

CHAPTER 4

RESULT AND DISCUSSION

In the model simulations effect of three parameters, emulsifier concentration, initiator concentration and mean residence time, are considered. The model equations shown above are solved numerically on IBM PC compatible microcomputer with mathcoprocessor by fourth order Runge-Kutta method, half an hour is used for each run. The effect of each stated parameter will be shown separately. The shown simulations are in the range of 0 - 12 mean residence time. The graphical results of the simulation are shown in appendix E.

The simulation results of conversion, particle diameter, average molecular weights, of 0.01 mole/dm^3 initiator concentration with 0.01, 0.03, 0.05 mole/dm^3 emulsifier concentrations and 30 minute mean residence time will be compared with Lee and Mallinson's experiment.

One of the most important aspects in mathematical modeling is a suitable rate parameters. Appendix D shown rate parameters determined by various researchers and those used in work. In the model calculation a set of rate parameters were selected from the available literatures and simulations that give the best result for conversion and average molecular weight. As illustrate in Appendix D a wide range of rate parameters has been reported in literatures for vinyl acetate polymerization at 60°C . These variations are due to somewhat different in operating conditions.

Kinetic parameters shown in Appendix D are modified kinetic parameters for Chiang and Thompson's model. All units used in this model are based on unit volume of emulsion, according to Kiparissided(1980).

4.1 Effect of emulsifier concentration.

Three concentrations of emulsifier, 0.01, 0.03 and 0.05 mole/dm³ with 0.01 mole/dm³ initiator concentration and 30 minute mean residence time are considered. Effect of emulsifier concentrations on polymer properties are presented.

Figure 4.1 - 4.6 show the results of Chiang and Thompson's differential equations for conversion and average particle diameter using the stated parameters. The simulation results at 60 °C for three emulsifier concentration are compared with Lee and Mallinson's work. The model predictions of conversion agree very well with the experimental data at low emulsifier concentration, 0.01 and 0.03 mole/dm³, figure 4.1 and 4.2, but underestimate the experimental conversion at high emulsifier concentration, 0.05 mole/dm³, figure 4.3. At high emulsifier concentrations simulation results of conversion are lower than that of experiments may be due to the assumption that particle surface are completely cover by emulsifier molecule thus there are lesser free emulsifier concentration to generate the polymer particles. But in the actual situation particle surface should not be completely covered by emulsifier molecule then higher free emulsifier concentration exist in the actual system and more particles are generated. High numbers of polymer particles give rise in reaction rate and conversion, thus the observed conversions are higher than the simulated conversion at high emulsifier concentration.

Figure 4.4 - 4.6 show the comparison between Lee and Mallinson's experimental results for particle size and the simulations. At emulsifier concentration of 0.01 mole/dm³, figure 4.4, the agreement is reasonable although the reduction in particle size at the second generation of particles, the experimental results are less compared to those of model. Figure 4.5 shows that the agreement at high emulsifier concentration is poor. At higher emulsifier concentration, 0.05 mole/dm³, figure 4.6, the results are like those in figure 4.5, the model result are less than those of experiment.

Figure 4.4 - 4.6 show that the simulation results agree with the experimental results at the first generation of particles. Those astonishing phenomena can be explained by the two following cases. Firstly, according to Edelhauser(1969), sodium dodecyl sulfate, which has a relatively short carbon chain length, tends to penetrate into the interior of the poly(vinyl acetate) particle, causing swelling and gradual dissolution of polymer chain by generating of solubilized polymeric complexes in the manner of polyelectrolyte. However, this disintegration of polymers chains leads only to limited swelling of the particles. The reason for this is that formation of poly(vinyl alcohol) layer by hydrolysis of poly(vinyl acetate) around the particle inhibit the swelling. The interaction between emulsifier and polymer chain is not considered in the theoretical model. Secondly, according to Kiparissides et al.(1980), they suggested that in the hetero-dispersed system, small particles may preferentially flocculate with large particles. Bierman(1955) extended the theory of coalescence to non-identical particles and showed that colloids which are most different in size will have the greatest chance of coalescence, quote from Kiparissides et al. At t/τ of 4.0 and t/τ of 3.0, for 0.03 and 0.05 mole/dm³ of emulsifier concentration respectively, are the time when the second generation of particles are generated, then there are two types of particle in the reactor, one is the remaining first generation, the other is the newly generated second generation. Thus, heterogenous particle sizes are generated and flocculation of old and new particle is occurred. This phenomenon gives rise in the observed particle size. Also, in some cases laser light scattering is known to undercount or ignore particles in smallest range, and this could be a contributing cause to discrepancy in simulated and experimental results.

