

CHAPTER 3

THE EMULSION POLYMERIZATION MODEL

Earlier emulsion polymerization theories have been developed largely from batch experimental data since emulsion polymerization in a semi-batch reactor or a continuous stirred tank reactor is more complicated and difficult to carry out with increasing difficulty in data interpretation. Since last decade, there are many theoretical and experimental works on CSTR emulsion polymerization. Polymerization in CSTR has many advantages over batch and semi-batch emulsion polymerization such as offers large scale production, minimum manpower maintenance and downtime, easier operation and control, more consistent product quality and higher throughputs (Kiparissides et al., 1990 and Piirma, 1982).

A successful model for reactor is one which is versatile enough utilize a common set of kinetic mechanisms and parameters to predict behavior of a batch, semi-batch or continuous stirred tank reactor. The unique kinetic in CSTR, such as broad and multi-peaked particle size distributions, the intermittent nucleation of particles with consequent sustained oscillation of conversion and/or multiple steady state conditions and the strong influence of start up procedure on the steady state behavior, can be modeled from a basic knowledge of batch kinetic.

Continuous stirred tank reactor of emulsion polymerization for various type of monomers have been known to exhibit isothermal multiple steady state and sustained oscillations for a wide range of operating conditions. Indeed the persistence of these unwanted oscillation is one of the obstacles to the acceptance of continuous processes for emulsion polymerization. Table 3.1 summerizes the pertinent experimental studies displaying sustained oscillations and multiple steady states. Note that oscillations have been reported for the styrene-

butadiene, vinyl chloride, methylmethacrylate, vinyl acetate and styrene systems. The period of these oscillations ranges from three to ten reactor residence times, depending on operating condition.

According to the study of Kirillov and Ray(1978), Kiparissides et al.(1980), Rawlings and Ray(1978), vinyl acetate polymerization is known to exhibit sustained oscillation. This case can be explained from the fact that there is insufficient free emulsifiers to cover the surface of particle during the particle generation period.

Many investigators have simulated the batch and continuous emulsion polymerization reactor with mathematical model in an attempt to understand its phenomena. Concluded experimental and theoretical works are shown in table 3.2.

Table 3.1 Experimental studies displaying sustained oscillation and multiple steady state(Killov and Ray, 1978; Rawlings and Ray, 1978).

Investigators	System	Observation
Owne et al.(1947)	Styrene-butadiene	Oscillation
Jacobi(1952)	Vinyl chloride	Oscillation
Gershberg and Longfield(1961)	Styrene	Oscillation
Gerrens et al.(1971)	Styrene	Multiple steady states
Gorber(1973)	Styrene	Multiple steady states
Ley and Gerrens(1974)	Styrene	Multiple steady states
Greene et al.(1976)	Methylmethacrylate	Oscillation
	Vinyl acetate	Oscillation
Brooks et al.(1978)	Styrene	Oscillation
Kiparissides et al.(1978)	Vinyl acetate	Oscillation
Nomura et al.(1980)	Vinyl acetate	Oscillation
Schork et al.(1980)	Methylmethacrylate	Multiple steady states
Schork and Ray(1981)	Methylmethacrylate	Multiple steady states
Lee and Mallinson(1988)	Vinyl acetate	Oscillation

Table 3.2 Previous experimental and theoretical works on emulsion polymerization and the related works.

Investigator(s)	Details
Harkins(1945,1947)	He proposed the mechanism of batch emulsion polymerization, nucleation of polymer particles and the progression of the reaction, based on his experimental works. Full details of Harkin's works are shown in Section 2.1
Smith and Ewart (1948)	They proposed the kinetic of batch emulsion polymerization based on Harkins's work. Their kinetic is divided into three cases, each case they developed the equation to calculate the average number of free radicals per particle, reaction rate, mean polymerizing lifetime of radical and the number of polymer particles. The full details of Smith and Ewart kinetic are shown in Section 2.2.
Stockmayer(1957) O'Tools(1965)	Stockmayer presented the general equations for the Smith and Ewart's model which are later corrected by O'Tools. O'Tools applied a modified form of the recurrent formular to produce the general solution. Their simplified equations are $(R_a/N)P_n = [k_{de} + (nk_{tp}/VN_A)](n+1)P_{n+1} + (n+1)(n+2)(k_{tp}/VN_A)P_{n+2}$ $N_n = \frac{a^n 2^{(m-1-3n)/2} I_{m-1+n}(a/2)}{n! I_{m-1}(a)}$ $q = \begin{cases} \frac{a I_m(a)}{4 I_{m-1}(a)} & \text{for } 0 < m < 1 \\ \frac{a I_0(a)}{4 I_1(a)} & \text{for } m = 0 \\ \frac{(1-m) + a I_{m-2}(a)}{2 \cdot 4 I_{m-1}(a)} & \text{for } m > 1 \end{cases}$ $a = 8\sqrt{\alpha}$ $\alpha = R_a VN_A / Nk_{tp}$ $m = k_{de} VN_A / k_{tp}$ $I_k(x) - \text{modified Bessel function of the first kind.}$

Table 3.2 (continued)

Investigator(s)	Details
Ugelstad et al. (1967)	<p>They proposed the method for the calculation of q in batch emulsion polymerization by considering the possibility that desorbed radicals being accumulated in the water phase may become re-absorbed by the particle or undergo biradical termination in the aqueous phase. Thus the radical production rate can be expressed as</p> $R_a = R_i + \sum_{n=1}^{\infty} k_{de} N_n n - 2k_{tw} [R_w]^2$
Min and Ray(1974), Kirillove and Ray (1978), Min and Ray(1978), Rawling and Ray (1987)	<p>They studied the effect of reactor type on polymer properties of methylmethacrylate continuous emulsion polymerization. They studied both steady state and dynamic conditions. The developed dynamic model was fitted well with experimental data with limited cycle oscillations. Their model was developed via the discrete particle generation due to the particle generated time. Rawling and Rays simplified the previous works and developed the model that included the particle size distribution, average number of radicals per particle and couple the particle generation rate to the particle size distribution. The simplified model equations for j th generation of particle are</p> $q(t, t) = k_q r$ $N(t, t) = k_f m_s(t) H(m_s) e^{-(t-t)}$ $r(t, t) = k_r ((t-t) + v)^{1/3}$ $m_s(t) = 1 - k_m \int_0^t m_s(t) H(m_s) e^{-(t-t)} (t-t+v)^{2/3} dt$ $x(t) = k_x \int_0^t m_s(t) H(m_s) e^{-(t-t)} (t-t) dt$ <p>k_q, k_f, k_r, k_x - constants.</p>
Friis and Hamielec (1975)	<p>They proposed the model for the average chain length of batch emulsion polymerization based on Smith and Ewart case II kinetic. The model is divided into two cases.</p> <p>Case A transfer reactions control molecular weight at $X < X_c$</p> $r_N = \frac{1 + KX_c / (1 - X_c)}{C_m}$

Table 3.2 (continued)

Investigator(s)	Details
Friis and Hamielec (continued)	$r_w = \frac{2(1 + KX_c/(1-X_c))^2}{(C_m + C_p X_c/(1-X_c)) - (2C_p X_c/(1-X_c))(1 + KX_c/(1-X_c))}$ $B_N = \frac{C_p r_N X_c/(1-X_c) + KX_c/(1-X_c)}{C_m + C_p X_c/(1-X_c)}$ <p>at $X > X_c$</p> $\frac{d[M_o]}{dX} = C_m [M_{p,o}] - \frac{K[M_o][M_{p,o}]}{[M_p]}$ $\frac{d[M_1]}{dX} = [M_{p,o}]$ $\frac{d[M_2]}{dt} = [M_{p,o}] + \frac{2 \left[\frac{[M_{p,o}] + K[M_1][M_{p,o}]}{[M_p]} \right] \left[\frac{[M_p] + C_p [M_2] + K[M_1]}{C_m [M_p] + C_p [M_1]} \right]}{C_m [M_p] + C_p [M_1]}$ $\frac{d([M_o]B_N)}{dX} = \frac{(C_p [M_1] + K[M_o])[M_{p,o}]}{[M_p]}$ $r_w = [M_2]/[M_1]$ $r_N = [M_1]/[M_o]$ $C_m = k_{fm}/k_p$ $C_p = k_{fp}/k_p$ $K = k_{pdb}/k_p$
	<p>Case B termination reaction control the molecular weight.</p> $\theta = \frac{k_p [M_p]}{k_p [M_p] + k_{fm} [M_p] + k_{fx} [x] + (R_i/N_p)N_A}$ $r_N = 1/(1 - \theta)$ $r_w/r_N = 2$
Kiparissides(1978) Kiparissides et al. (1980)	They developed the comprehensive dynamic model for continuous emulsion polymerization of vinyl acetate based on the particle age distribution. The model equations are in the form of integrodifferential equations. Full details of the model and the extensive works are shown in section 3.1.
Chiang and Thompson (1979)	They simplified Kiparissides's model by changing the integrodifferential equations into full differential equations, which can easily be solved by Laplace transform.

Table 3.2 (continued)

Investigator(s)	Details
Chiang and Thompson	They considered number of particles, particle surface area, particle diameter, particle volume and conversion. The model results fitted very well with Green's experimental data of vinyl acetate continuous emulsion polymerization. The full details of the model are shown in Section 3.2.

Normura et al. (1981) They proposed the rate coefficient for radical desorption from polymer particles in emulsion polymerization system to explain the kinetic deviation of water soluble monomers such as vinyl acetate and vinyl chloride from classical Smith & Ewart theory. The model equations for radical desorption coefficient and average number of radicals per particle are

$$k_{de} = \frac{12D_p \delta z}{md_p^2} \cdot \frac{k_{fm}}{k_p} \quad \text{for low conversion}$$

$$k_{de} = \frac{2D_p \delta z}{d_p^2} \cdot \frac{k_{fm}}{k_p} \quad \text{for high conversion}$$

$$z = \sum_{j=1}^s \left[\frac{k_p [M_p]}{K_o q + k_p [M_p]} \right]^j \quad 0 < z < s$$

For vinyl acetate and vinyl chloride system, $z = 1$

$$q = \frac{1}{2} \left[\left| \frac{r_1}{k_f N_t} \right|^2 + \left| \frac{r_1}{k_f N_t} \right| \right]^{1/2} - \left| \frac{r_1}{k_f N_t} \right|$$

The above equation can be simplified into two limiting cases.

$$q = 1/2 \quad \text{when } (r_1/k_f N_t)^{1/2} \rightarrow \infty$$

$$q = (r_1/k_f N_t)^{1/2} \quad \text{when } (r_1/k_f N_t)^{1/2} < 10^{-2}$$

$$r_1 = 2fk_d [I_w]$$

Baaded et al. (1982) They studied the kinetic of vinyl acetate polymerization in suspension polymerization upto high conversion. They found that the change of volume of the polymerizing system has no significant effect on kinetic. The narrowest molecular weight distribution of obtained poly(vinyl acetate) was achieved when polymerizing in the homogeneous continuous

Table 3.2 (continued)

Investigator(s)	Details
Baaded et al. (continued)	stirred tank reactors while the broadest molecular weight distribution was observed in the separated continuous stirred tank reactor. According to their proposed kinetic and mechanism, the calculated results are agree quite well with the experimental data.
Pramojaney(1982)	He developed a mathematical model to describe the kinetics of emulsion polymerization, the transient behavior of conversion, particle size distribution for vinyl acetate and styrene system in batch, semi-batch and continuous stirred tank reactor. The model is developed via material balance. The obtained calculation from the model was reasonably agree with experimental data.
Trimided et al. (1983)	<p>They ran an experimental study of batch emulsion polymerization of vinyl acetate and found that their polymerization data supported the general concepts of Smith and Ewart kinetic, the growth and termination of chain take place mainly inside the monomer-swollen polymer particles, but the polymerization rate is better predicted by the equation suggested by Harriott(1971). The rate of polymerization suggested by Harriott and this study is</p> $R_p = k_p [M_p] (2k_p [I_w] V_w V_p / k_t)^{1/2}$ <p>V_m - volume fraction of the aqueous phase V_p - volume fraction of the polymer phase</p>
Taylor and Reichert (1985)	<p>They developed model to describe the influence of reactor types and operating conditions on polymer properties for vinyl acetate polymerization. They took the gel effect into consideration and expressed as time dependent function because the model was developed based on the batch reactor conditions. The continuous model was developed after the batch model by taking time dependent</p>

Table 3.2 (continued)

Investigator(s)	Details
Taylor and Reichert (continued)	<p>function on the batch equations. They considered the differences between terminal double bond and non-terminal double bond species and the calculations from the proposed model were agree quite well with their experimental data.</p> <p>The equations were developed by moment method and are shown below.</p>
	$\frac{dX}{dt} = k_p(1 - X)[M^*_0]$
	$\frac{dX_i}{dt} = k_d(1 - X_i)$
	$[M^*_1] = C_1(k_p[M_p])(\sum_{i=0}^i \binom{i}{k} [M^*_k] - [M^*_1])$ $+ k_{fm}[M_p][M^*_0] + k_{fp}[M^*_0][M_{i+1}]$ $+ k_{pdb} \sum_{i=0}^i \binom{i}{k} ([M^*_k][M_{i-k}] - [M^*_0][M_i])$
	$[M^*_1] = C_1(k_p[M_p])(\sum_{i=0}^i \binom{i}{k} [M_k] - [M_1])$ $+ k_t[M^*_0]^2 + k_{fp}[M_0][M_{i+1}]$ $+ k_{pdb} \sum_{i=0}^i \binom{i}{k} ([M^*_k][M_{i-k}] - [M^*_0][M_i])$
	$[M_1] = k_p[M_p](\sum_{i=0}^i \binom{i}{k} [M^*_k] - [M^*_1])$ $+ k_{fm}[M_p][M^*_0] + (k_t/2)[M^*_1][M^*_0]$ $+ k_{pdb} \sum_{i=0}^i \binom{i}{k} ([M^*_k][M_{i-k}] - [M^*_1][M_0] - [M^*_0][M_i])$
	$[M_1] = k_p[M_p](\sum_{i=0}^i \binom{i}{k} [M_k] - [M_1]) + k_t[M^*_0]^2$ $+ k_{pdb} \sum_{i=0}^i \binom{i}{k} ([M^*_k][M_{i-k}] - [M^*_0][M_i])$ $- (k_t/2)[M^*_1][M^*_0]$
	$[M^*_0] = (2fk_d I/k_t)^{1/2}$
	$C_1 = 1/(k_{fm}[M_p] + k[M_1] + k_t[M^*_0])$
	$M_w = MW^* \left[\frac{([M^*_2] + [M_2]) + ([M_2] + [M_2])}{([M^*_1] + [M^*_1]) + ([M_1] + [M_1])} \right]$

Table 3.2 (continued)

Investigator(s)	Details
Taylor and Reichert (continued)	$M_n = MW \frac{([\underline{M}_1^*] + [\underline{M}_1^*]) + ([\underline{M}_1] + [\underline{M}_1])}{([\underline{M}_0^*] + [\underline{M}_0^*]) + ([\underline{M}_0] + [\underline{M}_0])}$ $PDI = M_w/M_n$

The model equations for homogeneous mixed continuous stirred tank reactor (HCSTR) and completely segregated continuous stirred tank reactor (SCSTR) were derived by taking time dependent functions on batch equations. Let P_1 is the property in batch reactor.

$$\frac{dP_{1, BR}}{dt} = F_1(P, t) \quad \text{for batch reactor}$$

$$P_{1, HCSTR} = \theta F_1(P, \theta) + P_{1, 0} \quad \text{for HCSTR}$$

$$P_{1, SCSTR} = \int_0^\infty P_{1, BR} e^{-t/\theta} d\theta \quad \text{for SCSTR}$$

Chern and Poehlein
(1987)

They proposed model for batch emulsion polymerization of vinyl acetate to calculate the average number of free radicals in the polymer particle based on the assumption that the particles in the system, N , consist of the following members, inactive particle, N_0 , particle with one monomer-unit free radical, N_m , particle with one polymeric radical, N_p , particle with one polymeric radicals and one monomer-unit free radical, N_{mp} and particle with two polymeric radical, N_{pp} . In this model q is defined as the ratio of number of particles with polymeric radical over total number of particles, the model equations are

$$N = N_0 + N_m + N_p + N_{mp} + N_{pp}$$

$$q = (N_p + N_{mp} + 2N_{pp})/N$$

$$N_p = ((E_2 - 4E_1E_3)^{1/2} - E_2)/2E_1$$

$$N_m = D_1 N_p + D_2$$

$$N_{pp} = B_1 N_m + B_2 N_p + B_3$$

$$N_{pm} = A_1 N_m + A_2 N_p + A_3 N_{pp} + A_4$$

$$dX/dt = (k_p [M_p] (MW) / M_0 N_A) / qN$$

A_1, B_1, D_1, E_1 - constants.

