

## KINETIC MODELLING OF FREE-RADICAL VINYL CHLORIDE POLYMERIZATION WITH A MIXTURE OF INITIATORS

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**Abstract.** The most critical unit operation in commercial manufacturing of poly(vinyl chloride) (PVC) is the polymerization reactor. Therefore, application of modelling techniques on polymerization reactors is essential to gain a clear understanding on the polymerization kinetics. In this paper, the kinetic behaviour of free-radical vinyl chloride polymerization in a suspension poly(vinyl chloride) (PVC) reactor is described. A kinetic model is used to describe the polymerization reaction. The isothermal model predicts the overall monomer conversion, the polymerization rate, reactor pressure and the monomer distribution in the gas, aqueous, and polymer phases for the polymerization cycle. In commercial reactors, mixtures of initiators are usually added to increase the polymerization rate. The model also explores the effect of initiators onto the polymerization rate and conversion. All algorithms are written in MATLAB 7.1.

*Keywords:* Polymerization; vinyl chloride; kinetic modelling; initiator

**Abstrak.** Unit operasi yang paling kritikal di dalam pembuatan komersial plastik polivinil klorida (PVC) adalah reaktor pempolimeran. Oleh itu, aplikasi teknik peragaan pada reaktor pempolimeran adalah penting bagi memperoleh pemahaman jelas tentang kinetik pempolimeran. Kerja ini menjelaskan kelakuan kinetik pempolimeran radikal bebas vinil klorida di dalam reaktor penggantung PVC. Sebuah model kinetik digunakan untuk menyifatkan tindak balas pempolimeran tersebut. Model suhu tetap tersebut meramalkan penukaran monomer keseluruhan, kadar pempolimeran, tekanan reaktor dan taburan monomer di dalam fasa gas, fasa air dan fasa polimer untuk kitar pempolimeran. Campuran bahan pemula biasanya ditambah untuk meningkatkan kadar pempolimeran di dalam reaktor komersial. Model ini turut meneroka kesan bahan pemula di atas kadar pempolimeran and penukaran monomer. Semua algoritma ditulis di dalam MATLAB 7.1.

*Kata kunci:* Pempolimeran; vinil klorida; peragaan kinetik; pemula

### 1.0 INTRODUCTION

First-principle modelling of vinyl chloride polymerisation is essential for the fundamental understanding of the polymerisation reaction kinetics. The mechanism of formation of PVC grains can be grouped into 5 stages as shown below. Figure 1.1 shows the mechanism [1].

