, since every molecular species (and there are an infinite number of possible polymer species) has to be treated by one ODE. Thus the method of moments is used to reduce the system to a small finite set of ODEs that is incorporated into the PaSPFR model. The model is validated against the predictions of PREDICI<sup>TM</sup> for the homogeneous case, and used to show the effect of mixing on the idealised MMA system.

The paper is organised as follows. In Section 2 the reaction system and method of moments are reviewed. Section 3 contains a description of the reactor model, the algorithm used to compute the numerical simulation of the reactor and a brief validation of the algorithm. The validation of the homogenous simulation is given in Section 4 and, finally, in Section 5, the numerical results are presented.

# 2 Free radical polymerisation mechanism

The following is an idealised mechanism for free radical polymerisation

Initiation

$$\begin{bmatrix} I & \longrightarrow & 2R \cdot \\ R \cdot & + & M & \longrightarrow & P_1 \cdot \\ & I & \stackrel{k_d}{\longrightarrow} & 2P_1 \cdot \end{bmatrix}$$
(1)

Propagation

Termination

Chain transfer

$$P_n \cdot + M \xrightarrow{k_p} P_{n+1} \cdot$$
 (2)

by combination	$P_n \cdot + P_m \cdot \xrightarrow{k_{tc}} D_{n+m}$	(3)
by disproportionation	$P_n \cdot + P_m \cdot \xrightarrow{k_{td}} D_n + D_m$	(4)

to monomer 
$$P_n \cdot + M \xrightarrow{k_{trm}} D_n + P_1 \cdot$$
 (5)

$$n,m = 1,2,3\ldots$$

where I is initiator, M is monomer,  $P_n$  is a live polymer radical of length n and  $D_n$  is a dead polymer chain of length n.

### 2.1 Material balance equations

The material balances model the formation of live and bulk polymer as described by the kinetic mechanism. They form an infinite set of coupled ODEs.

#### Live polymer radicals of length 1

$$\frac{d}{dt}[P_1 \cdot] = 2f_d k_d [I] + k_{trm} [M] \sum_{n=1}^{\infty} [P_n \cdot] -[P_1 \cdot] \left[ (k_p + k_{trm}) [M] + (k_{tc} + k_{td}) \sum_{n=1}^{\infty} [P_n \cdot] \right].$$
(6)

Live polymer radicals of length m

$$\frac{d}{dt}[P_{m}\cdot] = k_{p}[M][P_{m-1}\cdot] - [P_{m}\cdot]\left[(k_{p}+k_{trm})[M] + (k_{tc}+k_{td})\sum_{n=1}^{\infty}[P_{n}\cdot]\right]$$

$$m = 2, 3, \dots$$
(7)

Bulk polymer (dead and living) of length 1

$$\frac{d}{dt} \left( [D_1] + [P_1 \cdot] \right) = 2f_d k_d [I] + k_{trm} [M] \sum_{n=1}^{\infty} [P_n \cdot] - [P_1 \cdot] \left[ k_p [M] + k_{tc} \sum_{n=1}^{\infty} [P_n \cdot] \right].$$
(8)

Bulk polymer (dead and living) of length m

$$\frac{d}{dt} \left( [D_m] + [P_m \cdot] \right) = k_p[M][P_{m-1} \cdot] + \frac{1}{2} k_{tc} \sum_{n=1}^{m-1} [P_n \cdot][P_{m-n} \cdot] 
- [P_m \cdot] \left[ k_p[M] + k_{tc} \sum_{n=1}^{\infty} [P_n \cdot] \right]$$

$$m = 2, 3, \dots$$
(9)

Initiator

$$\frac{d}{dt}[I] = -k_d[I]. \tag{10}$$

Monomer

$$\frac{d}{dt}[M] = -k_p[M] \sum_{n=1}^{\infty} [P_n \cdot] - k_{trm}[M] \sum_{n=1}^{\infty} [P_n \cdot] - 2f_d k_d[I]$$
  
=  $-\mu_0[M](k_p + k_{trm}) - 2f_d k_d[I].$  (11)

where  $\mu_0$  is defined in (12) with k = 0.

### 2.2 Moments of the degree of polymerisation

The degree of polymerisation distribution can be approximately described by the first few statistical moments of the set of material balance equations. The method of moments can therefore be used to reduce the infinite set of material balance ODEs to a finite set of coupled moment ODEs.

The moments of the polymer distribution are defined, for the live polymer radicals

$$\mu_j = \sum_{n=1}^{\infty} n^j [P_n \cdot]$$
(12)

and for the **bulk polymer radicals** 

$$\lambda_j = \sum_{n=1}^{\infty} n^j \left( [D_n] + [P_n \cdot] \right).$$
(13)

Thus, using the material balance equations, we obtain a finite set of coupled ODEs to describe the evolution of the polymer distribution in terms of the live and the bulk moments.