Table 3.2 (continued)

Investigator(s)	Details
Chern and Poehlein (1987)	<p>They proposed the model based on nonuniform free radical distribution in the polymer particles of styrene emulsion polymerization system. The primary assumption of the model is that the generated free radicals are hydrophilic and often ionic. Thus, the free radicals that enter monomer-swollen particles are likely to be low molecular weight oligomer with hydrophilic end groups and these end groups will have a strong tendency to stay on the surface of particles and constrain the movement of the growing radicals into the particle interior, then particles with nonuniform radical distribution are generated. Due to Monte Carlo simulation, this model predicted that the free radical concentration will be greater near the particle surface. Such a nonuniform distribution could have a significant influence on reaction kinetics and product quality. According to the model postulation, the desorption rate constant is expressed as</p> $k_{de} = \frac{k_{fm} (4\pi/3)^{2/3} D_w}{k_p a (1/k - 2/k^2 + 2/k^3) - (2e^{-k})/k^3}$ <p>a, k - constants.</p>
Lee and Mallinson (1988)	<p>They developed the model for continuous vinyl acetate emulsion polymerization but they did not consider the differences between terminal double bond and non-terminal double bond species and the termination mode is the reaction of active polymer chain and adsorbed water phase radical only. The model agreed only with the observed experimental data at low initiator and low emulsifier concentration. The model equations were developed by making the balance equation over the specific species and are shown below.</p> $\begin{aligned} d[M_0]/dt &= K_2[M_0^*] - (K_3 + K_4 + 1/\theta)[M_0] \\ d[M_1]/dt &= K_2[M_1^*] - (K_3 + K_4 + 1/\theta)[M_1] \\ d[M_2]/dt &= K_2[M_2^*] - (K_3 + K_4 + 1/\theta)[M_2] \\ d[M_0^*]/dt &= K_1[P_0^*] - (K_2 + 1/\theta)[M_0^*] + K_3[M_0] \end{aligned}$

Table 3.2 (continued)

Investigator(s)	Details
Lee and Mallinson (continued)	$d[M_1^*]/dt = K_1([P_o^* + [M_o^*]]) - (K_2 + 1/\theta)[M_1^*]$ $+ (K_3 + K_4)[M_1]$ $d[M_2^*]/dt = K_1([P_o^* + 2[M_1^*] + [M_o^*]]) - (K_2 + 1/\theta)[M_2^*]$ $+ (K_3 + K_4)[M_2] + 2k_{pdb}[M_1^*][M_1]$ $M_w = MW*([M_2] + [M_2^*])/([M_1] + [M_1^*])$ $M_n = MW*([M_1] + [M_1^*])/([M_o] + [M_o^*])$ $K_1 = k_p[M_p]$ $K_2 = k_t[R_w] + k_{fm}[M_p] + k_{fp}[M_o]$ $K_3 = k_{fp}[M_o^*]$ $K_4 = k_{pdb}[M_o^*]$

Asau et al. (1989) They derived the rate coefficient for radical desorption in batch emulsion polymerization. The study included the competition between radical desorption and termination within particles with more than one free radicals and the possible reactions of the desorbed radecals in water phase. Due to the developed model, only monomeric radicals are allowed to desorbed from polymer particle and undergo several reabsorption - rededesorption steps provided that they react in neither the polymer particle nor aqueous phase. The general equations for rate of generation of monomeric radicals in water phase and desorption coefficient are

$$r_{sm} = k_{de}q(1 - \beta)$$

$$k_{de} = k_{fm}[M_p]/\beta$$

$$\beta = \frac{k_p[M]_w + k_{tw}[R_w]}{k_p[M]_w + k_{tw}[R_w] + k_a N_t \phi_w / N_A}$$

$$k_a = 2\Gamma D_w \delta d_p$$

$$\delta = (1 + 6D_w / mD_p)^{-1}$$

The Proposed Model
(1991)

This work, the developed model equations are based on Smith and Ewart theory and Chiang and Thompson model. The differences between terminal double bond and non-terminal double bond species and effects of branch points are taken into consideration. All assumptions and methods of model derivation are shown in Section 3.3.

3.1 Chiang and Thompson model.

Kiparissides(1978) developed a comprehensive model for continuous emulsion polymerization of vinyl acetate based on Harkins (1947) and Smith and Ewart(1948). The model equations are in the form of integrodifferential equations. Their comprehensive model agrees quite well with the experimental work.

Basic assumptions for Kiparissides's model.

- 1 Particles are nucleated by micellar nucleation and homogeneous nucleation.
- 2 Particles are produced until micelles are disappeared.
- 3 No particles coalescence during the reaction period.
- 4 Polymer particle is the main locus of polymerization.
- 5 Radical desorption rate is the function of particle size.
- 6 Desorption and reabsorption of free radicals.

The main model equations are :

$$\frac{dN(t)}{dt} = - \frac{N(t)}{\theta} + f(t) \quad (3.1)$$

$$\frac{dV_p(t)}{dt} = - \frac{V_p(t)}{\theta} + \int_0^t u_p(t,t') q(t,t') n(t,t') dt' \quad (3.2)$$

$$\frac{dA_p(t)}{dt} = - \frac{A_p(t)}{\theta} \quad (3.3)$$

$$+ 2(36\pi)^{1/3} \int_0^t V_p(t,t')^{-1/3} u(t,t') q(t,t') n(t,t') dt'$$

$$\frac{dX(t)}{dt} = \frac{X(t)}{\theta} + \frac{d_p}{M_p M_w} \int_0^t u_p(t,t') q(t,t') n(t,t') dt' \quad (3.4)$$

where

$$N_p(t) = \int_0^t n_p(t,t') dt' \quad \text{is the total number of particles}$$

$$V_p(t) = \int_0^t V_p(t,t') dt' \quad \text{is the total polymer volume}$$

$$A_p(t) = \int_0^t a_p(t,t') dt' \quad \text{is the total particle surface area}$$

$X(t)$ is the total conversion in the reactor at time t . $n(t, t')$ is the number of particles in the reactor at time t that were generated in the time interval $(t', t' + dt')$. $u(t, t')$ and $u_p(t, t')$ are the particle and polymer volume growth rates per radical respectively. $q(t, t')$ denotes the average number of radicals per particle and is given by

$$q(t, t') = \left[\frac{R_i}{2k_{de}(t, t')n(t, t')dt'} \right]^{1/2} \left[\frac{A_n(t, t')dt'}{A_p(t)} \right]^{1/2} \quad (3.5)$$

R_i is the total radical initiation rate, $A_n(t, t')dt'$ is the area of $n(t, t')dt'$ class of particles and k_{de} is the desorption coefficient of radicals from polymer particles and is given as

$$k_{de}(t, t') = \left[\frac{12D_w\delta}{m(t)D_{pp}^2} \left\| \frac{k_{fm}}{k_p} \right\| \right] \quad (3.6)$$

Where D_w is the diffusion coefficient of monomeric radicals in the water phase, D_{pp} is the diameter of a particle, m is a partition coefficient of monomeric radical between water and particle phases and k_p , k_{fm} are the rate coefficient of propagation and chain transfer to monomer respectively. δ is the parameter equal to $(1 + D_w/mD_p)^{-1}$, where D_p is the diffusion coefficient of monomeric radicals in the polymer particles. According to their proposed kinetic model, particles may be generated via micellar and homogeneous nucleation. Thus, the total rate of particle nucleation, $f(t)$, is

$$f(t) = \frac{P(t)}{1 + \frac{\xi A_p}{A_m} + \frac{u(1 - A_p L/4)}{k_v A_m}} + \frac{P(t)}{1 + \frac{\xi k_v A_p + k_v A_m}{u(1 - A_p L/4)}} \quad (3.7)$$

Where $P(t)$ is the total radical entry rate into all particles and equals $R_i + \int_0^t k_{ae} q(t, \dot{t}) n(t, \dot{t}) dt$. A_p is the total surface area of polymer particles. A_m is the total surface area of micelle. k_v is the volume of emulsion phase over the volume of the aqueous phase. L is defined as the distance which a growing radical will diffuse before it precipitates out to form a primary particle. ξ is defined to be the ratio of the transport coefficient for a radical from the aqueous phase into polymer particles, k_{ab} , over the rate coefficient for micellar nucleation, k_m . u is defined to be the ratio of the rate coefficient for homogeneous nucleation, k_{ho} , over the rate coefficient for micellar nucleation. Equation 3.1 to 3.7 represent a general model which is based on the age distribution of polymer particles. Solution of these equations with the proper balances for initiator, emulsifier and radicals will give information for the most important latex properties such as conversion, total particle surface area, free emulsifier concentration.

Chiang and Thompson (1979) simplified the model that developed by Kisparrisides et al. into the easier form. According to Kisparrisides's model equations, which are in the form of integrodifferential equations, Chiang and Thompson transformed them into pure differential equations, the solutions of which are easier to obtain should be more accurate than the solutions of integro-differential equations. Even though the non-linear differential equations are stiff.

The simplified equations and method of simplification by Chiang and Thompson are shown below.

The surface area of the $n(t, \dot{t}) dt$ class particles is given by

$$A_n(t, \dot{t}) dt = a_p(t, \dot{t}) n(t, \dot{t}) dt \quad (3.8)$$

Equation 3.5 and 3.6 combine with equation 3.8 obtain

$$q(t, \dot{t}) = \left[\frac{k_p R_i(t) m(t) D_p^2(t, \dot{t})}{24 \pi D_w \delta k_{r,m} n(t, \dot{t}) dt} \right]^{1/2} \left[\frac{a_p(t, \dot{t}) n(t, \dot{t}) dt}{A_p(t)} \right]^{1/2}$$

$$= \left[\frac{k_p R_i(t) m(t)}{24 D_w k_{fm}} \right]^{1/2} \left[\frac{a_p^2(t,t)}{A_p(t)} \right]^{1/2} \quad (3.9)$$

where we use

$$a_p(t,t) = \pi D_p^2(t,t) \quad (3.10)$$

$R_i(t)$ and $m(t)$ are time dependent functions and are given as

$$R_i(t) = 2fk_d [I]_{feed} (1 - e^{-t/\theta}) \quad (3.11)$$

$$m(t) = m_0 (1 - e^{-t/\theta}) \quad (3.12)$$

The volumetric growth rate of particles is related to the reactor environment and is given by

$$\frac{\partial v_p(t,t)}{\partial t} = \frac{k_p d_m \phi(t) q(t,t)}{N_A d_p (1 - \phi(t))} \quad (3.13)$$

When combine equation 3.13 with equation 3.10, 3.11 and 3.12 equation 3.13 becomes

$$\begin{aligned} \frac{\partial v_p(t,t)}{\partial t} &= \frac{k_p d_m \phi(t)}{N_A d_p [1 - \phi(t)]} \left[\frac{k_p R_i(t) m(t)}{24 D_w \delta k_{fm}} \right]^{1/2} \left[\frac{a_p^2(t,t)}{A_p(t)} \right]^{1/2} \\ &= \frac{k_p d_m \phi(t)}{N_A d_p [1 - \phi(t)]} \left[\frac{k_p 2fk_d [I]_{feed} m_0}{24 D_w \delta k_{fm}} \right]^{1/2} (1 - e^{-t/\theta}) \left[\frac{a_p^2(t,t)}{A_p(t)} \right]^{1/2} \\ &= \frac{k_p d_m \phi(t)}{N_A d_p [1 - \phi(t)]} \left[\frac{k_p f k_d [I]_{feed} m_0}{12 D_w \delta k_{fm}} \right]^{1/2} (1 - e^{-t/\theta}) \left[\frac{a_p(t,t)}{A_p^{1/2}(t)} \right] \quad (3.14) \end{aligned}$$

Equation 3.14 may be simplified into three separated parts as

$$\frac{\partial v_p(t,t)}{\partial t} = \lambda \zeta(t) a_p(t,t) \quad (3.15)$$

$$\lambda = \frac{k_p d_m \left[k_p f k_d [I]_{feed} m_0 \right]^{1/2}}{N_A d_p \left[12 \pi D_w \delta k_{fm} \right]}$$

$$\zeta(t) = \frac{(1 - e^{-t/\theta}) \phi(t)}{(1 - \phi(t)) A_p^{-1/2}(t)}$$

The particle nucleation function is simplified from equation 3.7, as

$$f(t) = \rho(t) \left[\frac{k_v A_m(t) + u(1 - LA_p(t)/4)}{k_v A_m(t) + k_v A_p + u(1 - LA_p(t)/4)} \right] \quad (3.16)$$

$$k_v = V_p(t) / (1 - V_p(t)) \quad (3.17)$$

$$A_m(t) = (S_F(1 - e^{-t/\theta}) - S_{cmc}) S_x - A_p(t) \quad (3.18)$$

The free radical production rate, $\rho(t)$ is comprised of contributions from initiator decomposition and radical desorption from particles.

$$\rho(t) = R_i(t) + \int_0^t k_{de}(t, \dot{t}) q(t, \dot{t}) n(t, \dot{t}) dt \quad (3.19)$$

Using equation 3.6, 3.8 and 3.9 the integrand in equation 3.19 can be shown as

$$\begin{aligned} & \int_0^t k_{de}(t, \dot{t}) q(t, \dot{t}) n(t, \dot{t}) dt \\ &= \int_0^t k_{de}(t, \dot{t}) \left[\frac{R_i(t)}{2k_{de}(t, \dot{t}) n(t, \dot{t}) dt} \right]^{1/2} \left[\frac{A_n(t, \dot{t}) dt}{A_p(t)} \right]^{1/2} n(t, \dot{t}) dt \\ &= \int_0^t \left[\frac{R_i(t) k_{de}(t, \dot{t})}{2n(t, \dot{t}) dt} \right]^{1/2} \left[\frac{A_n(t, \dot{t}) dt}{A_p(t)} \right]^{1/2} n(t, \dot{t}) dt \end{aligned}$$

$$\begin{aligned}
&= \int_0^t \left[\frac{R_i(t) 6D_w \delta k_{fm}}{n(t,t) dt m(t) D_{pp}^2 k_p} \right]^{1/2} \left[\frac{a_p(t,t) n(t,t) dt}{A_p(t)} \right]^{1/2} n(t,t) dt \\
&= \int_0^t \left[\frac{R_i(t)}{m(t) A_p(t)} \right]^{1/2} \left[\frac{6D_w \delta k_{fm}}{k_p} \right]^{1/2} n(t,t) dt \\
&= \left[\frac{12D_w \delta k_{fm} f k_d [I]_{feed}}{m_o k_p} \right]^{1/2} \frac{N(t)}{A_p^{1/2}(t)} \quad (3.20)
\end{aligned}$$

The integration in equation 3.19 is respected to the nucleation time, t , and all time dependent equations are independent of nucleation time. Thus equation 3.19 may be simplified as

$$n(t) = 2f k_d [I]_{feed} (1 - e^{-t/\theta}) + \left[\frac{12D_w \delta k_{fm} f k_d [I]_{feed}}{m_o k_p} \right]^{1/2} \frac{N(t)}{A_p^{1/2}(t)} \quad (3.21)$$

The set of differential equations which must be solved to completely describe the continuous emulsion polymerization system are developed. The transient balance on total number of polymer particles is given by

$$\frac{dN(t)}{dt} = - \frac{N(t)}{\theta} + f(t) \quad (3.1)$$

The time derivative of the total particle diameter, total particle surface area, total particle volume and total conversion are simplified by age distribution approach.