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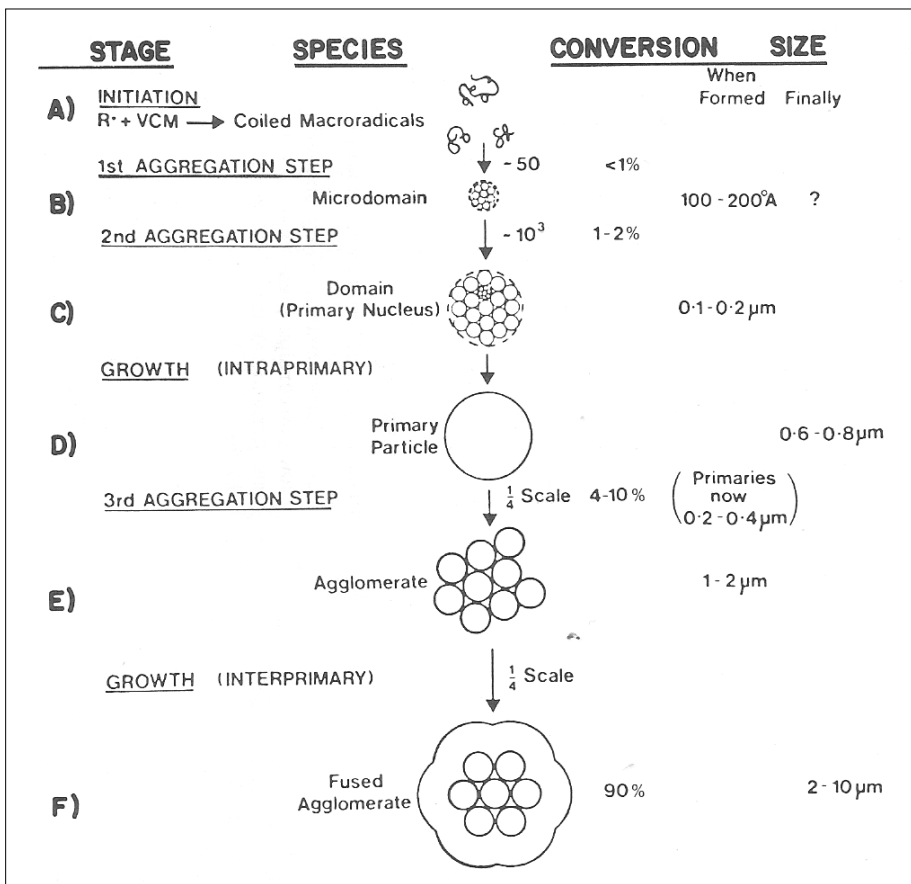
Stage 1: Macroradicals or macromolecules with chain length more than a critical value  $r_c$  begin to precipitate from the monomer phase (at  $H \approx 0.001\%$  conversion).

Stage 2: Aggregation of macroradicals and macromolecules after precipitation produces microdomains ( $0.01 - 0.02 \mu\text{m}$ , at  $<0.01\%$  conversion). The microdomain is not well-defined.

Stage 3: Aggregation of microdomains produces domains ( $0.1 - 0.3 \mu\text{m}$ ,  $<1\%$  conversion) stabilized by negative charge. This stage is completed at  $5 - 10\%$  conversion.

Stage 4: Aggregation and growth of domain causes formation of primary particles until the formation of continuous networks in droplets (about  $15 - 30\%$  conversion).

Stage 5: Primary particles grow and aggregate until free monomer phase disappears. The diameter of final primary particles is  $H \approx 1.2 - 1.5 \mu\text{m}$  ( $50 - 70\%$  conversion).



**Figure 1** Scheme of PVC grain formation

## 2.0 METHODOLOGY

### 2.1 Assumptions and Mechanism

A rigorous kinetic treatment of this mechanism leads to immense complexities. In order to derive a basic kinetic model, it is necessary to introduce some simplifying assumptions and approximations. Two important assumptions are discussed next.

VCM polymerisation is a heterogenous process occurring in two phases. Therefore, a two-stage kinetic model is used to describe the reaction [2]. In the first stage, polymerisation occurs in two phases (the monomer phase and the polymer phase) up to a critical conversion,  $X_f$ . As the reaction proceeds, the mass of the monomer phase decreases while the mass of the polymer phase increases. However, the composition of each phase is assumed to remain constant, because the rapid diffusion of monomer and initiator diffusion into and out of the polymer phase maintains the equilibrium partition. Pressure in the reactor remains constant at this stage. After the critical conversion is reached, the pure monomer phase disappears. When conversion exceeds  $X_f$ , polymerisation proceeds in the polymer phase. The reactor pressure decreases in the absence of the monomer phase. This is due to vapour volume increase and monomer vapour diffusing into the polymer phase. Reaction continues in the polymer phase until a limiting conversion is reached.

The following assumptions are adapted from [2] in developing this kinetic model.