### Live moments

$$\frac{d}{dt}\mu_0 = 2f_d k_d [I] - {\mu_0}^2 (k_{tc} + k_{td})$$
(14)

$$\frac{d}{dt}\mu_{1} = 2f_{d}k_{d}[I] - (\mu_{1} - \mu_{0})k_{trm}[M] - \mu_{1}\mu_{0}(k_{tc} + k_{td}) + \mu_{0}k_{p}[M]$$
(15)

$$\frac{d}{dt}\mu_2 = 2f_d k_d [I] - (\mu_2 - \mu_0) k_{trm} [M] - \mu_2 \mu_0 (k_{tc} + k_{td}) + (2\mu_1 + \mu_0) k_p [M]$$
(16)

$$\frac{d}{dt}\mu_{3} = 2f_{d}k_{d}[I] - (\mu_{3} - \mu_{0})k_{trm}[M] - \mu_{3}\mu_{0}(k_{tc} + k_{td}) + (3\mu_{2} + 3\mu_{1} + \mu_{0})k_{p}[M]$$
(17)

$$\frac{d}{dt}\mu_4 = 2f_d k_d [I] - (\mu_4 - \mu_0) k_{trm} [M] - \mu_4 \mu_0 (k_{tc} + k_{td}) + (4\mu_3 + 6\mu_2 + 4\mu_1 + \mu_0) k_p [M]$$
(18)

$$\frac{d}{dt}\mu_5 = 2f_d k_d [I] - (\mu_5 - \mu_0)k_{trm}[M] - \mu_5\mu_0(k_{tc} + k_{td}) + (5\mu_4 + 10\mu_3 + 10\mu_2 + 5\mu_1 + \mu_0)k_p[M]$$
(19)

$$\frac{d}{dt}\mu_{j} = 2f_{d}k_{d}[I] - (\mu_{j} - \mu_{0})k_{trm}[M] - \mu_{j}\mu_{0}(k_{tc} + k_{td}) + \sum_{i=0}^{j-1} {j \choose i}\mu_{i}k_{P}[M]$$
(20)

#### **Bulk** moments

$$\frac{d}{dt}\lambda_0 = 2f_d k_d [I] + \mu_0 k_{trm} [M] - \frac{1}{2}{\mu_0}^2 k_{tc}$$
(21)

$$\frac{d}{dt}\lambda_1 = 2f_d k_d [I] + \mu_0 (k_p + k_{trm})[M]$$
(22)

$$\frac{d}{dt}\lambda_{2} = 2f_{d}k_{d}[I] + \mu_{0}(k_{p} + k_{trm})[M] + 2\mu_{1}k_{p}[M] + {\mu_{1}}^{2}k_{tc}$$
(23)

$$\frac{d}{dt}\lambda_3 = 2f_d k_d [I] + \mu_0 (k_p + k_{trm})[M] + (3\mu_2 + 3\mu_1)k_p[M] + 3\mu_1\mu_2k_{tc}$$
(24)

$$\frac{d}{dt}\lambda_4 = 2f_d k_d [I] + \mu_0 (k_p + k_{trm})[M] + (4\mu_3 + 6\mu_2 + 4\mu_1)k_p[M] + (4\mu_1\mu_3 + 3\mu_2^2)k_{tc}$$
(25)

$$\frac{d}{dt}\lambda_5 = 2f_d k_d [I] + \mu_0 (k_p + k_{trm})[M] + (5\mu_4 + 10\mu_3 + 10\mu_2 + 5\mu_1)k_p[M] + (5\mu_1\mu_4 + 10\mu_2\mu_3)k_{tc}$$
(26)

### 2.3 MMA kinetics and initial conditions

The kinetic parameters and initial conditions are taken from Budde [3].

Parameter	Value	Unit	Parameter	Value	Unit
C	0.9		1	1 5 . 10-5	_1
Jd	0.3	-	$\kappa_d$	$1.5 \times 10^{-6}$	S 1
$\langle [M]_0 \rangle$	4.32	$kmol \ m^{-3}$	$k_p$	$7.594 \times 10^{2}$	$m^3 \ kmol^{-1} \ s^{-1}$
$\langle [I]_0 \rangle$	0.01508	$kmol \ m^{-3}$	$k_{tc}$	$24.15 \times 10^{6}$	$m^3 \ kmol^{-1} \ s^{-1}$
$M_M$	100.0	$kg \; kmol^{-1}$	$k_{td}$	$10.35 \times 10^{6}$	$m^3 \ kmol^{-1} \ s^{-1}$
$M_I$	100.0	$kg \; kmol^{-1}$	$k_{trm}$	$1.78 \times 10^{-2}$	$m^3 \ kmol^{-1} \ s^{-1}$

Table 1: Parameters  $(T = 65^{\circ}C)$  for MMA polymerisation.

where  $[M]_0 = [M](t=0)$  and  $[I]_0 = [I](t=0)$ .