Using an age distribution approach, if we defined the function $n(t,t)dt$ to be the number of particles in the reactor at time t that were born in the time interval $(t,t+dt)$ and $p(t,t)$ to be a property of the latex associated with this class of particle, then the total property $P(t) = \int_0^t p(t,t)n(t,t)dt$. The time derivative of the total property given by

$$\begin{aligned}
\frac{dP(t)}{dt} &= \frac{d}{dt} \int_0^t p(t, \tau) n(t, \tau) d\tau \\
&= \frac{d}{dt} \int_0^t p(t, \tau) f(\tau) e^{-(t-\tau)/\theta} d\tau \\
&= \int_0^t \frac{\partial p(t, \tau) f(\tau) e^{-(t-\tau)/\theta}}{\partial t d\tau} dt \\
&\quad - \frac{1}{\theta} \int_0^t p(t, \tau) f(\tau) e^{-(t-\tau)/\theta} d\tau + p(t, t) f(t) \\
\frac{dP(t)}{dt} &= \int_0^t \frac{\partial p(t, \tau) f(\tau) e^{-(t-\tau)/\theta}}{\partial t d\tau} dt - \frac{P(t)}{\theta} + p(t, t) f(t)
\end{aligned}$$

Where Liebnitz's rule and the chain rule have been used simultaneously to simplify above equation. The following expression was used to relate the number of particles to their age.

$$n(t, \tau) d\tau = f(\tau) e^{-(t-\tau)/\theta} d\tau$$

The time derivation of total particles diameter is found simply by changing equation 3.15 from a volume to diameter basis.

$$\begin{aligned}
\frac{dD(t)}{dt} &= \int_0^t \frac{\partial D_p(t, \tau) f(\tau) e^{-(t-\tau)/\theta}}{\partial t d\tau} dt - \frac{D(t)}{\theta} + D_p(t, t) f(t) \\
&= 2\lambda \bar{g}(t) N(t) - \frac{D(t)}{\theta} + D_p(t, t) f(t) \quad (3.22)
\end{aligned}$$

Time derivative of total particles surface area and total particles volume are

$$\frac{dA_p(t)}{dt} = 4\lambda\zeta(t)D(t) - \frac{A_p(t)}{\theta} + a_p(t,t)f(t) \quad (3.23)$$

$$\frac{dV_p(t)}{dt} = \lambda\zeta(t)A_p(t) - \frac{V_p(t)}{\theta} + v_p(t,t)f(t) \quad (3.24)$$

The rate of polymerization is given by

$$\begin{aligned} R(t) &= \int_0^t k_p [M_p] q(t,t) n(t,t) dt \\ &= \int_0^t \frac{k_p d_m \phi(t) q(t,t) n(t,t) dt}{N_A M_w} \\ &= \frac{k_p d_m \phi(t)}{N_A M_w} \int_0^t \left[\frac{k_p f k_d [I]_{feed} m_o}{12\pi D_w \delta k_{fm}} \right]^{1/2} (1 - e^{-t/\theta}) \frac{a_p(t,t) n(t,t) dt}{A_p^{1/2}(t)} \\ &= \frac{d_p k_p d_m}{M_w N_A d_p} \left[\frac{k_p f k_d [I]_{feed} m_o}{12\pi D_w \delta k_{fm}} \right]^{1/2} \phi(t) (1 - e^{-t/\theta}) A_p^{1/2}(t) \\ &= \frac{1 - \phi(t) d_p \lambda \zeta(t) A_p(t)}{M_w} \quad (3.25) \end{aligned}$$

The equation for monomer conversion is developed from the material balance for monomer.

$$\frac{dM(t)}{dt} = \frac{M_F - M(t)}{\theta} - R(t) \quad (3.26)$$

Using

$$x(t) = 1 - \frac{M(t)}{M_F (1 - e^{-t/\theta})} \quad (3.27)$$

Then we have

$$\frac{dX(t)}{dt} = \frac{1}{(1 - e^{-t/\theta})} \left[\frac{R(t)}{M_F} - \frac{X(t)}{\theta} \right] \quad (3.28)$$

The monomer volume function in polymer particle, $\phi(t)$, is constant if monomer droplets exist or $X(t) < X_c$. Thus $\phi(t)_{sat}$ is

$$\phi(t)_{sat} = \frac{1 - X_c}{1 - X_c(1 - d_m/d_p)} \quad (3.29)$$

If $X(t)$ is exceed X_c or monomer droplet is not exist $\phi(t)$ is

$$\phi(t) = \frac{1 - X}{1 - X(1 - d_m/d_p)} \quad (3.30)$$

The monomer concentration in polymer particle is obtained from the monomer volume fraction function, $\phi(t)$, as

$$[M_p] = \frac{\phi(t)d_m}{MW} \quad (3.31)$$

The calculated monomer concentration in polymer particle and the calculated number of polymer particle in this model are used to calculate the polymer molecular weight in the proposed model. Thus, it is necessary to solve Chiang and Thompson model with respect to time to obtain time dependent parameters for the calculation of molecular weight in the developed model.

3.2 The proposed model

3.2.1 Introduction

This model is developed to explain the oscillatory behavior of molecular weight of poly(vinyl acetate) from emulsion polymerization system. The model equations are developed by making balance equations over specific species. The differential equations of zero, first and second moment of dead polymers and living polymers with and without terminal double bond are obtained from infinite series of balance equations. Assuming unsteady state hypothesis, the system differential equations of moments are solved numerically by fourth order Runge-Kutta method. Average molecular weights of polymer are calculated from the obtained moments.

The observed oscillatory of molecular weight, conversion, particle size can be explained as follow, according to Kisparissides et al.(1980), Rawling and Ray(1987). At the beginning of the reaction, a large number of particles and surface area consume the available emulsifiers. The rate of emulsifier consumption exceeds the feed rate of emulsifier to the reactor then free emulsifiers are quickly disappeared. This leads to a period which particle generation rate is close to zero. The duration of this period depends on the feed rate of emulsifier, the washout rate of polymer particles and particle growth rate. Eventually the emulsifiers saturate the organic surface and free emulsifier is again available for particle generation. This mechanism leads to the formation of discrete particles and fluctuations in the number of particles, polymerization rate and conversion. It appears that under many operating conditions of a continuous stirred tank reactor, oscillations will prevail and steady state is impossible to achieve.

3.2.1.2 Advantages of the model

1 The different characteristics of terminal double and non-terminal double bond species and effects of chain branching are taken into consideration, thus a more comprehensive description of emulsion polymerization must be obtained and this consideration should provide a more satisfactory and useful explanation of a number of intricate and astonishing phenomena reported in the literatures and for the reactor design.

2 Microcomputer is used for model calculation and little time is used to complete calculating process.

3.2.2.1 Objectives of this work

1 To construct of an effective non-steady state mathematical model for molecular weight of poly(vinyl acetate) polymer obtained from continuous emulsion polymerization by the moment method.

2 To compare the result from the model calculation with an experimental data reported in literatures.

3.2.1.3 Limitation of this model.

This work considers the theoretical study of vinyl acetate emulsion polymerization and focus on the molecular weight. The model equations are derived by making balance equations over all species in the system. The differential equations of various moments are solved numerically by fourth order Runge-Kutta method.

3.2.1.4 Assumptions for the proposed model.

The important kinetic considerations in the proposed model are shown below.

1 Gel effect occurs at high conversion.

2 Particles are nucleated by micellar nucleation and by homogeneous nucleation.

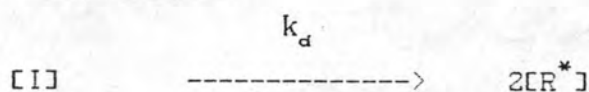
3 The monomer concentration and average number of radicals per particle are considered as the function of particle size.

4. Polymer particles shrink during the monomer-starved period.
5. Uniform distribution of free radicals in particles.
6. The reaction rate constant is independent of the polymer chain length and constant throughout the polymerization period.
7. The initiators decomposition take place in the water phase and these primary radicals from decomposition process enter newly generated micelles or polymer particles.
8. Polymer particles are the major locus for polymerization.
9. Only monomeric radicals can desorb from the particles.
10. The monomer concentration in monomer-swollen polymer particle remains constant if monomer droplets are exist.
11. The equilibrium between solubilized monomers and monomers in monomer droplets exists as long as monomer droplets are presented. The transfer rate of solubilized monomer into micelles or polymer particles is higher than consumption rate of monomer in the reaction loci.
12. No particle coalescence during the reaction period.
13. Each polymer chain has no more than one radical and one terminal double bond.

3.2.2 Specification of the reaction scheme.

A kinetic scheme was employed for vinyl acetate polymerization in which species with and without terminal double bond were considered. It involves numerous elementary chemical and physical processes which operate simultaneously in both polymer phase and water phase. The free radical reactions considered in this model are described by 6 consecutive steps which are obtained from batch experiments, according to Friis and Hamielec(1975), Baade et al.(1982), Pramojaney(1982), Taylor and Reichert(1985), Lee and Mallinson(1988).

1 Initiator decomposition



Primary radicals are generated by initiator decomposition. Monomeric radicals in water phase are generated by desorption of monomeric radicals in polymer particles. Two kinds of monomeric radical are considered, one with a terminal double bond and the other without this bond. It is assumed that water phase radicals comprise of primary radicals and desorbed monomeric radicals. In this study, effects of desorbed oligomeric radicals are neglected because high viscosity of polymer particles and there molecule is too big to desorb from polymer particles.

$$[R_w] = [R^*] + [M^*_{1,w}] + [\underline{M}^*_{1,w}]$$

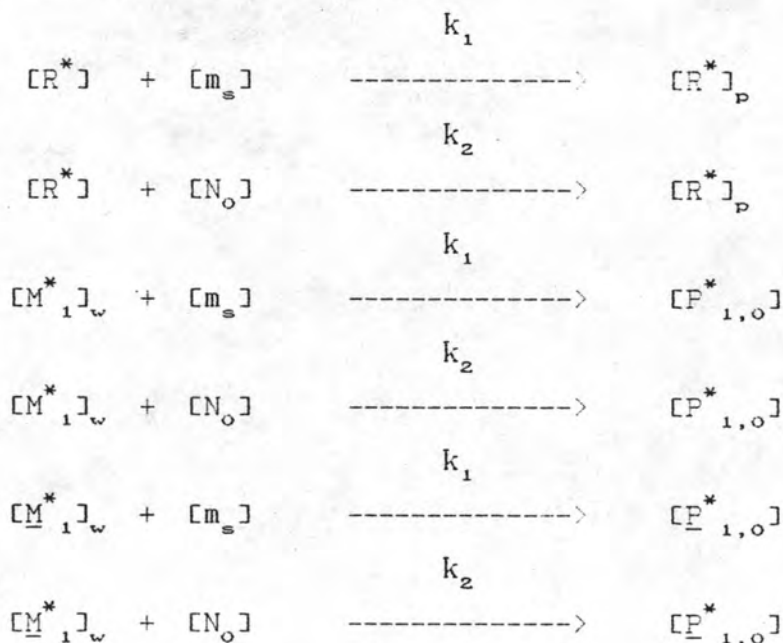
Thus, rate of water phase radical generation is

$$\frac{d[R_w]}{dt} = 2fk_d[I_w] + k_{de}[P^*_{1,o}] + k_{de}[\underline{P}^*_{1,o}]$$

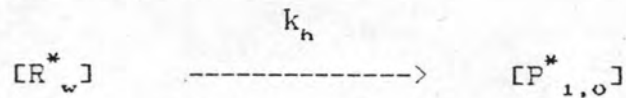
2 Chain initiation reaction

Chain initiation reaction comprises of two modes, micellar nucleation and homogeneous nucleation.

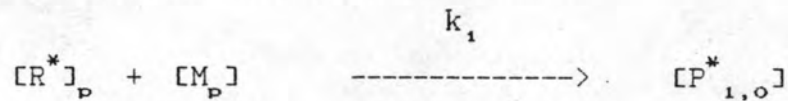
2.1 Micellar nucleation



2.2 Homogeneous nucleation



As soon as a primary radical enters polymer particle it reacts with a monomer molecule in polymer particle and a monomeric radical without terminal double bond is generated.



Assuming that rate of monomeric radical generation by absorbed primary radical is much greater than the absorption rate, $k_1 \gg k_1, k_2$. Thus, rate of monomeric radical generation by primary radicals is controlled by rate of diffusion of water phase radicals into particle.

Rate of monomeric radical generation in polymer particle by absorbed primary radical can be shown as

$$\frac{d[P_{1,o}^*]}{dt} = k_1 [R_p^*] [M_p] = k_1 [R^*] [M_s] + k_2 [R^*] [N_o]$$

Monomeric radical in water phase transforms into monomeric radical in polymer particle whenever it enters the particle.

$$\frac{d[P_{1,o}^*]}{dt} = k_1 [M_1^*] [M_s] + k_2 [M_1^*] [N_o] + k_h [M_1^*]$$

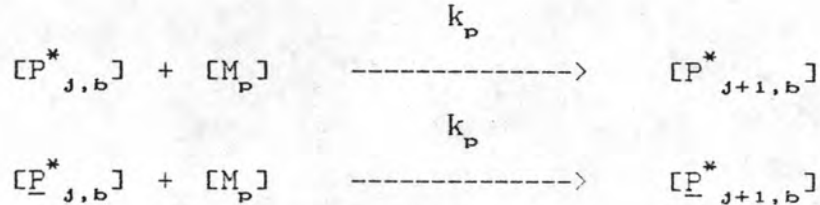
$$\frac{d[\underline{P}_{1,o}^*]}{dt} = k_1 [\underline{M}_1^*] [M_s] + k_2 [\underline{M}_1^*] [N_o] + k_h [\underline{M}_1^*]$$

Water phase radicals are consumed by two modes of reaction, micellar nucleation and homogeneous nucleation, thus rate of disappearance of water phase radicals is

$$\begin{aligned} - \frac{d[R_w]}{dt} &= k_1 ([R^*] + [M_1^*] + [\underline{M}_1^*]) [M_s] + k_2 ([R^*] + [M_1^*] + [\underline{M}_1^*]) [N_o] + k_h [R_w] \\ &= k_1 [R_w] [M_s] + k_2 [R_w] [N_o] + k_h [R_w] \end{aligned}$$

3 Chain propagation reaction

Propagation reaction occurs by the reaction between a polymeric radical and a monomer molecule in monomer-swollen polymer particle.

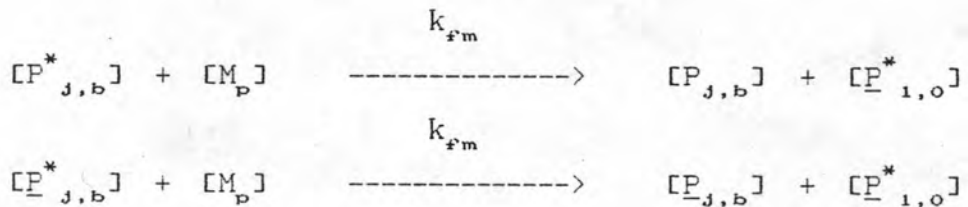


Assuming that propagation rate constant, k_p , is independent of the polymer chain length and constant throughout the polymerization period. Propagation reaction is mainly responsible for the development of polymer chain micro structure, a polymeric radical is going on propagation reaction till it is terminated by transfer to monomer, by transfer to polymer and by termination reactions.

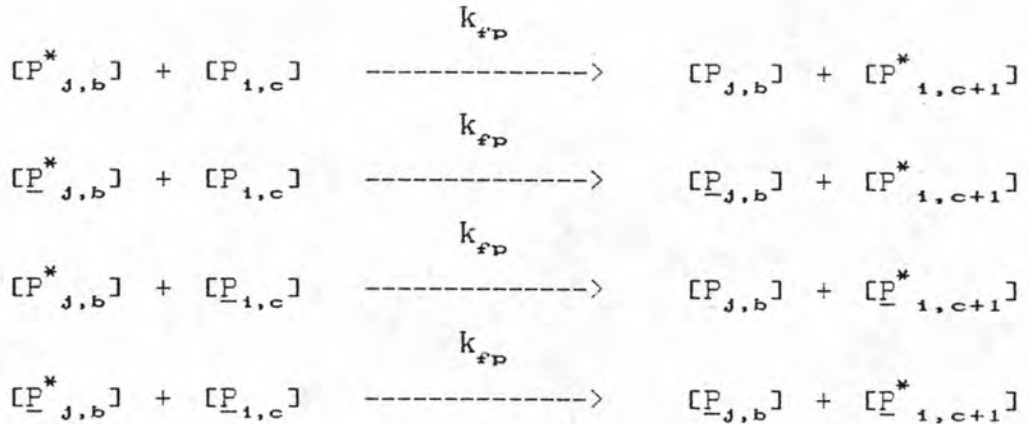
4 Transfer reaction

During the free radical polymerization, transfer reaction may take place by the reaction of living polymer with monomer molecule, other living polymer, transfer agent, initiator or solvent molecule. Transfer reactions in this study are transfer to monomer and transfer to dead polymer chain. Transfer to initiator and transfer to solvent are not considered in this system.