- (i) Polymerisation of VCM in the water and vapour phases is negligible.
- (ii) When conversion is less than critical conversion,  $X_f$ , polymerisation of VCM proceeds in two phases, the monomer phase and the polymer phase. When conversion exceeds  $X_f$ , polymerisation proceeds in the polymer phase.
- (iii) Monomer distribution in the water and vapour phases are taken into account.
- (iv) Monomer and initiators diffuse into and out of the polymer phase rapidly so that equilibrium partition of these species is assumed at all times.
- (v) Bimolecular termination of polymer radicals in the monomer phase is chemically controlled. But bimolecular termination in the polymer phase is diffusion controlled over the entire conversion range.
- (vi) Propagation reactions are diffusion controlled at  $X > X_f$ .
- (vii) The solubility of VCM in PVC follows the Flory-Huggins equation.

In addition, this model also assumes that no transfer of radicals occurs between monomer phase and polymer phase. Using the above simplifications, a kinetic model is developed for the free-radical polymerization of vinyl chloride initiated by a mixture of initiators.

## 2.1 Reaction Kinetic Scheme

A free radical polymerisation mechanism includes initiation, propagation, chain transfer to small molecules and bimolecular termination steps. For free-radical VCM suspension polymerisation, the elementary reactions are shown below.

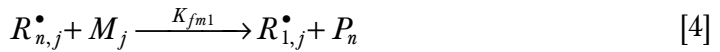
Initiation:



Propagation:



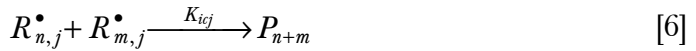
Chain transfer to monomer:



Termination by disproportionation:



Termination by combination:



In the above kinetic scheme, the symbols  $I$  and  $M$  denote the initiator and monomer molecules respectively. Radicals formed by the fragmentation of the initiation reaction are denoted by  $R^{\bullet}$  while  $i$  and  $N_d$  stands for the number of initiators used in the polymerisation.  $R_x^{\bullet}$  and  $P_x$  represents the live macroradicals and the dead polymer chains containing  $x$  monomer units. All the reactions shown above may occur in both monomer phase ( $j=1$ ) and polymer phase ( $j=2$ ) simultaneously.

## 2.2 Reactor Design Equations

### 2.2.1 Phase 1 ( $0 < X < X_f$ )

If the long chain approximation is valid for monomer and polymer phase, the polymerisation rate of VCM can be expressed as following [2].

$$\frac{dX}{dt} = \frac{K_p}{N_o M_m} \left( [R^{\bullet}]_1 M_1 + [R^{\bullet}]_2 M_2 \right) \quad [1]$$

$$[R^{\bullet}]_1 = \sqrt{\frac{(RI_{a1} + RI_{b1})}{K_{t1}}} \quad [2]$$

$$[R^\bullet]_2 = \sqrt{\frac{(RI_{a2} + RI_{b2})}{K_{t2}}} \quad [3]$$

In equation [2] and [3],  $[R^\bullet]_1$  and  $[R^\bullet]_2$  are the polymer radical concentrations in monomer phase and polymer phase respectively. During suspension polymerisation, monomer partitions in monomer, polymer, water and vapour phases. The total amount of monomer in the water and vapour phases is  $H \approx 4\%$  under commercial reactor operations. Hence it is important to consider monomer distributions for valid kinetic reactor modelling. The main equations according to [2] are as below.

$$M_1 = M_0(1 - X) - M_g - M_w - M_2 \quad [4]$$

$$M_2 = X[M_0(1 - X_f) - M_{gX_f} - M_w] / X_f \quad [5]$$

$$M_g = \frac{M_m P_m^\circ}{RT} \left[ (1 - W_i) V_r + \frac{X M_0 (1/D_m - 1/D_p)}{1 - D_{g0}/D_m} \right] \quad [6]$$

$$M_w = K W_w \quad [7]$$

$$M_{gX_f} = \frac{M_m P_m^\circ}{RT} \left[ (1 - W_i) V_r + \frac{X_f M_0 (1/D_m - 1/D_p) D_m}{D_m - D_{g0}} \right] \quad [8]$$

$$W_i = \left[ \frac{(W_w/D_w + M_0/D_m - D_{g0}V_r/D_m)}{V_r(1 - D_{g0}/D_m)} \right] \quad [9]$$