### 3 Stochastic reactor model

The degree of polymerisation distribution could be obtained by direct numerical simulation of the governing set of ODEs if perfect mixing were to be assumed [13]. If the assumption of perfect mixing is relaxed however, spatial inhomogeneities must now be considered and this approach becomes computationally infeasible.

An alternative to direct numerical simulation is the use of statistical methods. Assuming statistical homogeneity, a single PDF may be used to model the spatial inhomogeneities. Thus in the case of the PDF being a delta function, for example, all points in space have the same composition and we relax back to the perfectly mixed case studied by Seeßelberg [13].

The unknown quantities are represented as **random variables**. The time evolution of these random variables are given by a transport equation for their joint PDF. Here we combine the idealised polymerisation model, based on the moments of the degree of polymerisation distribution function, with the joint scalar PDF transport equation for a **partially** stirred reactor. The unknown scalar quantities are the first five live and bulk moments of the degree of polymerisation, and the monomer and initiator concentrations. These can be written in the **joint scalar random vector** 

$$\underline{\phi} = (\mu_0, \mu_1, \mu_2, \mu_3, \mu_4, \lambda_0, \lambda_1, \lambda_2, \lambda_3, \lambda_4, [M], [I])^T.$$
(27)

This vector has a corresponding joint scalar PDF,  $f_{\phi}(\underline{\psi}, t)$ , at time t.

The temporal evolution of the PDF of a batch or plug flow reactor is given by the **partially stirred plug flow reactor** (PaSPFR) model, as described by Kraft [9]

$$\frac{\partial f_{\underline{\phi}}(\underline{\psi}, t)}{\partial t} + \frac{\partial}{\partial \psi_k} \left( \left( S_k(\underline{\psi}) + A_k(\underline{\psi}) \right) f_{\underline{\phi}}(\underline{\psi}, t) \right) = 0$$
(28)

where reaction is described by the  $S_k(\underline{\psi})$  term (discussed in Section 3.2), mixing is described by the IEM model

$$A_k(\underline{\psi}) = -\frac{1}{\tau_{mix}} (\psi_k - \langle \phi_k \rangle)$$

in which  $\langle \cdot \rangle$  denotes the mean, and the initial condition is

$$f_{\underline{\phi}}(\underline{\psi}, 0) = f_{\underline{\phi}}^{\ 0}(\underline{\psi}).$$

The mixing time parameter,  $\tau_{mix}$ , is assumed to be constant during the course of the reaction.

The interaction by exchange with the mean (IEM) has been shown to be consistent for the use of moments of the degree of polymerisation in Balthasar *et al.* [1]. The model implies that the property of a stochastic particle moves towards the average of all stochastic particles.

### **3.1** Definition of functionals

The functionals of interest in the description of polymerisation reactions may be defined in terms of the scalars in the joint scalar random vector (27) for each stochastic particle in the model:

#### Number average degree of polymerisation

$$\bar{X}_N = \frac{\lambda_1 - \mu_1}{\lambda_0 - \mu_0} \tag{29}$$

and weight average degree of polymerisation

$$\bar{X}_W = \frac{\lambda_2 - \mu_2}{\lambda_1 - \mu_1}.$$
(30)

Justification of the form of the degrees of polymerisation is given in Appendix A.1. Since conversion is a descriptor of the total extent of reaction, the only definition of **monomer conversion** that makes sense in a non-homogeneous system is

$$x_M = 1 - \frac{\langle [M] \rangle}{\langle [M]_0 \rangle} \tag{31}$$

where  $[M]_0 = [M](t = 0)$ .

### 3.2 Numerical treatment of PaSPFR-LMSE model

The particle model uses an ensemble of stochastic particles, each with a joint scalar random vector of properties (27), to approximate the distributions of the scalars within the reactor.

The algorithm consists of generating trajectories of the reactor model (28) for each particle, and averaging over the appropriate functionals. This is done at a sequence

of points in time, separated by the time interval  $\Delta t$ . A flow diagram for the main algorithm is given in **Figure 1**.



Figure 1: Main algorithm.

The number and mass fraction distributions were estimated using the Schulz-Flory distribution with the empirical mean (over all particles in the ensemble) number average degree of polymerisation as a parameter.