4.1 Transfer to monomer



4.2 Transfer to dead polymer



In vinyl acetate polymerization, transfer reactions largely control the molecular weights of polymer. Transfer to monomer causes a shift in molecular weight distribution to the lower molecular weight. Transfer to dead polymer leads to branching which cause a shift to higher molecular weight. Transfer to polymer does not change the total number of polymer molecules, thus the number average molecular weight is unaffected. Weight average molecular weight increases very appreciably and gives a large increase in polydispersity. Transfer reaction does not change the total number of radicals in the system then rate of polymerization is unaffected.

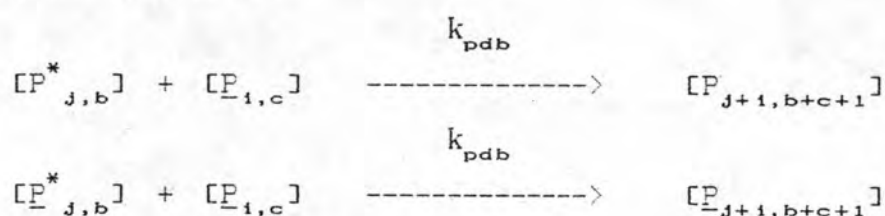
In transfer to dead polymer, a polymeric radical randomly abstract a labile atom, usually -hydrogen, from dead polymer chain leaving a radical center somewhere along the chain. This radical can react with monomer to form branch. In vinyl acetate polymerization, there are two different types of active positions in polymer chain, methyl group of the acetate and the tertiary hydrogen atoms. It is believed that most of the reactions occur at the methyl groups.

In transfer to monomer, a small and rather mobile monomeric radical which can diffuse out of the particle is generated. The desorption process plays an important role in the emulsion polymerization of vinyl acetate. Chern and Poehlein(1987) showed that the major transfer to monomer takes place on the vinyl hydrogen instead of the acetyl hydrogen. The monomeric radicals are rather stable and escape

form the particle. The desorbed monomeric radicals can be reabsorbed into the particles and repeat this process until they either reinitiate or are terminated in particles. The process of transport of free radicals out of the latex particles reduce the average number of free radical per particle and consequently lower the polymerization rate. Transfer to the acetyl hydrogen of vinyl acetate can also happen, but this chain transfer reaction has no kinetic significance because the generated monomeric radical is so reactive that it should reinitiate instantly before escapes from the particle.

5 Terminal double bond polymerization

Terminal double bond is generated by transfer to monomer. These terminal double bond species may react with a polymeric radical and produce a radical center somewhere along the chain of the combined polymer molecule. The terminal double bond reaction is a type of multiple propagation which leads to a dramatic increase in molecular weight. To include this effect, it is necessary to distinguish between two type of polymer chains, one with a terminal double bond and the other without this bond. The differences in reaction details of the two species are



6 Termination reaction

Termination reaction occurs by bimolecular reaction between two polymeric radicals or by the reaction between a polymeric radical and a adsorbed water phase radical.

6.1 Termination by bimolecular reaction

This mode of reaction are termination by combination and termination by disproportionation.

in the palisade layer due to its relatively hydrophilic nature. The exact location at which solubilization may occur varies with dipole attraction of H-bonding. The polymeric radical, located near the emulsifier head group, captures monomer molecules or adsorbed water phase radicals. If there are both monomer molecules and highly reactive adsorbed water phase radicals present, the polymeric radical may preferentially be terminated by a small radical. Therefore, assume that the adsorbed water phase radical quickly terminates the polymeric radical without further propagation. Due to the rapid rate of termination, the termination rate constant is a lumped parameter which accounts for the fact that $[R_w]$ and $[P^*]$ are actually concentrations in different phases. Thus, this lumps both the adsorption and termination steps.

3.2.3 Model formulation

Let us consider the reactor of volume V with steady flow rate F , thus its residence time, θ , equals V/F . Mass flow and phase separation in the reactor are shown in figure 3.1

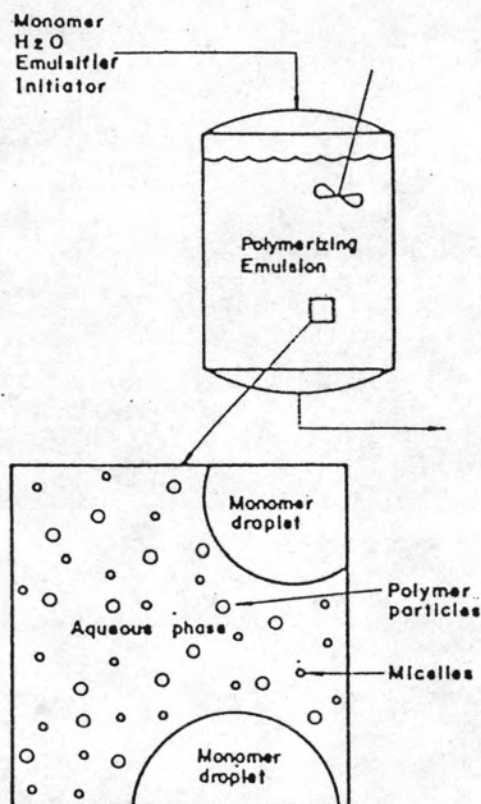


Figure 3.1 Schematic illustration of materials flow and phase separation in single continuous stirred tank emulsion polymerization reactor (Kirillov and Ray, 1978; Rawlings and Ray, 1987).

3.2.3.1 Balance equations.

The model equations are developed by making balance equations over the specific species. In the model, ten essential species for molecular weights calculation are initiator, primary radical, monomeric radical with and without terminal double bond in water phase, monomeric radical with and without terminal double bond in particle, polymeric radical with and without terminal double bond, dead polymer with and without terminal double bond. The balance equations of the stated species are derived from the kinetic schemes and are shown below.

1 Monomer balance equation.

Monomers are supplied to the system by feed stream and consumed by the propagation reaction in monomer-swollen polymer particles and discharged with the effluent stream.

rate of accumulation = rate of flow in - rate of flow out
+ rate of generation - rate of consumption

$$\begin{aligned} \frac{dM(t)}{dt} = & F(M_F - M(t)) && ; \text{ net flow of mass} \\ & + V(-k_p[M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^* \right]) && ; \text{ reaction in particle} \\ & - k_p[M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} \underline{P}_{j,b}^* \right]) && ; \text{ reaction in particle} \\ & - k_{fm}[M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^* \right]) && ; \text{ transfer to monomer} \\ & - k_{fm}[M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} \underline{P}_{j,b}^* \right]) && ; \text{ transfer to monomer} \end{aligned}$$

$k_p[M_p] \left(\left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^* \right] + \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} \underline{P}_{j,b}^* \right] \right)$ is total rate of polymerization and $k_{fm} \ll k_p$, thus

$$\frac{dM(t)}{dt} = \frac{M_F - M(t)}{\theta} - R_p \quad (3.32)$$

Equation 3.32 is the same as equation 3.26 that used in simplified Chiang and Thompson's model.

2 Emulsifier balance equation.

2.1 Overall emulsifier balance equation.

Emulsifiers in the reactor are supplied by feed stream and consumed by effluent stream.

$$\begin{aligned} \text{rate of accumulation} &= \text{rate of flow in} - \text{rate of flow out} \\ &+ \text{rate of generation} - \text{rate of consumption} \end{aligned}$$

$$\frac{VdS(t)}{dt} = F(S_F - S(t)) \quad ; \text{ net flow of mass}$$

$$\frac{dS(t)}{dt} = \frac{S - S(t)}{\theta}$$

By Laplace transform, the overall emulsifier concentration in reactor is

$$S(t) = S_F(1 - e^{-t/\theta}) \quad (3.33)$$

2.2 Free emulsifier concentration

Emulsifiers in the reaction exist in three different parts, dissolved free emulsifier molecules in water phase, micelles and absorbed emulsifier molecules on the surface of polymer particles. Assuming that the particle surface is completely covered by emulsifier molecule, free emulsifier concentration in the reactor is

$$S_{free} = S(t) - S_{cmc} - A_p(t)/S_a \quad (3.34)$$

If free emulsifier concentration, S_{free} , exceeds the critical micelle concentration, S_{cmc} , then micelles are exist and new particles are generated.

3 Initiator balance equation.

Initiators are supplied to the system by feed stream and consumed by initiator decomposition and discharged with effluent stream.

rate of accumulation = rate of flow in - rate of flow out
+ rate of generation - rate of consumption

$$\frac{Vd[I_w]}{dt} = F([I]_{\text{feed}} - [I_w]) \quad ; \text{ net flow of mass}$$

$$+ V(2fk_d[I_w]) \quad ; \text{ initiator decomposition}$$

$$\frac{d[I_w]}{dt} = \frac{[I]_{\text{feed}}}{\theta} - \frac{[I_w]}{\theta} + 2fk_d[I_w]$$

$2fk_d$ is so minute that $2fk_d[I_w]$ can be neglected when compared with $[I]_{\text{feed}}$ and $[I_w]$, then

$$\frac{d[I_w]}{dt} = \frac{[I]_{\text{feed}}}{\theta} - \frac{[I_w]}{\theta}$$

By Laplace transform, initiator concentration in water phase is given by

$$[I_w] = [I]_{\text{feed}}(1 - e^{-t/\theta}) \quad (3.35)$$

4 Water phase radical balance equation.

The water phase radicals consist of primary radicals from initiator decomposition and desorbed monomeric radicals. The radicals are consumed by the particle generation process. Mass balance equations of water phase radicals are shown below.

4.1 Primary radicals.

Primary radicals are generated by initiator decomposition and are consumed by particle generation process and by effluent stream.

rate of accumulation = rate of flow in - rate of flow out
+ rate of generation - rate of consumption

$$\begin{aligned} \frac{Vd[R^*]}{dt} = & F(C - [R^*]) && ; \text{ net flow of mass} \\ & + V(2fk_d[I_w] && ; \text{ initiator decomposition} \\ & - k_1[R^*][M_s] && ; \text{ micellar nucleation in micelle} \\ & - k_2[R^*][N_t] && ; \text{ micellar nucleation in particle} \\ & - k_h[R^*] && ; \text{ homogeneous nucleation} \end{aligned}$$

$$\frac{d[R^*]}{dt} = 2fk_d[I_w] - k_1[R^*][M_s] - k_2[R^*][N_t] - k_h[R^*] - [R^*]/\theta$$

Assume steady state hypothesis and all primary radicals are completely consumed, the above equation may be simplified to

$$[R^*] = \frac{2fk_d[I_w]}{(k_2[N_t] + k_1[M_s] + k_h)} \quad (3.36)$$

4.2 Monomeric radical without terminal double bond

Monomeric radicals without terminal double bond are generated by desorption of monomeric radicals without terminal double bond and are consumed by particle generation process and by effluent stream.

rate of accumulation = rate of flow in - rate of flow out
+ rate of generation - rate of consumption

$$\begin{aligned} \frac{Vd[M_1^*]}{dt} = & F(C_0 - [M_1^*]) && ; \text{ net flow of mass} \\ & + V(k_{de}[P_{1,0}^*] && ; \text{ desorption of monomeric radical} \\ & - k_1[M_1^*][M_s] && ; \text{ micellar nucleation in micelle} \\ & - k_2[M_1^*][N_t] && ; \text{ micellar nucleation in particle} \\ & - k_h[M_1^*] && ; \text{ homogeneous nucleation} \end{aligned}$$

$$\frac{d[M_1^*]}{dt} = k_{de}[P_{1,0}^*] - k_1[M_1^*][M_s] - k_2[M_1^*][N_t] - k_h[M_1^*] - [M_1^*]/\theta$$

Assume steady state hypothesis and all monomeric radicals without terminal double bond are consumed, the above equation may be simplified to

$$[M_1^*] = \frac{k_{de}[P_{1,0}^*]}{(k_2[N_t] + k_1[M_s] + k_h)} \quad (3.37)$$

4.3 Monomeric radical with terminal double bond

Monomeric radicals with terminal double bond are generated by desorption of monomeric radicals with terminal double bond and are consumed by particle generation process and by effluent stream.

rate of accumulation = rate of flow in - rate of flow out
+ rate of generation - rate of consumption

$$\begin{aligned} \frac{Vd[M_1^*]}{dt} = & F(O - [M_1^*]) && ; \text{ net flow of mass} \\ & + V(k_{de}[P_{1,o}^*] && ; \text{ desorption of monomeric radical} \\ & - k_1[M_1^*][M_s] && ; \text{ micellar nucleation in micelle} \\ & - k_2[M_1^*][N_t] && ; \text{ micellar nucleation in particle} \\ & - k_h[M_1^*] && ; \text{ homogeneous nucleation} \end{aligned}$$

$$\frac{d[M_1^*]}{dt} = k_{de}[P_{1,o}^*] - k_1[M_1^*][M_s] - k_2[M_1^*][N_t] - k_h[M_1^*] - [M_1^*]/\theta$$

Assume steady state hypothesis and all monomeric radicals with terminal double bond are completely consumed, the above equation may be simplified to

$$[M_1^*] = \frac{k_{de}[P_{1,o}^*]}{(k_2[N_t] + k_1[M_s] + k_h)} \quad (3.38)$$

Water phase radicals consist of primary radicals, monomeric radical with and without terminal double bond, thus

$$\begin{aligned} [R_w^*] &= [R^*] + [M_1^*] + [M_1^*] \\ &= \frac{2fk_d[I_w] + k_{de}[P_{1,o}^*] + k_{de}[P_{1,o}^*]}{(k_2[N_t] + k_1[M_s] + k_h)} \quad (3.39) \end{aligned}$$

5 Monomeric radicals in particle balance equation.

The monomeric radical in polymer particles consist of two kinds, one with terminal double bond and the other without this bond. Both monomeric radicals are different in generation sources and reaction characteristics, thus the balance equation of both radicals are treated separately.