where 
$$D_{g0} = \frac{P_{m0} M_m}{RT} \quad [10]$$

Assuming volume additivity, the volumes of the monomer and polymer phase are:

$$V_1 = M_1 / D_m \quad [11]$$

$$V_2 = M_2 / D_m + M_0 X / D_p \quad [12]$$

The total initiator mole balance can be written as below:

$$[I]_1 = I_0 \exp(-K_d t) / (V_1 + K_1 V_2) \quad [13]$$

$$[I]_2 = K_I [I]_1 \quad [14]$$

where  $[I]_1$  and  $[I]_2$  = Initiator concentrations in mol/L.

### 2.2.2 Phase 2 ( $X > X_f$ )

$$\frac{dX}{dt} = \frac{K_{t2}}{N_0 M_m} (R_{t2} / K_{t2})^{1/2} M_2 \quad [15]$$

where

$$M_2 = M_0 (1 - X_f) - M_g - M_w \quad [16]$$

$$M_g = \frac{M_m P_m}{RT} \left[ (1 - W_i) V_r + M_0 (1/D_m - 1/D_p) \times \left( X + X_f \frac{D_{g0}}{D_m - D_{g0}} \right) \right] \quad [17]$$

$$M_w = K W_w P_m / P_m^0 \quad [18]$$

$$R_{t2} = 2 f K_d I_0 \exp(1 - K_d t) V_2 \quad [19]$$

The kinetic rate constants can be obtained using the equations below.

$$K_{t2} = K_{t1} \exp \left[ -A * (1/V_{fp} - 1/V_{fcri}) \right] \quad [20]$$

$$K_p = K_{pxf} \exp \left[ -B * (1/V_{fp} - 1/V_{fxf}) \right] \quad [21]$$

$$K_d = K_{dxf} \exp \left[ -C * (1/V_{fp} - 1/V_{fxf}) \right] \quad [22]$$

where

$K_{t1}, K_{t2}$  = number average termination constants (accounts for chain length dependence of bimolecular termination)

$V_{fp}$  = free volume fraction of the polymer-monomer mixture for  $X > X_f$

$V_{fcri}$  = critical free volume fraction at which bimolecular termination reaction of polymer phase becomes diffusion-controlled.  $V_{fcri}$  is used as an adjustable parameter in the model.

Table 1.1 shows the reaction kinetic parameters used for Phase 1 when conversion is less than critical conversion,  $X_f$  while Table 1.2 shows the reaction kinetic parameters used for Phase 2.

The expression for critical conversion,  $X_f$  is as below. It is applicable for both phases in the polymerization of vinyl chloride.

$$X_f = \frac{M_0 - [D_{g0} (1 - W_i) V_r] + K W_w}{M_0 \left\{ \left[ 1 - D_{g0} (1/D_m - 1/D_p) \right] / (1 - D_{g0} - D_m) + D_m (1 - \phi_2) / \phi_2 D_p \right\}} \quad [23]$$

To obtain volume fraction of polymer phase using Flory-Huggins equation, the following expressions are used.

**Table 1.1** Reaction kinetic parameters for phase 1 ( $X < X_f$ )

Variable	Value	Unit	ref
Initiator: Perkadox 16-W40			
MW	398	g/mol	a
$K_d$	$K_d = 2.31 \times 10^{15} \exp(-29.1kcal/RT)$	$s^{-1}$	a
$K_p$	$K_p = 30 \times 10^8 \exp(-3320/T)^b$	$m^3/kmol/min$	b
$(K_{fm})_1$	$(K_{fm})_1 = 1.9 \times 10^5 \exp(-7800/RT)$	L/mol/s	a
$K_{t1}$	$K_{t1} = 1.3 \times 10^{12} \exp(-4200/RT)$	L/mol/s	a
$\left(\frac{K_{t1}}{K_{t2}}\right)^{1/2}$	$\left(\frac{K_{t1}}{K_{t2}}\right)^{1/2} = 24 \exp[1007(1/T - 1/333.15)]$	$m^3/kmol/min$	c
$K$	$K = 0.0472 - 11.6/T$		a
$P_{m0}$	$P_{m0} = 12722 \exp(2411.7/T)$	atm	a
$P_m$	$P_m = P_t - P_w$	atm	a
$\chi$	$\chi = 1286.4/T - 3.02$		a

<sup>a</sup>[2]. <sup>b</sup>[3]. <sup>c</sup>[4].