A discussion of the applicability of the Schulz-Flory distribution to the MMA mechanism is given in Appendix A.2.

#### 3.2.1 Initialisation of model

The ensemble is initialised to approximate a segregated mixture of monomer and initiator. The number of stochastic particles is specified

$$N = m(r+1) \tag{32}$$

where N, m and r are required to be integers, and r is the initial mass ratio of monomer to initiator

$$r = \frac{M_M \langle [M]_0 \rangle}{M_I \langle [I]_0 \rangle}.$$
(33)

Particles are specified as containing monomer or initiator, in the ratio of the mass of monomer to the mass of initiator:

$$\begin{bmatrix} M \end{bmatrix}_0^i = \langle [M]_0 \rangle \ (r+1)/r \\ \begin{bmatrix} I \end{bmatrix}_0^i = 0 \\ \end{bmatrix} \quad i \in \{1, \dots, m \ r\}$$
(34)

$$\begin{bmatrix} I \end{bmatrix}_{0}^{i} = \langle [I]_{0} \rangle (r+1) \\ \begin{bmatrix} M \end{bmatrix}_{0}^{i} = 0 \end{bmatrix} \quad i \in \{m \ r+1, \dots, N\}$$
 (35)

where i is the particle index. A worked example is given in Appendix B.1.

#### 3.2.2 IEM mixing algorithm

At each time step, the ensemble is updated according to the IEM mixing model over the incremental time interval  $\Delta t$ .

The empirical mean of each scalar  $\langle \phi_k \rangle$  was calculated over the ensemble at time  $t_{n-1}$ . The IEM model

$$\frac{d\psi_k^i}{dt} = A_k^i 
= \frac{-1}{\tau_{mix}} \left( \psi_k^i - \langle \phi_k \rangle \right).$$
(36)

was solved analytically for each particle in the ensemble

$$\psi_{k}{}^{i}{}_{n} = \langle \phi_{k} \rangle + (\psi_{k}{}^{i}{}_{n-1} - \langle \phi_{k} \rangle) \exp\left(\frac{-\Delta t}{\tau_{mix}}\right)$$
(37)

where i is the particle index,

$$\psi_k(t_n) = \psi_{k n}$$

and

$$\Delta t = t_n - t_{n-1}.$$

#### 3.2.3 Reaction algorithm

At each time step, the ensemble is updated according to the reaction model over the incremental time interval  $\Delta t$ .

For each particle in the ensemble, the simultaneous system of equations

$$\frac{d\psi}{dt} = \underline{S} \tag{38}$$

was solved using a fourth-order Runge-Kutta integration routine where

$$\underline{S} = (S_1, \dots, S_k)^T = \left(\frac{d\mu_0}{dt}, \dots, \frac{d[I]_0}{dt}\right)^T.$$
(39)

The elements of  $\underline{S}$  are given by (14) through (18), (21) through (25), (11) and (10).

### 3.3 Validation of the particle algorithm

The use of the particle method to approximate the evolution of the scalars in the reactor was validated by comparing the results of the model to those obtained for analytic solutions for the simple cases of a partially stirred plug flow reactor with mixing described by the linear mean square estimator model (PaSPFR-LMSE) and a PaSPFR-LMSE with first order reaction [2, 10], where the LMSE and IEM models are equivalent.

The particle algorithm was in very good agreement with the analytic solutions.

## 4 Validation of the homogeneous case

The model was validated for the homogeneous case by comparing the results of the model to those obtained from PREDICI<sup>TM</sup> for the mechanism, parameters and initial conditions presented in Section 2.

Figures 2 and 3 show that the time evolution of the degree of polymerisation and the monomer and initiator concentrations calculated by the model almost exactly match those obtained using PREDICI<sup>TM</sup>.



Figure 2: Degree of polymerisation against time, t.



Figure 3: Monomer and initiator concentration against time, t.

Figures 4 and 5 present a comparison between the approximate number and mass fraction distributions calculated by the model, using the Schulz-Flory distribution, and the distributions calculated by PREDICI<sup>TM</sup>. The general agreement between the model and PREDICI<sup>TM</sup> is again very good. It is noted that there is some discrepancy, but we accept the use of Schulz-Flory as a first approximation.



(e) Time, t = 50000 s.

Figure 4: Number fraction distributions.



Figure 5: Mass fraction distributions.

# 5 Results

The model was used to demonstrate the effect of the rate of mixing on the polymerisation of the idealised MMA system.