5.1 Monomeric radical without terminal double bond

Monomeric radicals without terminal double bond are produced by micellar and homogeneous nucleation of primary radical and monomeric radical without terminal double bond. The radicals are consumed by desorption process, propagation reaction, transfer to polymer, terminal double bond reaction and termination reactions.

rate of accumulation = rate of flow in - rate of flow out
+ rate of generation - rate of consumption

$$\begin{aligned}
 \frac{Vd[P_{1,0}^*]}{dt} = & F(O - [P_{1,0}^*]) && ; \text{ net flow of mass} \\
 & + V(k_1[M_s]R^* && ; \text{ micellar nucleation} \\
 & + k_2[N_o]R^* && ; \text{ micellar nucleation} \\
 & + k_1[M_s][M_1^*] && ; \text{ micellar nucleation} \\
 & + k_2[N_o][M_1^*] && ; \text{ micellar nucleation} \\
 & - k_{de}[P_{1,0}^*] && ; \text{ radical desorption} \\
 & - k_p[M_p][P_{1,0}^*] && ; \text{ chain propagation} \\
 & - k_{fp}[P_{1,0}^*]\left[\sum_{j=1}^{\infty}\sum_{b=1}^{\infty}P_{j,b}\right] && ; \text{ transfer to polymer} \\
 & - k_{fp}[P_{1,0}^*]\left[\sum_{j=1}^{\infty}\sum_{b=1}^{\infty}P_{j,b}\right] && ; \text{ transfer to polymer} \\
 & - k_{pdb}[P_{1,0}^*]\left[\sum_{j=1}^{\infty}\sum_{b=1}^{\infty}P_{j,b}\right] && ; \text{ terminal double bond} \\
 & - k_{td}[P_{1,0}^*]\left[\sum_{j=1}^{\infty}\sum_{b=1}^{\infty}P_{j,b}^*\right] && ; \text{ disproportionation} \\
 & - k_{td}[P_{1,0}^*]\left[\sum_{j=1}^{\infty}\sum_{b=1}^{\infty}P_{j,b}^*\right] && ; \text{ disproportionation} \\
 & - k_t[P_{1,0}^*][R_w] && ; \text{ termination with radicals}
 \end{aligned}$$

$$\begin{aligned}
\frac{d[CP^*_{1,0}]}{dt} = & k_1[M_s][CR^*] + k_2[N_0][CR^*] + k_1[M_s][CM^*_1] + k_2[N_0][CM^*_1] \\
& - k_{de}[CP^*_{1,0}] - k_p[M_p][CP^*_{1,0}] - k_{fp}[CP^*_{1,0}]\left[\sum_{j=1}^{\infty}\sum_{b=1}^{\infty}P_{j,b}\right] \\
& - k_{fp}[CP^*_{1,0}]\left[\sum_{j=1}^{\infty}\sum_{b=1}^{\infty}P_{j,b}\right] - k_{pdb}[CP^*_{1,0}]\left[\sum_{j=1}^{\infty}\sum_{b=1}^{\infty}P_{j,b}\right] \\
& - k_{td}[CP^*_{1,0}]\left[\sum_{j=1}^{\infty}\sum_{b=1}^{\infty}P^*_{j,b}\right] - k_{td}[CP^*_{1,0}]\left[\sum_{j=1}^{\infty}\sum_{b=1}^{\infty}P_{j,b}\right] \\
& - k_t[CP^*_{1,0}][R_w] - [CP^*_{1,0}]/\theta
\end{aligned}$$

Assume steady state hypothesis, the above equation may be simplified to

$$[CP^*_{1,0}] = \frac{k_1[M_s]([CR^*] + [CM^*_1]) + k_2[N_0]([CR^*] + [CM^*_1])}{k_{de} + k_p[M_p] + k_{fp}[M_0] + k_{fp}[M_0] + k_{pdb}[M_0] + k_{td}[M_0] + k_{td}[M_0] + k_t[R_w] + 1/\theta}$$

Using the simplified terms in Appendix C, the above equation may be simplified to

$$[CP^*_{1,0}] = \frac{A_9}{(k_{de} + A_1 + A_5 + A_8 + \theta)} \quad (3.40)$$

5.2 Monomeric radical with terminal double bond

Monomeric radicals with terminal double bond are produced by micellar nucleation, homogeneous nucleation and transfer to polymer reaction. The radicals are consumed by desorption process, propagation reaction, transfer to polymer, terminal double bond reaction and termination reactions.

rate of accumulation = rate of flow in - rate of flow out
+ rate of generation - rate of consumption

$$\frac{d[P_{1,0}^*]}{dt} = F(O - [P_{1,0}^*]) \quad ; \text{ net flow of mass}$$

$$+ V(k_1 [M_s] [M_1^*] \quad ; \text{ micellar nucleation}$$

$$+ k_2 [N_o] [M_1^*] \quad ; \text{ micellar nucleation}$$

$$- k_{de} [P_{1,0}^*] \quad ; \text{ radical desorption}$$

$$+ k_{fm} [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^* \right] \quad ; \text{ transfer to monomer}$$

$$+ k_{fm} [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^* \right] \quad ; \text{ transfer to monomer}$$

$$- k_p [M_p] [P_{1,0}^*] \quad ; \text{ chain propagation}$$

$$- k_{fp} [P_{1,0}^*] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b} \right] \quad ; \text{ transfer to polymer}$$

$$- k_{fp} [P_{1,0}^*] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b} \right] \quad ; \text{ transfer to polymer}$$

$$- k_{pdb} [P_{1,0}^*] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b} \right] \quad ; \text{ terminal double bond}$$

$$- k_{td} [P_{1,0}^*] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^* \right] \quad ; \text{ disproportionation}$$

$$- k_{td} [P_{1,0}^*] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^* \right] \quad ; \text{ disproportionation}$$

$$- k_t [P_{1,0}^*] [R_w] \quad ; \text{ termination with radicals}$$

$$\frac{d[P_{1,0}^*]}{dt} = (k_1 [M_s] + k_2 [N_o]) [M_1^*] + k_{fm} [M_p] \left(\left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^* \right] + \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b} \right] \right)$$

$$- k_{de} [P_{1,0}^*] \quad - k_p [M_p] [P_{1,0}^*] - k_{fp} [P_{1,0}^*] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b} \right]$$

$$- k_{fp} [P_{1,0}^*] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b} \right] - k_{pdb} [P_{1,0}^*] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b} \right]$$

$$- k_{td} [P_{1,0}^*] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^* \right] - k_{td} [P_{1,0}^*] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^* \right]$$

$$- k_t [P_{1,0}^*] [R_w] \quad - [P_{1,0}^*] / \theta$$

Assume steady state hypothesis, the above equation may be simplified to

$$[P_{1,0}^*] = \frac{(k_1[M_0] + k_2[N_0])[M_1^*] + k_{fm}[M_p][\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*] + [\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*]}{k_{de} + k_p[M_p] + k_{fp}[M_0] + k_{fp}[M_0] + k_{pdb}[M_0] + k_{td}[M_0] + k_{td}[M_0] + k_t[R_w] + 1/\theta}$$

Using the simplified terms in Appendix C, the above equation may be simplified to

$$[P_{1,0}^*] = \frac{A_{10}}{(k_{de} + A_1 + A_5 + A_8 + \theta)} \quad (3.41)$$

6 Dead polymer without terminal double bond balance equation.

Dead polymer chains without terminal double bond are generated and are consumed by the following reactions, transfer to monomer, transfer to polymer and termination reactions.

rate of accumulation = rate of flow in - rate of flow out
+ rate of generation - rate of consumption

$$\begin{aligned} \frac{Vd[\sum_{b=1}^{\infty} P_{j,b}]}{dt} &= F(O - [\sum_{b=1}^{\infty} P_{j,b}]) && ; \text{ net flow of mass} \\ &+ V(k_{fm}[M_p][\sum_{b=1}^{\infty} P_{j,b}^*] && ; \text{ transfer to monomer} \\ &+ k_{fp}[\sum_{b=1}^{\infty} P_{j,b}^*][\sum_{c=1}^{\infty} P_{1,c}] && ; \text{ transfer to polymer} \\ &+ k_{fp}[\sum_{b=1}^{\infty} P_{j,b}^*][\sum_{c=1}^{\infty} P_{1,c}] && ; \text{ transfer to polymer} \\ &- k_{fp}[\sum_{b=1}^{\infty} P_{j,b}][\sum_{c=1}^{\infty} P_{1,c}^*] && ; \text{ transfer to polymer} \\ &- k_{fp}[\sum_{b=1}^{\infty} P_{j,b}][\sum_{c=1}^{\infty} P_{1,c}^*] && ; \text{ transfer to polymer} \\ &+ (1/2)k_{td}[\sum_{b=1}^{\infty} P_{j,b}^*][\sum_{c=1}^{\infty} P_{1,c}^*] && ; \text{ disproportionation} \\ &+ (1/2)k_{td}[\sum_{b=1}^{\infty} P_{j,b}][\sum_{c=1}^{\infty} P_{1,c}^*] && ; \text{ disproportionation} \\ &+ (1/2)k_{td}[\sum_{b=1}^{\infty} P_{j,b}^*][\sum_{c=1}^{\infty} P_{1,c}] && ; \text{ disproportionation} \\ &+ k_t[R_w][\sum_{b=1}^{\infty} P_{j,b}^*] && ; \text{ termination reaction} \end{aligned}$$

$$\begin{aligned}
 \frac{d[\bar{\dot{P}}_{j,b}]}{dt} = & k_{fm}[M_p][\bar{\dot{P}}_{j,b}^*] + k_{fp}[\bar{\dot{P}}_{j,b}^*][\bar{\dot{P}}_{1,c}] \\
 & + k_{fp}[\bar{\dot{P}}_{j,b}^*][\bar{\dot{P}}_{1,c}] - k_{fp}[\bar{\dot{P}}_{j,b}][\bar{\dot{P}}_{1,c}^*] \\
 & - k_{fp}[\bar{\dot{P}}_{j,b}][\bar{\dot{P}}_{1,c}^*] + (1/2)k_{td}[\bar{\dot{P}}_{j,b}^*][\bar{\dot{P}}_{1,c}^*] \\
 & + (1/2)k_{td}[\bar{\dot{P}}_{j,b}^*][\bar{\dot{P}}_{1,c}^*] + (1/2)k_{td}[\bar{\dot{P}}_{j,b}][\bar{\dot{P}}_{1,c}^*] \\
 & + k_t[R_w][\bar{\dot{P}}_{j,b}^*] - [\bar{\dot{P}}_{j,b}]/\theta \quad (3.42)
 \end{aligned}$$

7 Dead polymer with terminal double bond balance equation.

Dead polymer chains with terminal double bond are generated and are consumed by the following reactions, transfer to monomer, transfer to polymer, terminal double bond reaction and termination reactions.

rate of accumulation = rate of flow in - rate of flow out
+ rate of generation - rate of consumption

$$\begin{aligned}
 \frac{Vd[\bar{\dot{P}}_{j,b}]}{dt} = & F(0 - [\bar{\dot{P}}_{j,b}]) && ; \text{ net flow of mass} \\
 & + V(k_{fm}[M_p][\bar{\dot{P}}_{j,b}^*] && ; \text{ transfer to monomer} \\
 & + k_{fp}[\bar{\dot{P}}_{j,b}^*][\bar{\dot{P}}_{1,c}] && ; \text{ transfer to polymer} \\
 & + k_{fp}[\bar{\dot{P}}_{j,b}^*][\bar{\dot{P}}_{1,c}] && ; \text{ transfer to polymer} \\
 & - k_{fp}[\bar{\dot{P}}_{j,b}][\bar{\dot{P}}_{1,c}^*] && ; \text{ transfer to polymer} \\
 & - k_{fp}[\bar{\dot{P}}_{j,b}][\bar{\dot{P}}_{1,c}^*] && ; \text{ transfer to polymer} \\
 & - k_{pdb}[\bar{\dot{P}}_{j,b}][\bar{\dot{P}}_{1,c}^*] && ; \text{ terminal double bond} \\
 & - k_{pdb}[\bar{\dot{P}}_{j,b}][\bar{\dot{P}}_{1,c}^*] && ; \text{ terminal double bond} \\
 & + (1/2)k_{td}[\bar{\dot{P}}_{j,b}^*][\bar{\dot{P}}_{1,c}^*] && ; \text{ disproportionation} \\
 & + (1/2)k_{td}[\bar{\dot{P}}_{j,b}^*][\bar{\dot{P}}_{1,c}^*] && ; \text{ disproportionation} \\
 & + (1/2)k_{td}[\bar{\dot{P}}_{j,b}][\bar{\dot{P}}_{1,c}^*] && ; \text{ disproportionation} \\
 & + k_{td}[\bar{\dot{P}}_{j,b}][\bar{\dot{P}}_{1,c}^*] && ; \text{ disproportionation} \\
 & + k_{td}[\bar{\dot{P}}_{j,b}][\bar{\dot{P}}_{1,c}^*] && ; \text{ disproportionation} \\
 & + k_t[R_w][\bar{\dot{P}}_{j,b}^*] && ; \text{ termination reaction}
 \end{aligned}$$

$$\begin{aligned}
\frac{d\left[\sum_{j,b} \bar{P}_{j,b}\right]}{dt} = & k_{fm}[M_p]\left[\sum_{j,b} \bar{P}_{j,b}^*\right] + k_{fp}\left[\sum_{j,b} \bar{P}_{j,b}^*\right]\left[\sum_{i,c} \bar{P}_{i,c}\right] \\
& + k_{fp}\left[\sum_{j,b} \bar{P}_{j,b}^*\right]\left[\sum_{i,c} \bar{P}_{i,c}\right] - k_{fp}\left[\sum_{j,b} \bar{P}_{j,b}\right]\left[\sum_{i,c} \bar{P}_{i,c}^*\right] \\
& - k_{fp}\left[\sum_{j,b} \bar{P}_{j,b}\right]\left[\sum_{i,c} \bar{P}_{i,c}^*\right] - k_{pdb}\left[\sum_{j,b} \bar{P}_{j,b}\right]\left[\sum_{i,c} \bar{P}_{i,c}^*\right] \\
& - k_{pdb}\left[\sum_{j,b} \bar{P}_{j,b}\right]\left[\sum_{i,c} \bar{P}_{i,c}^*\right] + (1/2)k_{td}\left[\sum_{j,b} \bar{P}_{j,b}^*\right]\left[\sum_{i,c} \bar{P}_{i,c}^*\right] \\
& + (1/2)k_{td}\left[\sum_{j,b} \bar{P}_{j,b}^*\right]\left[\sum_{i,c} \bar{P}_{i,c}^*\right] + (1/2)k_{td}\left[\sum_{j,b} \bar{P}_{j,b}^*\right]\left[\sum_{i,c} \bar{P}_{i,c}^*\right] \\
& + k_{td}\left[\sum_{j,b} \bar{P}_{j,b}^*\right]\left[\sum_{i,c} \bar{P}_{i,c}^*\right] + k_{td}\left[\sum_{j,b} \bar{P}_{j,b}^*\right]\left[\sum_{i,c} \bar{P}_{i,c}^*\right] \\
& + k_t[R_w]\left[\sum_{j,b} \bar{P}_{j,b}^*\right] - \left[\sum_{j,b} \bar{P}_{j,b}\right]/\theta \quad (3.43)
\end{aligned}$$

8 Living polymer without terminal double bond balance equation.

Living polymer chains without terminal double bond are generated and consumed by the following reactions, propagation reaction, transfer to monomer, transfer to polymer, terminal double bond reaction and termination reactions.

$$\begin{aligned}
\text{rate of accumulation} = & \text{rate of flow in} - \text{rate of flow out} \\
& + \text{rate of generation} - \text{rate of consumption}
\end{aligned}$$

$$\begin{aligned}
\frac{d[\sum_{b_1} \dot{P}_{j,b}^*]}{dt} = & F(0 - [\sum_{b_1} \dot{P}_{j,b}^*]) && ; \text{ net flow of mass} \\
& + V(k_p [M_p] [\sum_{b_1} \dot{P}_{j-1,b}^*] && ; \text{ propagation reaction} \\
& - k_p [M_p] [\sum_{b_1} \dot{P}_{j,b}^*] && ; \text{ propagation reaction} \\
& - k_{fm} [M_p] [\sum_{b_1} \dot{P}_{j,b}^*] && ; \text{ transfer to monomer} \\
& - k_{fp} [\sum_{b_1} \dot{P}_{j,b}^*] [\sum_{c_1} \dot{P}_{1,c}^*] && ; \text{ transfer to polymer} \\
& + k_{fp} [\sum_{b_1} \dot{P}_{j,b}^*] [\sum_{c_1} \dot{P}_{1,c}^*] && ; \text{ transfer to polymer} \\
& + k_{fp} [\sum_{b_1} \dot{P}_{j,b}^*] [\sum_{c_1} \dot{P}_{1,c}^*] && ; \text{ transfer to polymer} \\
& - k_{fp} [\sum_{b_1} \dot{P}_{j,b}^*] [\sum_{c_1} \dot{P}_{1,c}^*] && ; \text{ transfer to polymer} \\
& - k_{pdb} [\sum_{b_1} \dot{P}_{j,b}^*] [\sum_{c_1} \dot{P}_{1,c}^*] && ; \text{ terminal double bond} \\
& + k_{pdb} [\sum_{b_1} \dot{P}_{j-1,b}^*] [\sum_{c_1} \dot{P}_{1,c}^*] && ; \text{ terminal double bond} \\
& - k_{td} [\sum_{b_1} \dot{P}_{j,b}^*] [\sum_{c_1} \dot{P}_{1,c}^*] && ; \text{ disproportionation} \\
& - k_{td} [\sum_{b_1} \dot{P}_{j,b}^*] [\sum_{c_1} \dot{P}_{1,c}^*] && ; \text{ disproportionation} \\
& - k_t [R_w] [\sum_{b_1} \dot{P}_{j,b}^*] && ; \text{ termination reaction}
\end{aligned}$$

$$\begin{aligned}
\frac{d[\sum_{b_1} \dot{P}_{j,b}^*]}{dt} = & k_p [M_p] [\sum_{b_1} \dot{P}_{j-1,b}^*] && - k_p [M_p] [\sum_{b_1} \dot{P}_{j,b}^*] \\
& - k_{fm} [M_p] [\sum_{b_1} \dot{P}_{j,b}^*] && - k_{fp} [\sum_{b_1} \dot{P}_{j,b}^*] [\sum_{c_1} \dot{P}_{1,c}^*] \\
& + k_{fp} [\sum_{b_1} \dot{P}_{j,b}^*] [\sum_{c_1} \dot{P}_{1,c}^*] && + k_{fp} [\sum_{b_1} \dot{P}_{j,b}^*] [\sum_{c_1} \dot{P}_{1,c}^*] \\
& - k_{fp} [\sum_{b_1} \dot{P}_{j,b}^*] [\sum_{c_1} \dot{P}_{1,c}^*] && - k_{pdb} [\sum_{b_1} \dot{P}_{j,b}^*] [\sum_{c_1} \dot{P}_{1,c}^*] \\
& + k_{pdb} [\sum_{b_1} \dot{P}_{j-1,b}^*] [\sum_{c_1} \dot{P}_{1,c}^*] && - k_{td} [\sum_{b_1} \dot{P}_{j,b}^*] [\sum_{c_1} \dot{P}_{1,c}^*] \\
& - k_{td} [\sum_{b_1} \dot{P}_{j,b}^*] [\sum_{c_1} \dot{P}_{1,c}^*] && - k_t [R_w] [\sum_{b_1} \dot{P}_{j,b}^*] \\
& - [\sum_{b_1} \dot{P}_{j,b}^*] / \theta && (3.44)
\end{aligned}$$