However, the average particle size from the experiments and from the simulation agree very well at low emulsifier concentration and show no sensitivity of the emulsifier concentration in this range. This model has been shown to provide satisfactory results for modeling transient continuous stirred tank behavior of conversion. It is diffi-

cult to estimate the effect of uncertainty of parameters in such a complex model without extensive efforts in that direction.

Figure 4.7 - 4.9, the comparisons between Lee and Mallinson's experimental and simulated results and the model results. Figure 4.7 shows the result of the experiment and simulation of this system at emulsifier concentration of 0.01 mole/dm^3 , the observed weight average molecular weight and polydispersity index are around 0.78×10^6 and 4.3 respectively. When maximum average particle sizes are observed at the t/τ of 8 in figure 4.4 approximately minimum average molecular weight are observed. From a kinetic point of view, smaller particle size and higher particle number give higher molecular weight due to long propagation time. It can be seen that only the simulated weight average molecular weight agree very well with the experimental data but the calculated number average molecular weight is higher than that of experiment. The calculated weight average molecular weight show the oscillation that comparable to that of experiment. Polydispersity index from the simulations are in the range 2-3. Due to high value of calculated number average molecular weight, calculated polydispersity index are lower those that of experimental results.

Figure 4.8 shows average molecular weight at 0.03 mole/dm^3 emulsifier concentration. Observed weight average molecular weight and polydispersity index are 0.9×10^6 and 4.4 respectively. The simulated weight average molecular weight agree very well with the experimental result but do not shows oscillation. Number average molecular weight stills higher than that of experiment.

Like the results at 0.01 and 0.03 mole/dm^3 of emulsifier concentration, the calculated weight average molecular weight at 0.05 mole/dm^3 , figure 4.9, agrees very well with experimental result and number average molecular weight stills higher than the experiment. At this emulsifier concentration, the observed weight average molecular weight and polydispersity index are 1.2×10^3 and 7.8 respectively.

Theoretically, higher emulsifier concentrations result in smaller average particle sizes and smaller particle sizes give higher

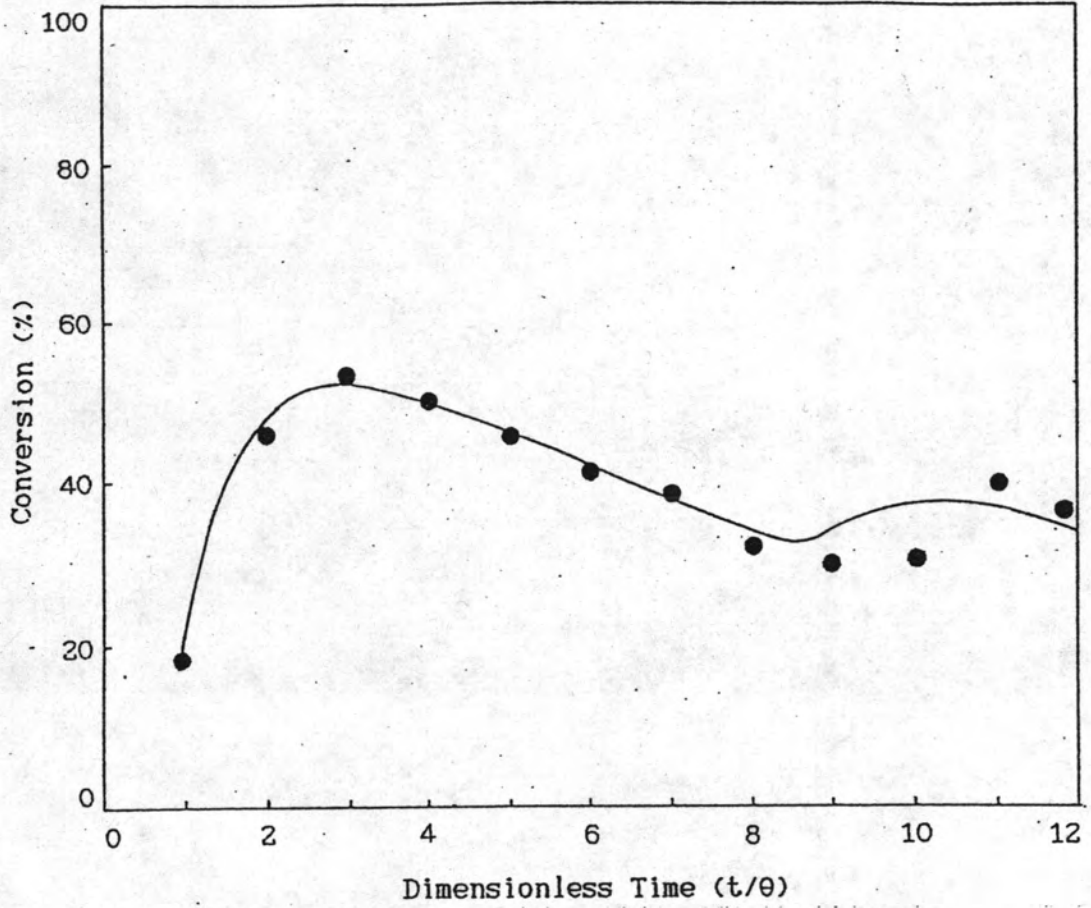


Figure 4.1 Comparison between experimental result and model result of conversion.