Figure 6 shows the time evolution of the mean number and weight average degrees of polymerisation,  $\langle \bar{X}_N \rangle$  and  $\langle \bar{X}_W \rangle$ , and the monomer conversion,  $x_M$ , against time t, as a function of the mixing time parameter,  $\tau_{mix}$ . Figure 7 shows the same data, now plotted against  $\tau_{mix}$ , as a function of the time t.



(a) Mean number average degree of polymerisation.

(b) Mean weight average degree of polymerisation.



(c) Monomer conversion curves.

(d) Monomer conversion curves (natural axes).

Figure 6: Monomer conversion, mean number and weight average degree of polymerisation against time t, as a function of the mixing parameter  $\tau_{mix}$  (in seconds).



(a) Mean number average degree of polymerisation (semi-natural axes).

(b) Mean weight average degree of polymerisation.



(c) Monomer conversion curves.

Figure 7: Monomer conversion, mean number and weight average degree of polymerisation against mixing parameter  $\tau_{mix}$ , as a function of time t (in seconds).

The time evolution of the mean number average degree of polymerisation and the monomer and initiator concentrations for the homogeneous and  $\tau_{mix} = 100s$  cases are shown in **Figure 8**.

In the homogeneous case,  $\langle \bar{X}_N \rangle$  increases rapidly over the first 10 seconds. As the reaction proceeds,  $\langle \bar{X}_N \rangle$  gradually decreases due to the differential consumption of monomer and initiator, such that the proportion of initiation reactions (1) increases with respect to propagation (2). Thus an increasing proportion of  $P_1$  polymers are born and  $\langle \bar{X}_N \rangle$  and  $\langle \bar{X}_W \rangle$  decrease, as observed. The time evolution of the mean number average degree of polymerisation and the monomer and initiator concentrations are shown for the homogeneous case in Figures 8(a) and 8(c).

Figures 8(b) and 8(d) show the time evolution of the mean number average degree of polymerisation and the monomer and initiator concentrations for the case  $\tau_{mix} =$ 100s. It is evident that the slower mixing (i.e. larger  $\tau_{mix}$ ) has a strong influence on the temporal evolution of  $\langle \bar{X}_N \rangle$ .

At low t,  $\langle \bar{X}_N \rangle$  is lower than for the homogeneous case, but increases much more quickly, and peaks well above the homogeneous curve. The value of  $\langle \bar{X}_N \rangle$  then decreases rapidly, falling below the homogeneous curve again, before steadying out and rising to join homogeneous curve, but not crossing above it.

These effects are caused by the initial segregation of the monomer and initiator. At low t, the segregation is such that little reaction occurs, since in the initiator dominated regions there will be insufficient monomer for significant propagation of any  $P_1$  polymers that are born, and in the monomer dominated regions there will be insufficient initiator to cause a significant birth rate of  $P_1$  polymers. This can be seen in Figures 8(b) and 8(d) for  $t \in [0, 2)s$ .

As mixing begins to occur, small concentrations of initiator will be introduced into pockets of monomer. Thus, initiation reactions gradually produce small concentrations of  $P_1$  radicals surrounded by monomer molecules. The low polymer concentration suppresses the termination reactions (3) and (4), such that once formed, the polymer radicals, surrounded by monomer molecules, simply propagate with little chain termination, causing a rapid increase in  $\langle \bar{X}_N \rangle$ , soon passing above the homogeneous curve, as can be seen in Figures 8(b) and 8(d) in the interval  $t \in [2, 10)s$ .

Further mixing introduces increasing concentrations of initiator into the monomer pockets. Thus the birth rate of  $P_1$  radicals increases, and the proportion of shorter chain polymers begins to grow. Consequently, the rate of increase of  $\langle \bar{X}_N \rangle$  begins to

fall, and eventually, as the initiator concentration continues to increase,  $\langle \bar{X}_N \rangle$  starts to fall rapidly, eventually passing below the homogeneous curve. See Figures 8(b) and 8(d) for  $t \in [10, 230)s$ .<sup>1</sup>

Ultimately complete mixing is achieved, and the contents of the reactor reach a homogeneous state. The initiator curve in Figure 8(d) is observed to rejoin the homogeneous initiator curve, shown in Figure 8(c), at about t = 650s. At this point, initiation reactions cease to dominate, and  $\langle \bar{X}_N \rangle$  rises to join the homogeneous curve at about  $t = 2 \times 10^4 s$ , due to propagation and termination by combination (3). As the reaction proceeds,  $\langle \bar{X}_N \rangle$  now follows the homogeneous curve, and gradually decreases by the mechanism described above for the homogeneous case.

The same reasoning may be applied to the effect of mixing on the evolution of  $\langle X_W \rangle$ .