9 Living polymer with terminal double bond balance equation.

Living polymer chains with terminal double bond are generated and consumed by the following reactions, propagation reaction, transfer to monomer, transfer to polymer, terminal double bond reaction and termination reactions.

rate of accumulation = rate of flow in - rate of flow out
 + rate of generation - rate of consumption

$$\frac{Vd[\sum_{b,1}^* \bar{P}_{j,b}]}{dt} = F(C_0 - [\sum_{b,1}^* \bar{P}_{j,b}])$$

; net flow of mass

$$+ V(k_p [M_p] [\sum_{b,1}^* \bar{P}_{j-1,b}]$$

; propagation reaction

$$- k_p [M_p] [\sum_{b,1}^* \bar{P}_{j,b}]$$

; propagation reaction

$$- k_{fm} [M_p] [\sum_{b,1}^* \bar{P}_{j,b}]$$

; transfer to monomer

$$- k_{fp} [\sum_{b,1}^* \bar{P}_{j,b}] [\sum_{c,1}^* \bar{P}_{1,c}]$$

; transfer to polymer

$$+ k_{fp} [\sum_{b,1}^* \bar{P}_{j,b}] [\sum_{c,1}^* \bar{P}_{1,c}]$$

; transfer to polymer

$$- k_{fp} [\sum_{b,1}^* \bar{P}_{j,b}] [\sum_{c,1}^* \bar{P}_{1,c}]$$

; transfer to polymer

$$+ k_{fp} [\sum_{b,1}^* \bar{P}_{j,b}] [\sum_{c,1}^* \bar{P}_{1,c}]$$

; transfer to polymer

$$- k_{pdb} [\sum_{b,1}^* \bar{P}_{j,b}] [\sum_{c,1}^* \bar{P}_{1,c}]$$

; terminal double bond

$$+ k_{pdb} [\sum_{b,1}^* \bar{P}_{j-1,b}] [\sum_{c,1}^* \bar{P}_{1,c}]$$

; terminal double bond

$$- k_{td} [\sum_{b,1}^* \bar{P}_{j,b}] [\sum_{c,1}^* \bar{P}_{1,c}]$$

; disproportionation

$$- k_{td} [\sum_{b,1}^* \bar{P}_{j,b}] [\sum_{c,1}^* \bar{P}_{1,c}]$$

; disproportionation

$$- k_t [R_w] [\sum_{b,1}^* \bar{P}_{j,b}])$$

; termination reaction

$$\frac{d[\sum_{b,1}^* \bar{P}_{j,b}]}{dt} = k_p [M_p] [\sum_{b,1}^* \bar{P}_{j-1,b}] - k_p [M_p] [\sum_{b,1}^* \bar{P}_{j,b}]$$

$$- k_{fm} [M_p] [\sum_{b,1}^* \bar{P}_{j,b}] - k_{fp} [\sum_{b,1}^* \bar{P}_{j,b}] [\sum_{c,1}^* \bar{P}_{1,c}]$$

$$+ k_{fp} [\sum_{b,1}^* \bar{P}_{j,b}] [\sum_{c,1}^* \bar{P}_{1,c}] - k_{fp} [\sum_{b,1}^* \bar{P}_{j,b}] [\sum_{c,1}^* \bar{P}_{1,c}]$$

$$+ k_{fp} [\sum_{b,1}^* \bar{P}_{j,b}] [\sum_{c,1}^* \bar{P}_{1,c}] - k_{pdb} [\sum_{b,1}^* \bar{P}_{j,b}] [\sum_{c,1}^* \bar{P}_{1,c}]$$

$$+ k_{pdb} [\sum_{b,1}^* \bar{P}_{j-1,b}] [\sum_{c,1}^* \bar{P}_{1,c}] - k_{td} [\sum_{b,1}^* \bar{P}_{j,b}] [\sum_{c,1}^* \bar{P}_{1,c}]$$

$$- k_{td} [\sum_{b,1}^* \bar{P}_{j,b}] [\sum_{c,1}^* \bar{P}_{1,c}] - k_t [R_w] [\sum_{b,1}^* \bar{P}_{j,b}]$$

$$- [\sum_{b,1}^* \bar{P}_{j,b}] / \theta$$

(3.45)

3.2.3.2 Moment expressions.

A system of differential equations for unsteady-state calculation of average molecular weights are derived from the infinite series of equation 3.42 to equation 3.45 and monomeric radicals mass balance. Moment expressions and series reductions of particular species are shown in Appendix A and Appendix B respectively. The infinite series of equation 3.42 to equation 3.45 can be generalized by using Appendix A, B and C. The generalized system equations for zero, first and second moment of dead polymer and living polymer with and without terminal double bond are shown below.

1 Zero moment of dead polymer without terminal double bond.

Differential equation for the zero moment of dead polymer without terminal double bond can be derived by infinite series of equation 3.42 and simplify the obtained equation by using series reductions and simplified notations in Appendix B and C.

$$\begin{aligned} \frac{d\left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}\right]}{dt} = & k_{fm}[M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right] + k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}\right] \\ & + k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}\right] - k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] \\ & - k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] + 0.5 * k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] \\ & + 0.5 * k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] + 0.5 * k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] \\ & + k_t [R_w] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right] - \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}\right] / \theta \end{aligned}$$

$$\begin{aligned} \frac{d[M_o]}{dt} = & k_{fm}[M_p][M_o^*] + k_{fp}[M_o^*][M_o] + k_{fp}[M_o^*][M_o] - k_{fp}[M_o][M_o^*] \\ & - k_{fp}[M_o][M_o^*] + 0.5 * k_{td}[M_o^*][M_o^*] + 0.5 * k_{td}[M_o^*][M_o^*] \\ & + 0.5 * k_{td}[M_o^*][M_o^*] + k_t [R_w][M_o^*] - [M_o] / \theta \end{aligned}$$

$$= (k_{fm}[M_p] + k_{fp}[M_o] + k_{fp}[M_o] + k_{td}[M_o^*] + 0.5 * k_{td}[M_o^*] + k_t[R_w])[M_o^*] \\ - (k_{fp}[M_o^*] + k_{fp}[M_o^*] + 1/\theta)[M_o]$$

$$\frac{d[M_o]}{dt} = (A_2 + A_6)[M_o^*] - (A_3 + 1/\theta)[M_o] \quad (3.46)$$

2 First moment of dead polymer without terminal double bond.

Differential equation for the first moment of dead polymer without terminal double bond can be derived by infinite series of the product of j and equation 3.42 then simplify the obtained equation by series reductions and simplified notations in Appendix B and C.

$$\frac{d\left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}\right]}{dt} = k_{fm}[M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] + k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}\right] \\ + k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}\right] - k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] \\ - k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] + 0.5 * k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] \\ + 0.5 * k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] + 0.5 * k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] \\ + k_t[R_w] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] - \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}\right] / \theta$$

$$\frac{d[M_1]}{dt} = k_{fm}[M_p][M_1^*] + k_{fp}[M_1^*][M_o] + k_{fp}[M_1^*][M_o] - k_{fp}[M_1][M_o^*] \\ - k_{fp}[M_1][M_o^*] + 0.5 * k_{td}[M_1^*][M_o^*] + 0.5 * k_{td}[M_1^*][M_o^*] \\ + 0.5 * k_{td}[M_1^*][M_o^*] + k_t[R_w][M_1^*] - [M_1] / \theta$$

$$= (k_{fm}[M_p] + k_{fp}[M_o] + k_{fp}[M_o] + k_{td}[M_o^*] + 0.5 * k_{td}[M_o^*] + k_t[R_w])[M_1^*] \\ - (k_{fp}[M_o^*] + k_{fp}[M_o^*] + 1/\theta)[M_1]$$

$$\frac{d[M_1]}{dt} = (A_2 + A_6)[M_1^*] - (A_3 + 1/\theta)[M_1] \quad (3.47)$$

3 Second moment of dead polymer without terminal double bond.

Differential equation for the second moment of dead polymer without terminal double bond can be derived by infinite series of the product of j^2 and equation 3.42 then simplify the obtained equation by series reductions and simplified notations in Appendix B and C.

$$\begin{aligned} \frac{d\left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j,b}\right]}{dt} = & k_{fp} [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j,b}^*\right] + k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}\right] \\ & + k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}\right] - k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j,b}\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] \\ & - k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j,b}\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] + 0.5 * k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] \\ & + 0.5 * k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] + 0.5 * k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j,b}\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] \\ & + k_t [R_w] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j,b}^*\right] - \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j,b}\right] / \theta \end{aligned}$$

$$\begin{aligned} \frac{d[M_2]}{dt} = & k_{fp} [M_p] [M_2^*] + k_{fp} [M_2^*] [M_0] + k_{fp} [M_2^*] [M_0] - k_{fp} [M_2] [M_0^*] \\ & - k_{fp} [M_2] [M_0^*] + 0.5 * k_{td} [M_2^*] [M_0^*] + 0.5 * k_{td} [M_2^*] [M_0^*] \\ & + 0.5 * k_{td} [M_2^*] [M_0^*] + k_t [R_w] [M_2^*] - [M_2] / \theta \end{aligned}$$

$$\begin{aligned} = & (k_{fp} [M_p] + k_{fp} [M_0] + k_{fp} [M_0] + k_{td} [M_0^*] + 0.5 * k_{td} [M_0^*] + k_t [R_w]) [M_2^*] \\ & - (k_{fp} [M_0^*] + k_{fp} [M_0^*] + 1/\theta) [M_2] \end{aligned}$$

$$\frac{d[M_2]}{dt} = (A_2 + A_0) [M_2^*] - (A_3 + 1/\theta) [M_2] \quad (3.48)$$

4 Zero moment of dead polymer with terminal double bond.

Differential equation for the zero moment of dead polymer with terminal double bond can be derived by infinite series of equation 3.43 then simplify the obtained equation by series reductions and simplified notation in Appendix B and C.

$$\begin{aligned} \frac{d\left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}\right]}{dt} = & k_{fm} [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right] + k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right] \left[\sum_{i=1}^{\infty} \sum_{c=1}^{\infty} P_{i,c}\right] \\ & + k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right] \left[\sum_{i=1}^{\infty} \sum_{c=1}^{\infty} P_{i,c}\right] - k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}\right] \left[\sum_{i=1}^{\infty} \sum_{c=1}^{\infty} P_{i,c}^*\right] \\ & - k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}\right] \left[\sum_{i=1}^{\infty} \sum_{c=1}^{\infty} P_{i,c}^*\right] - k_{pdb} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}\right] \left[\sum_{i=1}^{\infty} \sum_{c=1}^{\infty} P_{i,c}^*\right] \\ & - k_{pdb} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}\right] \left[\sum_{i=1}^{\infty} \sum_{c=1}^{\infty} P_{i,c}^*\right] + 0.5 * k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right] \left[\sum_{i=1}^{\infty} \sum_{c=1}^{\infty} P_{i,c}^*\right] \\ & + 0.5 * k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right] \left[\sum_{i=1}^{\infty} \sum_{c=1}^{\infty} P_{i,c}^*\right] + 0.5 * k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right] \left[\sum_{i=1}^{\infty} \sum_{c=1}^{\infty} P_{i,c}^*\right] \\ & + k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right] \left[\sum_{i=1}^{\infty} \sum_{c=1}^{\infty} P_{i,c}^*\right] + k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}\right] \left[\sum_{i=1}^{\infty} \sum_{c=1}^{\infty} P_{i,c}^*\right] \\ & + k_t [R_w] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right] - \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}\right] / \theta \end{aligned}$$

$$\begin{aligned} \frac{d[M_o]}{dt} = & k_{fm} [M_p] [M_o^*] + k_{fp} [M_o^*] [M_o] + k_{fp} [M_o^*] [M_o] - k_{fp} [M_o] [M_o^*] \\ & - k_{fp} [M_o] [M_o^*] - k_{pdb} [M_o] [M_o^*] - k_{pdb} [M_o] [M_o^*] \\ & + 0.5 * k_{td} [M_o^*] [M_o^*] + 0.5 * k_{td} [M_o^*] [M_o^*] \\ & + 0.5 * k_{td} [M_o^*] [M_o^*] + k_{td} [M_o^*] [M_o^*] + k_{td} [M_o^*] [M_o^*] \\ & + k_t [R_w] [M_o^*] - [M_o] / \theta \end{aligned}$$

$$\begin{aligned} = & (k_{fm} [M_p] + k_{fp} [M_o] + k_{fp} [M_o] + k_{td} [M_o^*] + k_{td} [M_o^*] + k_t [R_w]) [M_o^*] \\ & - (k_{fp} [M_o^*] + k_{fp} [M_o^*] + k_{pdb} [M_o^*] + k_{pdb} [M_o^*] + 1/\theta) [M_o] \\ & + (k_{td} [M_o^*] + 0.5 * k_{td} [M_o^*]) [M_o^*] \end{aligned}$$

$$\frac{d[M_o]}{dt} = (A_2 + A_5) [M_o^*] - (A_3 + A_4 + 1/\theta) [M_o] + (A_6) [M_o^*] \quad (3.49)$$

5 First moment of dead polymer with terminal double bond.

Differential equation for the first moment of dead polymer with terminal double bond can be derived by infinite series of the product of j and equation 3.43 then simplify the obtained equation by series reductions and simplified notations in Appendix B and C.

$$\begin{aligned} \frac{d\left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}\right]}{dt} = & k_{fp} [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] + k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}\right] \\ & + k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}\right] - k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] \\ & - k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] - k_{pdb} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] \\ & - k_{pdb} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] + 0.5 * k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] \\ & + 0.5 * k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] + 0.5 * k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] \\ & + k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] + k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] \\ & + k_t [R_w] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] - \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b} / \theta\right] \end{aligned}$$

$$\begin{aligned} \frac{d[M_1]}{dt} = & k_{fm} [M_p] [M_1^*] + k_{fp} [M_1^*] [M_0] + k_{fp} [M_1^*] [M_0] - k_{fp} [M_1] [M_0^*] \\ & - k_{fp} [M_1] [M_0^*] - k_{pdb} [M_1] [M_0^*] - k_{pdb} [M_1] [M_0^*] \\ & + 0.5 * k_{td} [M_1^*] [M_0^*] + 0.5 * k_{td} [M_1^*] [M_0^*] \\ & + 0.5 * k_{td} [M_1^*] [M_0^*] + k_{td} [M_1^*] [M_0^*] + k_{td} [M_1^*] [M_0^*] \\ & + k_t [R_w] [M_1^*] - [M_1] / \theta \end{aligned}$$

$$\begin{aligned} = & (k_{fm} [M_p] + k_{fp} [M_0] + k_{fp} [M_0] + k_{td} [M_0^*] + k_{td} [M_0^*] + k_t [R_w]) [M_1^*] \\ & - (k_{fp} [M_0^*] + k_{fp} [M_0^*] + k_{pdb} [M_0^*] + k_{pdb} [M_0^*] + 1/\theta) [M_1] \\ & + (k_{td} [M_0^*] + 0.5 * k_{td} [M_0^*]) [M_1^*] \end{aligned}$$

$$\frac{d[M_1]}{dt} = (A_2 + A_5) [M_1^*] - (A_3 + A_4 + 1/\theta) [M_1] + (A_5) [M_1^*] \quad (3.50)$$