**Table 1.2** Parameters used in Phase 2 ( $X > X_f$ ) [2]

Variable	Value	Unit
$A^*$	$A^* = 6.64 \times 10^6 \exp(-4986/T)$	
$B^*$	$B^* = 1.85 \times 10^3 \exp(-2595/T)$	
$C^*$	$C^* = 477 \exp(-2291/T)$	
$V_{fp}$	$V_{fp} = 0.025 + a_p (T - T_{gp})$	$cm^3/cm^3$
$V_{fm}$	$V_{fm} = 0.025 + a_m (T - T_{gm})$	$cm^3/cm^3$
$a_m$	$a_m = 9.98 \times 10^{-4}$	$K^{-1}$
$a_p$	$a_p = 5.47 \times 10^{-4}$	$K^{-1}$
$T_{gm}$	70	K
$T_{gp}$	$T_{gp} = 87.1 - 0.132(T - 273.15)$	C

For  $0 < X < X_f$ ,  $P_m = P_{m0}$

$$\ln(1 - \phi_2) + \phi_2 + \chi\phi_2^2 = 0 \quad [24]$$

For  $X > X_f$ ,

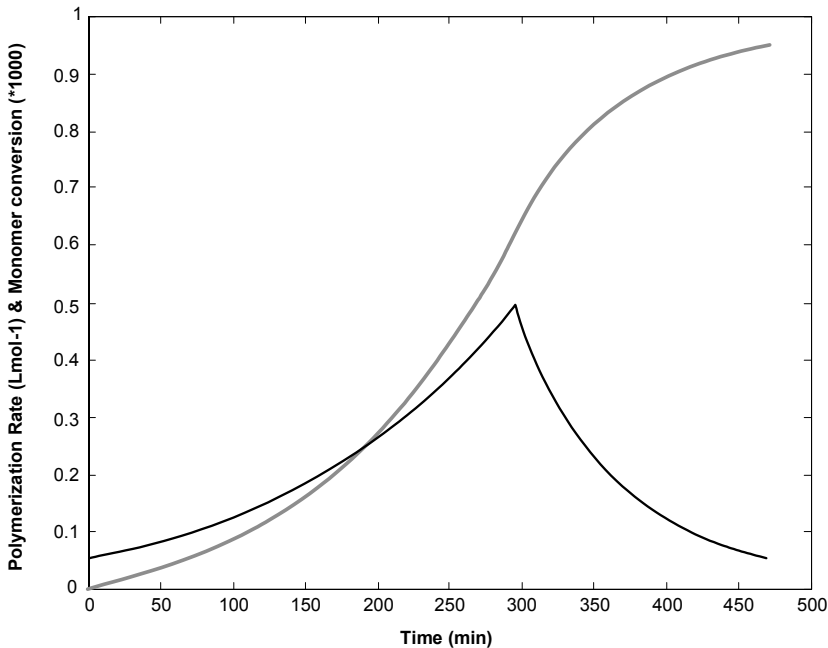
$$\ln(P_m / P_{m0}) = (1 - \phi_2) + \phi_2 + \chi\phi_2^2 \quad [25]$$

where  $\phi_2$  = volume fraction of polymer phase  
 $\chi$  = VCM-PVC interaction parameter  
 $P_m$  = Partial pressure of monomer (atm)  
 $P_{m0}$  = Vapour pressure of monomer (atm)