The effect of mixing on the number and mass distributions, as estimated from  $\langle \bar{X}_N \rangle$  using the Schulz-Flory distribution, is shown in **Figures 9 and 10**. It can be seen that the effect of mixing diminishes as  $t \to 1000s$ , and can be deduced from **Figures 6(a) and 7(a)** that the distributions will have all collapsed to the homogeneous curves by  $t = 10^4 s$ . It can also be seen that faster mixing cases (i.e. lower  $\tau_{mix}$ ) collapse to the homogeneous curves at lower times than slower mixing cases, as common sense would suggest.

<sup>&</sup>lt;sup>1</sup>Note, it can be deduced that it is the initiation reaction (1) that is responsible for the decrease in  $\langle \bar{X}_N \rangle$ , as opposed to chain transfer to monomer (5) (which is the only other reaction that can produce  $P_1$  radicals, and therefore lower  $\langle \bar{X}_N \rangle$ ), since the rate of chain transfer is directly coupled to the rate of propagation due to both reactions having the same kinetic form, and where the propagation rate constant,  $k_p$  is four orders of magnitude greater than the chain transfer rate constant,  $k_{trm}$ .



(a) Mean number average degree of polymerisation for homogeneous case,  $\tau_{mix} = 0s$ .

(b) Mean number average degree of polymerisation, case  $\tau_{mix} = 100s$ .



(c) Monomer and initiator concentration for homogeneous case,  $\tau_{mix} = 0s$ .

(d) Monomer and initiator concentration, case  $\tau_{mix} = 100s$ , for stochastic particles with initial condition  $[I]_0 = 0$  only.

Figure 8: Mean number average degree of polymerisation, monomer and initiator concentration against time t, as a function of the mixing parameter  $\tau_{mix}$  (in seconds).



Figure 9: Number fraction distributions, as a function of the mixing parameter  $\tau_{mix}$  (in seconds).



Figure 10: Mass fraction distributions, as a function of the mixing parameter  $\tau_{mix}$  (in seconds).

## 6 Conclusions

A stochastic particle model has been developed to describe the idealised free radical polymerisation of methyl methacrylate (MMA) in imperfectly mixed batch and plug flow reactors. Using the method of moments, the model allows efficient computation of the empirical moments of the number and weight average degrees of polymerisation, monomer conversion and (based on the Schulz-Flory distribution) the number and mass fraction distributions, as a function of time and mixing. The model can serve as a simplified reactor model for a subset of the cases covered by Tsai and Fox [15] and can be used to analyse the influence of the chemistry and micro-mixing on the full PDF transport equation.

The model was validated against PREDICI<sup>TM</sup> for the homogeneous case. For nonhomogeneous cases it was shown that the rate of mixing has several effects at low monomer conversions, corresponding to low residence times. At large residence times, the influence of mixing disappears and the reactions converge to the homogeneous case.

We can conclude that, for a typical set of initial conditions, the influence of mixing in our model is dependent on the relationship between the reaction time, characterised by the chemical kinetics, the mixing time,  $\tau_{mix}$  and the reactor residence time, t.

The next step in developing the model will be to add volume contraction and gel effects to the reaction kinetics (see Budde and Wulkow [4]), to investigate the effect of the increasing viscosity on the mixing behaviour, and to include non-isothermal kinetics and reactor cooling effects in the particle model and algorithm. At this point, the model should be validated against experimental data for real, non-perfectly mixed, reactors.

Further enhancements to the model would be to extend the algorithm to semi-batch reactors and CSTRs, and to extend the mechanism to co-polymerisations.

### **A** Descriptors of polymerisation reactions

#### A.1 Number and weight average degrees of polymerisation

Elias [5] defines the number and weight average degrees of polymerisation as

$$\bar{X}_N = \frac{\sum_{i=1}^{\infty} X_i N_i}{\sum_{i=1}^{\infty} N_i} \tag{40}$$

$$\bar{X}_W = \frac{\sum_{i=1}^{\infty} X_i M_i}{\sum_{i=1}^{\infty} M_i}$$

$$\tag{41}$$

where

 $X_i$  = degree of polymerisation.  $\overline{X}_N$  = number average degree of polymerisation  $\overline{X}_W$  = weight average degree of polymerisation  $N_i$  = number of polymers with degree of polymerisation  $X_i$  $M_i$  = molecular weight of polymers with degree of polymerisation  $X_i$ 

In our notation, the degree of polymerisation is given by n, and the number of dead (product) polymers of degree of polymerisation n is a linear function of the molar concentration  $[D_n]$ . The dimensions of the concentration terms cancel, and in our notation (40) may therefore be written as

$$\bar{X}_{N} = \frac{\sum_{n=1}^{\infty} n[D_{n}]}{\sum_{n=1}^{\infty} [D_{n}]} \\
= \frac{\sum_{n=1}^{\infty} n\left([D_{n}] + [P_{n} \cdot]\right) - \sum_{n=1}^{\infty} n[P_{n} \cdot]}{\sum_{n=1}^{\infty} ([D_{n}] + [P_{n} \cdot]) - \sum_{n=1}^{\infty} [P_{n} \cdot]} \qquad (42) \\
= \frac{\lambda_{1} - \mu_{1}}{\lambda_{0} - \mu_{0}}$$

as asserted in equation (29), and where  $\mu_j$  and  $\lambda_j$  are defined in (12) and (13).