6 Second moment of dead polymer with terminal double bond.

Differential equation for the second moment of dead polymer with terminal double bond can be derived by infinite series of the product of j^2 and equation 3.43 then simplify the obtained equation by series reductions and simplified notations in Appendix B and C.

$$\begin{aligned} \frac{d\left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}\right]}{dt} = & k_{fp} [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}^*\right] + k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c}\right] \\ & + k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c}\right] - k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}\right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c}^*\right] \\ & - k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}\right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c}^*\right] - k_{pdb} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}\right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c}^*\right] \\ & - k_{pdb} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}\right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c}^*\right] + 0.5 * k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c}^*\right] \\ & + 0.5 * k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c}^*\right] + 0.5 * k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c}^*\right] \\ & + k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c}^*\right] + k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c}^*\right] \\ & + k_t [R_w] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}^*\right] - \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}\right] / \theta \end{aligned}$$

$$\begin{aligned} \frac{d[M_2]}{dt} = & k_{fm} [M_p] [M_2^*] + k_{fp} [M_2^*] [M_0] + k_{fp} [M_2^*] [M_0] - k_{fp} [M_2] [M_0^*] \\ & - k_{fp} [M_2] [M_0^*] - k_{pdb} [M_2] [M_0^*] - k_{pdb} [M_2] [M_0^*] \\ & + 0.5 * k_{td} [M_2^*] [M_0^*] + 0.5 * k_{td} [M_2^*] [M_0^*] \\ & + 0.5 * k_{td} [M_2^*] [M_0^*] + k_{td} [M_2^*] [M_0^*] + k_{td} [M_2^*] [M_0^*] \\ & + k_t [R_w] [M_2^*] - [M_2] / \theta \end{aligned}$$

$$\begin{aligned} = & (k_{fm} [M_p] + k_{fp} [M_0] + k_{fp} [M_0] + k_{td} [M_0^*] + k_{td} [M_0^*] + k_t [R_w]) [M_2^*] \\ & - (k_{fp} [M_0^*] + k_{fp} [M_0^*] + k_{pdb} [M_0^*] + k_{pdb} [M_0^*] + 1/\theta) [M_2] \\ & + (k_{td} [M_0^*] + 0.5 * k_{td} [M_0^*]) [M_2^*] \end{aligned}$$

$$\frac{d[M_2]}{dt} = (A_2 + A_5) [M_2^*] - (A_3 + A_4 + 1/\theta) [M_2] + (A_6) [M_2^*] \quad (3.51)$$

7 Zero moment of living polymer without terminal double bond.

Differential equation for the zero moment of living polymer without terminal double bond can be derived by infinite series of the equation 3.44 then simplify the obtained equation by series reduction and simplified notation in Appendix B and C.

$$\begin{aligned}
 \frac{d\left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right]}{dt} &= k_p [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j-1,b}^*\right] - k_p [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right] \\
 &- k_{fm} [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right] - k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \sum_{1,c} P_{1,c}\right] \\
 &+ k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}\right] \left[\sum_{c=1}^{\infty} \sum_{1,c} P_{1,c}^*\right] + k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}\right] \left[\sum_{c=1}^{\infty} \sum_{1,c} P_{1,c}^*\right] \\
 &- k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \sum_{1,c} P_{1,c}\right] - k_{pdb} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \sum_{1,c} P_{1,c}\right] \\
 &+ k_{pdb} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} \left(\sum_{c=1}^{\infty} \sum_{1,c} P_{j-1,b}^* \sum_{c=1}^{\infty} P_{1,c}\right)\right] - k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \sum_{1,c} P_{1,c}^*\right] \\
 &- k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \sum_{1,c} P_{1,c}^*\right] - k_t [R_w] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right] - \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right] / \theta \\
 &= k_p [M_p] \left(\left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j-1,b}^*\right] - \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} P_{j,b}^*\right]\right) - k_{fm} [M_p] [M_o^*] \\
 &- k_{fp} [M_o^*] [M_o] + k_{fp} [M_o] [M_o^*] + k_{fp} [M_o] [M_o^*] \\
 &- k_{fp} [M_o^*] [M_o] - k_{pdb} [M_o^*] [M_o] + k_{pdb} [M_o^*] [M_o] \\
 &- k_{td} [M_o^*] [M_o^*] - k_{td} [M_o^*] [M_o] - k_t [R_w] [M_o^*] - [M_o^*] / \theta \\
 &= k_p [M_p] [P_{1,0}^*] - k_{fm} [M_p] [M_o^*] - k_{fp} [M_o^*] [M_o] \\
 &+ k_{fp} [M_o] [M_o^*] + k_{fp} [M_o] [M_o^*] - k_{fp} [M_o^*] [M_o] \\
 &- k_{td} [M_o^*] [M_o^*] - k_{td} [M_o^*] [M_o] - k_t [R_w] [M_o^*] - [M_o^*] / \theta \\
 &= k_p [M_p] [P_{1,0}^*] + (k_{fp} [M_o^*] + k_{fp} [M_o]) [M_o] - (k_{fm} [M_p] \\
 &+ k_{fp} [M_o] + k_{fp} [M_o] + k_{td} [M_o^*] + k_{td} [M_o] + k_t [R_w] + 1/\theta) [M_o^*] \\
 \frac{d[M_o^*]}{dt} &= A_1 [P_{1,0}^*] + A_3 [M_o] - (A_2 + A_5 + 1/\theta) [M_o^*] \quad (3.52)
 \end{aligned}$$

8 First moment of living polymer without terminal double bond.

Differential equation for the first moment of living polymer without terminal double bond can be derived by infinite series of the product of j and equation 3.44 then simplify the obtained equation by series reductions and simplified notations in Appendix B and C.

$$\begin{aligned}
 \frac{d\left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right]}{dt} &= k_p [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j-1,b}^*\right] - k_p [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \\
 &- k_{fm} [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] - k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] \\
 &+ k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] + k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] \\
 &- k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] - k_{pdb} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] \\
 &+ k_{pdb} \left[\sum_{j=1}^{\infty} j \left[\sum_{b=1}^{\infty} \left(\sum_{c=1}^{\infty} P_{j-1,b}^* \sum_{c=1}^{\infty} P_{1,c}^*\right)\right]\right] - k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] \\
 &- k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] - k_t [R_w] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \\
 &- \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] / \theta \\
 &= k_p [M_p] ([P_{1,0}^*] + [M_0^*]) - k_{fm} [M_p] [M_1^*] - k_{fp} [M_1^*] [M_0] \\
 &+ k_{fp} [M_1] [M_0^*] + k_{fp} [M_1] [M_0^*] - k_{fp} [M_1^*] [M_0] \\
 &+ k_{pdb} [M_0^*] [M_1] - k_{td} [M_1^*] [M_0^*] - k_{td} [M_1^*] [M_0^*] \\
 &- k_t [R_w] [M_1^*] - [M_1^*] / \theta \\
 &= k_p [M_p] ([P_{1,0}^*] + [M_0^*]) + (k_{fp} [M_0^*] + k_{fp} [M_0^*]) [M_1] \\
 &- (k_{fm} [M_p] + k_{fp} [M_0] + k_{fp} [M_0] + k_{td} [M_0^*] + k_{td} [M_0^*] + k_t [R_w] \\
 &+ 1/\theta) [M_1^*] + k_{pdb} [M_0^*] [M_1] \\
 \frac{d[M_1^*]}{dt} &= A_1 ([P_{1,0}^*] + [M_0^*]) + A_3 [M_1] \\
 &- (A_2 + A_5 + 1/\theta) [M_1^*] + A_7 [M_1] \tag{3.53}
 \end{aligned}$$

9 Second moment of living polymer without terminal double bond.

Differential equation for the second moment of living polymer without terminal double bond can be derived by infinite series of the product of j^2 and equation 3.44 then simplify the obtained equation by series reductions and simplified notations in Appendix B and C.

$$\begin{aligned}
 \frac{d\left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j,b}^*\right]}{dt} &= k_p [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j-1,b}^*\right] - k_p [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j,b}^*\right] \\
 &- k_{fm} [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j,b}^*\right] - k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \sum_{1,c} P_{1,c}^*\right] \\
 &+ k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \sum_{1,c} P_{1,c}^*\right] + k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \sum_{1,c} P_{1,c}^*\right] \\
 &- k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \sum_{1,c} P_{1,c}^*\right] - k_{pdb} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \sum_{1,c} P_{1,c}^*\right] \\
 &+ k_{pdb} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \left[\sum_{c=1}^{\infty} \left(\sum_{b=1}^{\infty} P_{j-1,b}^* \sum_{c=1}^{\infty} P_{1,c}^*\right)\right]\right] - k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \sum_{1,c} P_{1,c}^*\right] \\
 &- k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \sum_{1,c} P_{1,c}^*\right] - k_t [R_w] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j,b}^*\right] \\
 &- \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 P_{j,b}^*\right] / \theta \\
 &= k_p [M_p] ([P_{1,0}^*] + 2[M_1^*] + [M_0^*]) - k_{fm} [M_p] [M_2^*] - k_{fp} [M_2^*] [M_0^*] \\
 &+ k_{fp} [M_2] [M_0^*] + k_{fp} [M_2] [M_0^*] - k_{fp} [M_2^*] [M_0] \\
 &+ 2k_{pdb} [M_1^*] [M_1] + k_{pdb} [M_0^*] [M_2] - k_{td} [M_2^*] [M_0^*] \\
 &- k_{td} [M_2^*] [M_0^*] - k_t [R_w] [M_2^*] - [M_2^*] / \theta \\
 &= k_p [M_p] ([P_{1,0}^*] + 2[M_1^*] + [M_0^*]) + (k_{fp} [M_0^*] + k_{fp} [M_0^*]) [M_2] \\
 &- (k_{fm} [M_p] + k_{fp} [M_0] + k_{fp} [M_0] + k_{td} [M_0^*] + k_{td} [M_0^*] + k_t [R_w] \\
 &+ 1/\theta) [M_2^*] + 2k_{pdb} [M_1^*] [M_1] + k_{pdb} [M_0^*] [M_2] \\
 \frac{d[M_2^*]}{dt} &= A_1 ([P_{1,0}^*] + 2[M_1^*] + [M_0^*]) + A_3 [M_2] - (A_2 + A_5 + 1/\theta) [M_2^*] \\
 &+ 2k_{pdb} [M_1^*] [M_1] + A_7 k_{pdb} [M_2] \quad (3.54)
 \end{aligned}$$

10 Zero moment of living polymer with terminal double bond.

Differential equation for the zero moment of living polymer with terminal double bond can be derived by infinite series of equation 3.45 then simplify the obtained equation by series reductions and simplified notations in Appendix B and C.

$$\begin{aligned}
 \frac{d\left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} \underline{P}_{j,b}^*\right]}{dt} &= k_p [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} \underline{P}_{j-1,b}^* \right] - k_p [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} \underline{P}_{j,b}^* \right] \\
 &- k_{fm} [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} \underline{P}_{j,b}^* \right] - k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} \underline{P}_{j,b}^* \right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c} \right] \\
 &+ k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} \underline{P}_{j,b} \right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c}^* \right] - k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} \underline{P}_{j,b}^* \right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c} \right] \\
 &+ k_{fdb} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} \underline{P}_{j,b} \right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c}^* \right] - k_{fdb} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} \underline{P}_{j,b}^* \right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c} \right] \\
 &+ k_{pdb} \left[\sum_{j=1}^{\infty} \left[\sum_{b=1}^{\infty} (\underline{P}_{j-1,b}^* \underline{P}_{1,c}) \right] \right] - k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} \underline{P}_{j,b}^* \right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c}^* \right] \\
 &- k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} \underline{P}_{j,b}^* \right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c}^* \right] - k_t [R_w] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} \underline{P}_{j,b}^* \right] - \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} \underline{P}_{j,b}^* \right] / \theta \\
 &= k_p [M_p] \left(\left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} \underline{P}_{j-1,b}^* \right] - \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} \underline{P}_{j,b}^* \right] \right) - k_{fm} [M_p] [M_o^*] \\
 &- k_{fp} [M_o^*] [M_o] + k_{fp} [M_o] [M_o^*] - k_{fp} [M_o^*] [M_o] + k_{fp} [M_o] [M_o^*] \\
 &- k_{fdb} [M_o^*] [M_o] + k_{fdb} [M_o] [M_o^*] - k_{td} [M_o^*] [M_o^*] \\
 &- k_{td} [M_o^*] [M_o^*] - k_t [R_w] [M_o^*] - [M_o^*] / \theta \\
 &= k_p [M_p] [P_{1,0}^*] - k_{fm} [M_p] [M_o^*] - k_{fp} [M_o^*] [M_o] + k_{fp} [M_o] [M_o^*] \\
 &- k_{fp} [M_o^*] [M_o] + k_{fp} [M_o] [M_o^*] - k_{td} [M_o^*] [M_o^*] \\
 &- k_{td} [M_o^*] [M_o^*] - k_t [R_w] [M_o^*] - [M_o^*] / \theta \\
 &= k_p [M_p] [P_{1,0}^*] + (k_{fp} [M_o^*] + k_{fp} [M_o]) [M_o] - (k_{fm} [M_p] + k_{fp} [M_o] \\
 &+ k_{fp} [M_o] + k_{td} [M_o^*] + k_{td} [M_o^*] + k_t [R_w] + 1/\theta) [M_o^*] \\
 \frac{d[M_o^*]}{dt} &= A_1 [P_{1,0}^*] + (A_3) [M_o] - (A_2 + A_5 + 1/\theta) [M_o^*] \quad (3.55)
 \end{aligned}$$

11 First moment of living polymer with terminal double bond.

Differential equation for the first moment of living polymer with terminal double bond can be derived by infinite series of the product of j and equation 3.45 then simplify the obtained equation by series reductions and simplified notations in Appendix B and C.

$$\begin{aligned}
 \frac{d\left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right]}{dt} &= k_p [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j-1,b}^*\right] - k_p [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \\
 &- k_{fp} [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] - k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] \\
 &+ k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] - k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] \\
 &+ k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] - k_{pdb} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] \\
 &+ k_{pdb} \left[\sum_{j=1}^{\infty} j \left[\sum_{b=1}^{\infty} P_{j-1,b}^* \left(\sum_{c=1}^{\infty} P_{1,c}^*\right)\right]\right] - k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] \\
 &- k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \left[\sum_{c=1}^{\infty} P_{1,c}^*\right] - k_t [R_w] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] \\
 &- \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right] / \theta \\
 &= k_p [M_p] \left(\left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j-1,b}^*\right] - \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j P_{j,b}^*\right]\right) - k_{fp} [M_p] [M_1^*] \\
 &- k_{fp} [M_1^*] [M_0] + k_{fp} [M_1] [M_0^*] - k_{fp} [M_1^*] [M_0] \\
 &+ k_{fp} [M_1] [M_0^*] - k_{pdb} [M_1^*] [M_0] + k_{pdb} [M_1^*] [M_0] \\
 &+ k_{pdb} [M_0^*] [M_1] - k_{td} [M_1^*] [M_0^*] - k_{td} [M_1^*] [M_0^*] \\
 &- k_t [R_w] [M_1^*] - [M_1^*] / \theta \\
 &= k_p [M_p] ([P_{1,0}^*] + [M_0^*]) - k_{fp} [M_p] [M_1^*] - k_{fp} [M_1^*] [M_0] \\
 &+ k_{fp} [M_1] [M_0^*] - k_{fp} [M_1^*] [M_0] + k_{fp} [M_1] [M_0^*] + k_{pdb} [M_0^*] [M_1] \\
 &- k_{td} [M_1^*] [M_0^*] - k_{td} [M_1^*] [M_0^*] - k_t [R_w] [M_1^*] - [M_1^*] / \theta \\
 \frac{d[M_1^*]}{dt} &= A_1 ([P_{1,0}^*] + [M_0^*]) + (A_3 + A_7) [M_1] - (A_2 + A_5 + 1/\theta) [M_1^*] \quad (3.56)
 \end{aligned}$$