### 3.0 RESULTS AND DISCUSSION

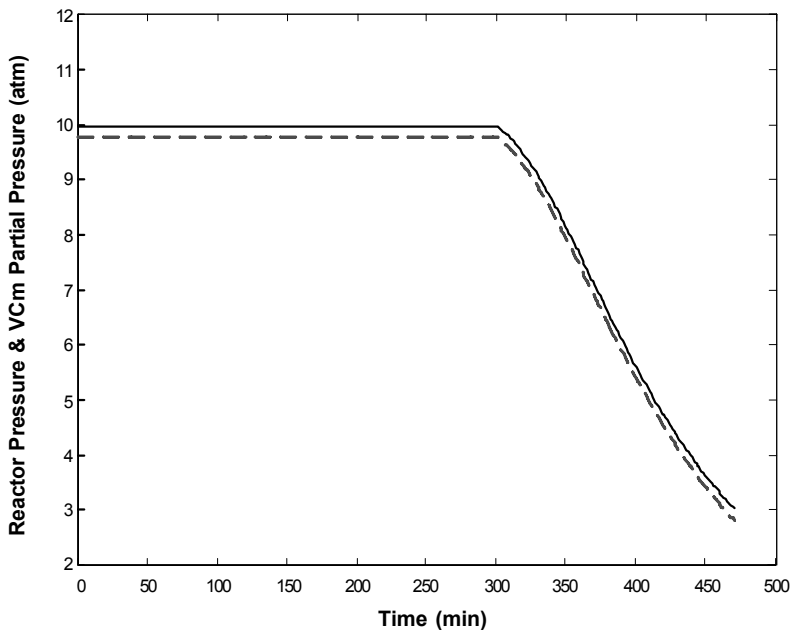
The capability of the model to predict vinyl chloride polymerization is shown with the following results.

In Figures 1 – 2, the model results on polymerization rate, monomer conversion, reactor pressure and VCM partial pressure are plotted with respect to the polymerization time at polymerization temperature of 60 °C. The results agree well with model and experimental results by Xie *et al.* (1991). In Figure 1, the polymerization rate peaks at critical conversion,  $X_f$  and decreases drastically after that. This peak in polymerization rate will result in large temperature increase in the reactor and should be given due attention in the dynamic modelling of the reactor. Monomer conversion reaches 0.95 in the model predictions. In Figure 2, the reactor pressure also drops after critical conversion. This is due to the reduction of the termination rate constant in polymer phase after critical conversion. The termination rates in the polymer phase are diffusion controlled due to the high volume of polymer.