Noting that the mass concentration of polymer of length n,  $[\hat{D}_n]$  is still a linear function of the molar concentration, where

$$[P_n \cdot] = M_n [P_n \cdot]$$
$$= n M_1 [P_n \cdot]$$

and

$$[\hat{D}_n] = M_n[D_n]$$
  
=  $nM_1[D_n]$ 

then

$$\hat{\lambda}_{j} = \sum_{n=1}^{\infty} n^{j} \left( [\hat{D}_{n}] + [\hat{P}_{n} \cdot ] \right)$$

$$= M_{1} \sum_{n=1}^{\infty} n^{j+1} \left( [D_{n}] + [P_{n} \cdot ] \right)$$

$$= M_{1} \lambda_{j+1}.$$
(43)

Thus following the argument leading to (42), the weight average degree of polymerisation may be written

$$\bar{X}_W = \frac{\hat{\lambda}_1 - \hat{\mu}_1}{\hat{\lambda}_0 - \hat{\mu}_0}$$
$$= \frac{\lambda_2 - \mu_2}{\lambda_1 - \mu_1}$$

as asserted in equation (30).

### A.2 Schulz-Flory distribution

The number and mass fraction distributions, given by the Schulz-Zimm (SZ) distribution, are given by Elias [5] and cross-referenced with IUPAC  $[11]^2$ :

$$x = \frac{(\zeta/\bar{X}_n)^{\zeta+1} X^{\zeta-1} \bar{X}_n \exp(-\zeta X/\bar{X}_n)}{\Gamma(\zeta+1)}$$
(44)

$$w = \frac{(\zeta/\bar{X}_n)^{\zeta+1} X^{\zeta} \exp(-\zeta X/\bar{X}_n)}{\Gamma(\zeta+1)}$$
(45)

<sup>&</sup>lt;sup>2</sup>Note, there appears to be a typographical error in Elias' definition of w, such that the number fraction distribution is no longer normalised, hence the cross-reference with the IUPAC definition.

where  $\Gamma(\zeta + 1)$  is the gamma-function of  $(\zeta + 1)$ , and the *degree of coupling*,  $\zeta$ , denotes the number of independently grown chains that have coupled to a dead chain. X is the degree of polymerisation and  $\bar{X}_N$  is the number average degree of polymerisation as before.

The Schulz-Zimm distribution tends to the Schulz-Flory (SF) distribution for  $\zeta = 1$  and  $X \to \infty$ . Thus in our notation, the distributions become:

$$x = (1/\bar{X}_n)^2 \, \bar{X}_n \exp(-n/\bar{X}_n) \tag{46}$$

$$w = (1/\bar{X_n})^2 n \exp(-n/\bar{X_n})$$
 (47)

where n is the degree of polymerisation.

Elias [5] asserts that free radical polymerisations lead to the SF distribution because the addition of monomers occurs at random. The derivation given assumes:

- 1. Chain termination by disproportionation.
- 2. Ideal polymerisation kinetics.
  - a Only initiator decomposition and start, propagation and termination have to be considered (no kinetic chain transfer).
  - b All reactions are irreversible.
  - c The effective concentration of initiator radicals is stationary.
  - d The concentration of polymer radicals is stationary.
  - e The principle of equal chemical reactivity applies to propagation and termination reactions (no dependence on molar mass).
  - f Termination occurs only by mutual deactivation of two polymer radicals (combination or disproportionation).
  - g Constant initiator concentration [I] = [I](t = 0).

A termination by disproportionation generates one dead polymer from one polymer radical (the degree of coupling  $\zeta = 1$ ). A termination by combination couples two polymer radicals to one dead chain ( $\zeta = 2$ ). Clearly, the inclusion of a termination by combination step in our MMA mechanism ( $k_{tc} \neq 0$  in Table 1) places us in violation of condition 1. In terms of the ideal polymerisation kinetics, we have a chain transfer to monomer step, and we simulate reaction to high monomer conversion. We are therefore also in violation of conditions 2a and likely to be in violation of 2c, 2d and 2g. However, all reactions in the mechanism are specified as being irreversible with constant kinetic parameters, and termination occurs only by combination and disproportionation. Thus we are still in compliance with conditions 2b, 2e and 2f.