12 Second moment of living polymer with terminal double bond.

Differential equation for the second moment of living polymer with terminal double bond can be derived by infinite series of the product of j^2 and equation 3.45 then simplify the obtained equation by series reductions and simplified notations in Appendix B and C.

$$\begin{aligned}
 \frac{d\left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}^*\right]}{dt} &= k_p [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j-1,b}^*\right] - k_p [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}^*\right] \\
 &- k_{fm} [M_p] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}^*\right] - k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c}^*\right] \\
 &+ k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c}^*\right] - k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c}^*\right] \\
 &+ k_{fp} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c}^*\right] - k_{pdb} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c}^*\right] \\
 &+ k_{pdb} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \left[\sum_{c=1}^{\infty} \left(\underline{P}_{j-1,b}^* \underline{P}_{1,c}^*\right)\right]\right] - k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c}^*\right] \\
 &- k_{td} \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}^*\right] \left[\sum_{c=1}^{\infty} \underline{P}_{1,c}^*\right] - k_t [R_w] \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}^*\right] \\
 &- \left[\sum_{j=1}^{\infty} \sum_{b=1}^{\infty} j^2 \underline{P}_{j,b}^*\right] / \theta \\
 &= k_p [M_p] ([\underline{P}_{1,0}^*] + 2[\underline{M}_1^*] + [\underline{M}_0^*]) - k_{fm} [M_p] [\underline{M}_2^*] - k_{fp} [\underline{M}_2^*] [\underline{M}_0] \\
 &+ k_{fp} [\underline{M}_2] [\underline{M}_0^*] - k_{fp} [\underline{M}_2^*] [\underline{M}_0] + k_{fp} [\underline{M}_2] [\underline{M}_0^*] + 2k_{pdb} [\underline{M}_1^*] [\underline{M}_1] \\
 &+ k_{pdb} [\underline{M}_0^*] [\underline{M}_2] - k_{td} [\underline{M}_1^*] [\underline{M}_0^*] - k_{td} [\underline{M}_1^*] [\underline{M}_0^*] \\
 &- k_t [R_w] [\underline{M}_1^*] - [\underline{M}_1^*] / \theta \\
 &= k_p [M_p] ([\underline{P}_{1,0}^*] + 2[\underline{M}_1^*] + [\underline{M}_0^*]) + (k_{fp} [\underline{M}_0^*] + k_{fp} [\underline{M}_0^*] + k_{pdb} [\underline{M}_0^*]) [\underline{M}_2] \\
 &- (k_{fm} [M_p] + k_{fp} [\underline{M}_0] + k_{fp} [\underline{M}_0] + k_{td} [\underline{M}_0^*] + k_{td} [\underline{M}_0^*] + k_t [R_w] + 1/\theta) [\underline{M}_2^*] \\
 &+ 2k_{pdb} [\underline{M}_1^*] [\underline{M}_1] \\
 \frac{d[\underline{M}_2^*]}{dt} &= A_1 ([\underline{P}_{1,0}^*] + 2[\underline{M}_1^*] + [\underline{M}_0^*]) + (A_3 + A_7) [\underline{M}_2] \quad (3.57) \\
 &- (A_2 + A_5 + 1/\theta) [\underline{M}_2^*] + 2k_{pdb} [\underline{M}_1^*] [\underline{M}_1]
 \end{aligned}$$

Average molecular weights and polydispersity index can be simply calculated in terms of the zero, first and second moment of dead and living polymer with and without terminal double bond, according to Taylor and Riechert(1985), Lee and Mallinson(1988) as

$$M_w = (MW) * \left[\frac{([M_2] + [\underline{M}_2]) + ([M_2^*] + [\underline{M}_2^*])}{([M_1] + [\underline{M}_1]) + ([M_1^*] + [\underline{M}_1^*])} \right] \quad (3.58)$$

$$M_n = (MW) * \left[\frac{([M_1] + [\underline{M}_1]) + ([M_1^*] + [\underline{M}_1^*])}{([M_0] + [\underline{M}_0]) + ([M_0^*] + [\underline{M}_0^*])} \right] \quad (3.59)$$

$$PDI = M_w / M_n \quad (3.60)$$

All developed differential equations together with those of Chiang and Thompson's model will be solved numerically by fourth order Runge-Kutta method on IBM PC compatible 386 microcomputer. TURBO PASCAL Version 5.0 Language are used in computer programing.

3.3 The model restriction

All basic parameters are calculated from Chiang and Thompson's model which based on Kiparissides and Kiparissides et al. experimental and theorietical study, thus this work is related to those works too. Continuous stirred tank reactor and the reaction porcedure in this work are the same as those of Kiparissides and Kiparessides et al. Figure 3.2 shows the diagram of the system configuration of Kisparissides reaction system. Any of experimerntal data or experimental works to be fitted with this proposed model must have the same reaction proce- dures as those of Kisparissides et al.(1980).

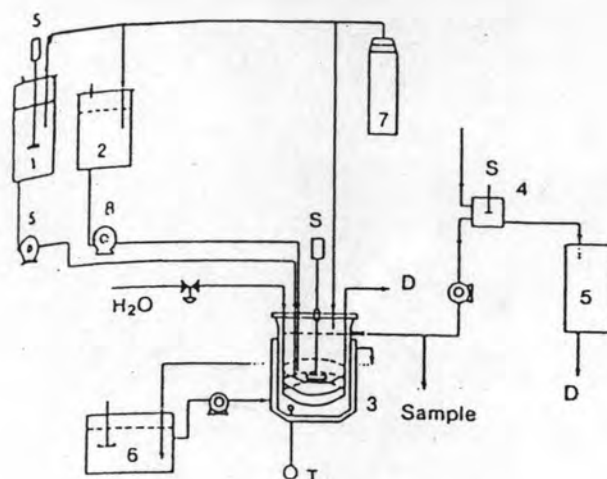


Figure 3.2 Schematic diagram for the reactor set-up in Kisparissides et al.(1980) experimental works.

- 1 Storage tank contains monomer, water and emulsifier and is stirred with a flat blade paddle.
- 2 Storage tank contains water and initiator.
- 3 2 L, jacketed glass kettle reactor with an overflow arm attached to its side to give a required volume.
- 4 Dilution vessel.
- 5 Spectrophotometer
- 6 Constant temperature bath
- 7 Nitrogen supply,
- 8 Constant flowrate pump
- D Drain
- S Stirrer

3.4 Reactor start up procedure.

To begin the reaction, both storages tanks are blanketed with nitrogen to reduce oxygen retardation. The reactants in both vessels and glass kettle reactor are bubble continuously with nitrogen throughout the reaction period. Two continuous feed streams are introduced separately with constant flow rate to the glass kettle reactor which was initially filled with distilled water. The reactants in reactor are stirred continuously with flat blade paddle stirrer.

The stainless steel cooling coil inside the reactor provides baffling to ensure proper mixing. The reactor temperature is maintained at 60 ± 2 °C. The polymer properties are continuously measured from the latex product. In Lee and Mallinson(1988) experimental work the effluence product is quenched by concentrated hydroquinone solution before examine its properties. The particle size is measured by Culter Model N4-SD laser light scattering system while molecular weights and molecular weight distribution are measured by gel permeation chromatography by Waters Associates model GPC1 apparatus with a differential refractometer and three 7.8 mm x 30 cm columns packed with ultrastyrigel having norminal size of $1 \cdot 10^3$, $1 \cdot 10^5$ and $1 \cdot 10^6$ Å. Tetrahydrofuran are used as the solvent in molecular weight measurement.

3.5 Recipe components

This vinyl acetate emulsion polymerization consists of the following reactants, according to Lee and Mallinson(1988)'s experiment.

- 1 Monomer is purified vinyl acetate, VAc. Monomer feed stream consists of 1.33 dm^3 vinyl acetate, 9.6 g SDS (for 0.01 mole/dm^3 emulsifer) and 2 dm^3 distilled water.
- 2 Dispersion medium is distilled water.
- 3 Initiator is potassium persulphate(PFS). Initiator feed stream consists of 1.35 dm^3 water and 9.12 g PFS(for 0.01 mole/dm^3 initiator).
- 4 Emulsifier is sodium dodecyl sulphate(SDS).
- 5 Nitrogen is used to reduce oxygen content in the mixture.
- 6 Quenching agent is concentrated hydroquinone solution.

To start up the reactor, the 1 dm^3 glass kettle reactor is initially filled with 294 cm^3 distilled water. The reactor temperature is maintained at the constant valus 60 ± 2 °C. By the above recipe component, the monomer to water ratio(VAc/Water) is 4/10 wt/wt.

3.6 Studying method.

This model is developed for predicting the average molecular weights of vinyl acetate polymer. Moment method is used for model development. This model considers the differences between terminal and non-terminal double bond species in the sense of reaction characteristics. Studying methods are shown below.

1 Develop balance equations of all reaction species, initiator, water phase radical, monomeric radical, dead polymer chain with and without terminal double and living polymer chain with and without terminal double bond.

2 Develop the model equations, which are differential equations of zero, first and second moment of dead polymer chains and living polymer chains with and without terminal double bond, from the infinite series of the balance equations.

3 Simultaneously solve the system differential equations which comprise of the equations from Chiang and Thompson's model and form the proposed model with respect to reaction time. The results are the moments of dead polymer and living polymer chain as time dependent function. Average molecular weight and polydispersity index are calculated from the obtained moments.

4 Compare the calculated results, conversion, average particle diameter and average molecular weights with the reported experimental data. In this study the compared experimental data are taken from Lee and Mallinson(1988) experimental work.

5 In this study, effects of emulsifier concentration, initiator concentration and resident time are considered. All studies are taken at 60 °C in continuous stirred tank reactor of Kiparissides (1980) configuration. The variation of the stated effect are

Initiator	0.01, 0.03, 0.05	mole/dm ³ .
Emulsifier	0.01, 0.03, 0.05	mole/dm ³ .
Mean residence time	20, 30, 40	minute

6 The computer program for the model calculation is developed for the microcomputer. TURBO PASCAL Version 5.0 is used in the developed program and fourth order Runge-Kutta method is used in numerical calculation.

All kinetic parameters in model calculation from various sources are shown in appendix D.

3.7 Summary of the model equations.

The following equations are the model equations which must be solved simultaneously with respect to reaction time. Equation 3.1 - 3.31 are the equations from Chiang and Thompson's model. Equation 3.32 - 3.60 are the equations from the proposed model. Average molecular weights and polydispersity index are defined in equation 3.58 - 3.60. Chiang and Thompson's model equations must be solved first because the proposed model use basic parameters from that model. This system differential equations are solved numerically by fourth order Runge-Kutta method.

$$f(t) = \rho(t) \left[\frac{k_v A_m(t) + u(1 - LA_p(t)/4)}{k_v A_m(t) + k_v \xi A_p + u(1 - LA_p(t)/4)} \right] \quad (3.16)$$

$$k_v = V_p(t)/(1 - V_p(t)) \quad (3.17)$$

$$A_m(t) = (S_F(1 - e^{-t/\theta}) - S_{cmc})S_d - A_p(t) \quad (3.18)$$

$$\rho(t) = 2fk_d[I]_{feed}(1 - e^{-t/\theta}) + \left[\frac{12TD\delta k_{fm}fk_d[I]_{feed}}{m_0 k_p} \right]^{1/2} \frac{N(t)}{A_p^{1/2}(t)} \quad (3.21)$$

$$\frac{dN(t)}{dt} = -\frac{N(t)}{\theta} + f(t) \quad (3.1)$$

$$\frac{dD(t)}{dt} = \frac{2\lambda\zeta(t)N(t)}{\theta} - \frac{D(t)}{\theta} + D_p(t,t)f(t) \quad (3.22)$$

$$\frac{dA_p(t)}{dt} = 4\pi\lambda\zeta(t)D(t) - \frac{A_p(t)}{\theta} + a_p(t,t)f(t) \quad (3.23)$$

$$\frac{dV_p(t)}{dt} = \lambda\zeta(t)A_p(t) - \frac{V_p(t)}{\theta} + v_p(t,t)f(t) \quad (3.24)$$

$$R(t) = \frac{1 - \phi(t)d_p\lambda\zeta(t)A_p(t)}{M_w} \quad (3.25)$$

$$\frac{dX(t)}{dt} = \frac{1}{(1 - e^{-t/\theta})} \left[\frac{R(t)}{M_F} - \frac{X(t)}{\theta} \right] \quad (3.28)$$

$$\phi(t)_{\text{sat}} = \frac{1 - X_c}{1 - X_c(1 - d_m/d_p)} \quad X < X_c \quad (3.29)$$

$$\phi(t) = \frac{1 - X}{1 - X(1 - d_m/d_p)} \quad X > X_c \quad (3.30)$$

$$[M_p] = \phi(t)d_m/MW \quad (3.31)$$

$$[I_w] = [I]_{\text{feed}}(1 - e^{-t/\theta}) \quad (3.35)$$

$$[R_w] = \frac{2fk_d[I_w] + k_{de}[P^*_{1,0}] + k_{de}[P^*_{\underline{1},0}]}{k_2[N_t] + k_1[M_s] + k_h} \quad (3.39)$$

$$[P^*_{1,0}] = \frac{A_9}{k_{de} + A_1 + A_5 + A_8 + 1/\theta} \quad (3.40)$$

$$[P^*_{\underline{1},0}] = \frac{A_{10}}{k_{de} + A_1 + A_5 + A_8 + 1/\theta} \quad (3.41)$$

$$d[M_0]/dt = (A_2 + A_6)[M^*_0] - (A_3 + 1/\theta)[M_0] \quad (3.46)$$

$$d[M_1]/dt = (A_2 + A_5)[M_1^*] - (A_3 + 1/\theta)[M_1] \quad (3.47)$$

$$d[M_2]/dt = (A_2 + A_5)[M_2^*] - (A_3 + 1/\theta)[M_2] \quad (3.48)$$

$$d[M_0]/dt = (A_2 + A_5)[M_0^*] - (A_3 + A_4 + 1/\theta)[M_0] + (A_6)[M_0^*] \quad (3.49)$$

$$d[M_1]/dt = (A_2 + A_5)[M_1^*] - (A_3 + A_4 + 1/\theta)[M_1] + (A_6)[M_1^*] \quad (3.50)$$

$$d[M_2]/dt = (A_2 + A_5)[M_2^*] - (A_3 + A_4 + 1/\theta)[M_2] + (A_6)[M_2^*] \quad (3.51)$$

$$d[M_0^*]/dt = A_1[P_{1,0}^*] + A_3[M_0] - (A_2 + A_5 + 1/\theta)[M_0^*] \quad (3.52)$$

$$d[M_1^*]/dt = A_1([P_{1,0}^*] + [M_0^*]) + A_3[M_1] - (A_2 + A_5 + 1/\theta)[M_1^*] + A_7[M_1] \quad (3.53)$$

$$d[M_2^*]/dt = A_1([P_{1,0}^*] + 2[M_1^*] + [M_0^*]) + A_3[M_2] - (A_2 + A_5 + 1/\theta)[M_2^*] + 2k_{pdb}[M_1^*][M_1] + A_7[M_2] \quad (3.54)$$

$$d[M_0^*]/dt = A_1[P_{1,0}^*] + (A_3)[M_0] - (A_2 + A_5 + 1/\theta)[M_0^*] \quad (3.55)$$

$$d[M_1^*]/dt = A_1([P_{1,0}^*] + [M_0^*]) + (A_3 + A_7)[M_1] - (A_2 + A_5 + 1/\theta)[M_1^*] \quad (3.56)$$

$$d[M_2^*]/dt = A_1([P_{1,0}^*] + 2[M_1^*] + [M_0^*]) + (A_3 + A_7)[M_2] - (A_2 + A_5 + 1/\theta)[M_2^*] + 2k_{pdb}[M_1^*][M_1] \quad (3.57)$$

$$M_w = (MW) * \left[\frac{([M_2] + [M_2^*]) + ([M_2^*] + [M_2^*])}{([M_1] + [M_1^*]) + ([M_1^*] + [M_1^*])} \right] \quad (3.58)$$

$$M_n = (MW) * \left[\frac{([M_1] + [M_1^*]) + ([M_1^*] + [M_1^*])}{([M_0] + [M_0^*]) + ([M_0^*] + [M_0^*])} \right] \quad (3.59)$$

$$PDI = M_w/M_n \quad (3.60)$$