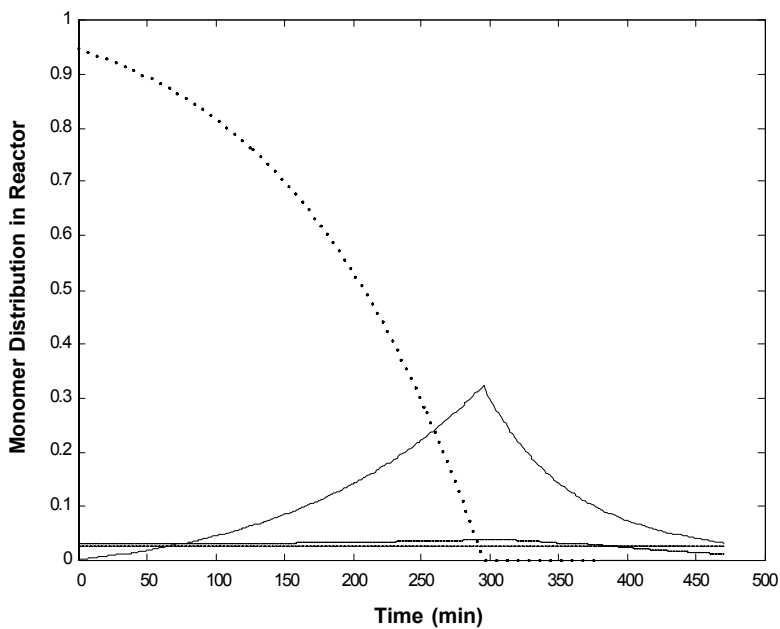


**Figure 1** Polymerization rate and monomer conversion at polymerization temperature of 60 °C



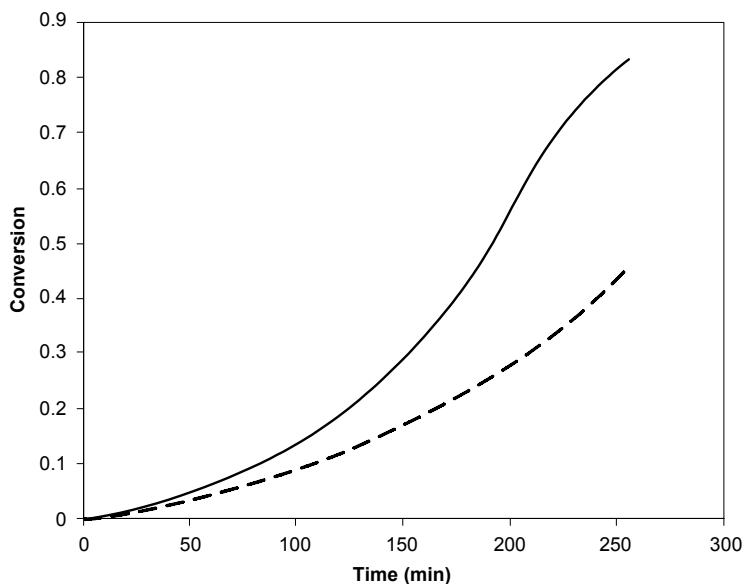


**Figure 2** Reactor pressure and VCM partial pressure at polymerization temperature of 60 °C



**Figure 3** Monomer distributions in four different phases at polymerization temperature of 60 °C (Monomer, Polymer, Water and Gas)

At any time of polymerization, monomer will be distributed in four phases in the reactor. Figure 3 shows the monomer distributions in four different phases in the reactor, which are the monomer phase, polymer phase, water phase and gas phase. The model predictions are accurate as according to literature, the amount of monomer in the water phase and gas phase accounts for around 4% of the total monomer. Monomer in monomer phase is consumed continuously and is fully consumed at critical conversion.



**Figure 4** Monomer conversion using different mixtures of initiators

#### 4.0 CONCLUSION

Initiator concentration affects the conversion of vinyl chloride polymerization. Increasing the initiator concentration will reduce batch time and therefore increase productivity. However, increasing the initiator concentration might affect the molecular weight distribution of PVC produced. This effect will be studied next. Polymer models are valuable and applicable for future use in industries only if they correctly compute and track polymer product quality and properties as process conditions change. Therefore, it is essential that polymer models relate end-use properties to polymer molecular structure. A complete dynamic model complete with polymerisation kinetics and mechanism is essential to accurately model the VCM polymerisation. Besides polymerization chemistry, it is even more important to investigate the molecular weight distributions characterizing polymer quality. These are the measurable variables that are critical to VCM polymerisation and will be studied in future research.