It seems unlikely that our mechanism will lead exactly to SF distributions of the number and mass fractions of polymers, as the differences to the distributions obtained with PREDICI<sup>TM</sup> show (see Figures 4 and 5). Nevertheless, in the absence of other information, SF is accepted as a first approximation.

# **B** Supplementary algorithm information

### B.1 Example initialisation of model

The ensemble is initialised according to the initial conditions specified in Table 1:

$$\langle [M]_0 \rangle = 4.32 \ kmol \ m^{-3}$$
  
 $\langle [I]_0 \rangle = 0.01508 \ kmol \ m^{-3}$   
 $M_M = 100.0 \ kg \ kmol^{-1}$   
 $M_I = 100.0 \ kg \ kmol^{-1}$ .

Thus from (33):

$$r = \frac{M_M \langle [M]_0 \rangle}{M_I \langle [I]_0 \rangle}$$
  
= 286.47214854111405  
= 286 truncating to form an integer.

Set the number of stochastic particles using (32):

$$N = m(r+1)$$
$$= 287$$

where m = 1, noting that fewer particles will result in a faster calculation<sup>3</sup>. Specify the segregated distribution of monomer and initiator in the ensemble using (34) and (35):

$$\begin{bmatrix} M \end{bmatrix}_{0}^{i} = 4.32 \times (287/286) \\ \approx 4.33510 \\ \begin{bmatrix} I \end{bmatrix}_{0}^{i} = 0 \\ \end{bmatrix}^{i} = 0 \\ i \in \{1, \dots, 286\} \\ i \in \{1, \dots, 286\} \\ i \in \{287\}. \\ \begin{bmatrix} M \end{bmatrix}_{0}^{i} = 0 \\ \end{bmatrix}$$

 $<sup>^{3}</sup>$ It is therefore apparent that there is a minimum number of particle required in the model to correctly represent the specified initial conditions.

# List of symbols

$A_k$	Coefficient of first order differential mixing operator	
	of the $k^{\text{th}}$ scalar.	
$D_n$	Dead polymer of degree of polymerisation $n$ .	
f	Probability density function (PDF).	[—]
$f_d$	Efficiency parameter in initiation reaction.	[—]
i	Particle index in the stochastic particle ensemble.	[—]
Ι	Initiator.	
$k_d$	Initiation rate constant.	$[s^{-1}]$
$k_p$	Propagation rate constant.	$[m^3 \ kmol^{-1} \ s^{-1}]$
$k_{tc}$	Termination by combination rate constant.	$[m^3 \ kmol^{-1} \ s^{-1}]$
$k_{td}$	Termination by disproportionation rate constant.	$[m^3 \ kmol^{-1} \ s^{-1}]$
$k_{trm}$	Chain transfer to monomer rate constant.	$[m^3 \ kmol^{-1} \ s^{-1}]$
M	Monomer.	
$M_I$	Molecular weight of initiator.	$[kg \ kmol^{-1}]$
$M_M$	Molecular weight of monomer.	$[kg \ kmol^{-1}]$
$M_n$	Molecular weight of polymer of length $n$ .	$[kg \ kmol^{-1}]$
n	Degree of polymerisation.	[—]
N	Number of stochastic particles in ensemble.	[—]
$P_n$ .	Live polymer of degree of polymerisation $n$ .	
r	Initial mass ratio of monomer to initiator.	[—]
$S_k$	Coefficient of first order differential reaction operator	
	of the $k^{\text{th}}$ scalar.	
t	Time variable.	[s]
w	Mass fraction of polymer.	[—]
x	Number fraction of polymer.	[—]
$x_M$	Monomer conversion.	[—]
$\bar{X}_N$	Number average degree of polymerisation.	[—]
$\bar{X}_W$	Weight average degree of polymerisation.	[—]

# Greek symbols

$\lambda_j$	$j^{\rm th}$ moment of the bulk polymer concentration.	$[kmol \ m^{-3}]$
$\hat{\lambda_j}$	$j^{\rm th}$ moment of the bulk polymer mass concentration.	$[kg \ m^{-3}]$
$\mu_j$	$j^{th}$ moment of the live polymer concentration.	$[kmol \ m^{-3}]$
$\psi_k$	Scalar variable.	
$\overline{\psi}$	Scalar vector.	
$ au_{mix}$	Mixing time parameter.	[s]
$\phi_k$	Scalar random variable.	
$\overline{\phi}$	Scalar random vector.	

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