**NOMENCLATURE**

$A$	-	Adjustable parameter for empirical termination rate equation
$A^*$	-	Free volume factor used in $K_t$ equation
$A_J$	-	Area of jacket
$B$	-	Adjustable parameter for empirical termination rate equation
$B^*$	-	Free volume factor used in $K_p$ equation
$C$	-	Adjustable parameter for empirical termination rate equation
$C^*$	-	Free volume factor used in $K_d$ equation
$C_p$	-	Heat capacity
$D$	-	Adjustable parameter for empirical termination rate equation
$D_m$	-	Density of monomer (g/L)
$D_p$	-	Density of polymer (g/L)
$D_w$	-	Density of water (g/L)
$\Delta Hr$	-	Heat of reaction (kJ/kmol)
$f$	-	Initiator efficiency
$I$	-	Initiator
$[I]$	-	Concentration of initiator (mol/L)
$J$	-	Parameter defined in the model
$K$	-	Solubility constant of VCM in water
$K^*$	-	Parameter of precipitation defined in the model
$K_d$	-	Decomposition rate constant of the initiator (1/s)
$K_{de}$	-	Desorption rate constant of radicals
$K'_{de}$	-	Modified desorption rate constant of radicals
$K_{fm}$	-	Chain transfer to monomer rate constant ( $L \text{ mol}^{-1} \text{ s}^{-1}$ )
$K_{fp}$	-	Chain transfer to polymer rate constant ( $L \text{ mol}^{-1} \text{ s}^{-1}$ )
$K_i$	-	Initiation rate constant ( $L \text{ mol}^{-1} \text{ s}^{-1}$ )
$K_p$	-	Propagation rate constant ( $L \text{ mol}^{-1} \text{ s}^{-1}$ )
$K_t$	-	Termination rate constant ( $L \text{ mol}^{-1} \text{ s}^{-1}$ )
$K_I$	-	Initiator partition coefficient
$M$	-	Monomer
$M_1$	-	Mass of monomer in the monomer phase (g)
$M_2$	-	Mass of monomer in the polymer phase (g)
$[M]$	-	Concentration of monomer (mol/L)
$M_g$	-	Mass of monomer in gas phase (g)
$M_{gX_f}$	-	Mass of monomer in gas phase at $X_f$ (g)
$M_m$	-	Molecular weight of monomer
$M_0$	-	Initial monomer charged (g)
$N_0$	-	Initial number of moles of monomer charged
$N_D$	-	Number of initiators
$P$	-	Polymer
$P_m$	-	Partial pressure of monomer (atm)

$P_{m0}$	-	Vapour pressure of monomer (atm)
$Q$	-	Adjustable parameter
$R$	-	Gas constant (1 atm mol <sup>-1</sup> K <sup>-1</sup> )
$R^\bullet$	-	Live polymer radicals
$R_I$	-	Initiation rate (mol L <sup>-1</sup> s <sup>-1</sup> )
$[R^\bullet]$	-	Radical concentration (mol/L)
$t$	-	Reaction time (min) or temperature (°C) as specified
$T$	-	Temperature (K)
$T_0$	-	Reference temperature, 0 °C
$T_c$	-	Chilled water injection temperature
$U$	-	Overall heat transfer coefficient, kJ/ (m.s.K)
$U_a$	-	Heat transfer coefficient from jacket to ambient, kJ/(m.s.K)
VCM	-	Vinyl chloride monomer
$V$	-	Reaction volume (L)
$V_r$	-	Reactor volume (L)
$V_{fcri}$	-	Critical free volume fraction
$V_{fjp}$	-	Free volume fraction of the polymer-monomer mixture
$V_{fXf}$	-	Free volume fraction at $X_f$
$W_w$	-	Water charged
$W_i$	-	Initial fractional fillage of the reactor
$X$	-	Fraction conversion
$X_f$	-	Critical conversion at which monomer is fully consumed.

### Greek Letters

$\chi$	-	VCM –PVC interaction parameter
$\phi_2$	-	volume fraction of polymer phase
$\phi_p$	-	volume fraction of polymer in polymer phase
$\rho$	-	Density, kg/m <sup>3</sup>
$\tau_D$	-	Delay constant
$\mu_i$	-	ith moment of dead polymer chains
$\lambda_i$	-	ith moment of live radical chains

### Subscripts

0	-	Initial state
1	-	Monomer phase
2	-	Polymer phase
$m$	-	Monomer
$p$	-	Polymer
$n$	-	Chain number
$i$	-	Initiator species, $i = 0, 1, 2, \dots$
$j$	-	Phase number, $j = 1, 2.$

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