$T = 60\text{ }^{\circ}\text{C}$, $\theta = 30\text{ min}$, $V_{\text{Ac}}/V_{\text{Water}} = 4/10$, $[I] = 0.01\text{ mol/dm}^3$
 $[S] = 0.01\text{ mol/dm}^3$, ● Exp, — Model.

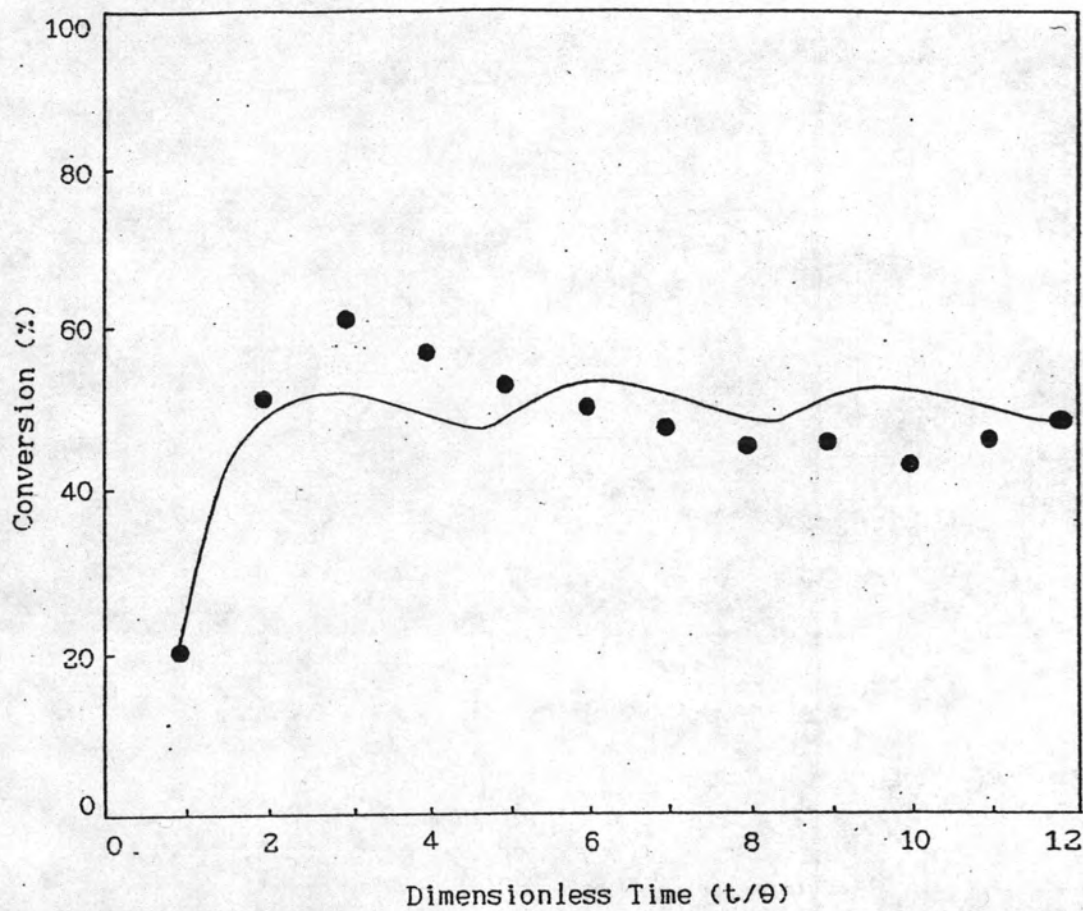


Figure 4.2 Comparison between experimental result and model result of conversion.

$T = 60\text{ }^{\circ}\text{C}$, $\theta = 30\text{ min}$, $V_{\text{Ac}}/V_{\text{Water}} = 4/10$, $[I] = 0.01\text{ mol/dm}^3$
 $[S] = 0.03\text{ mol/dm}^3$, ● Exp, — Model.

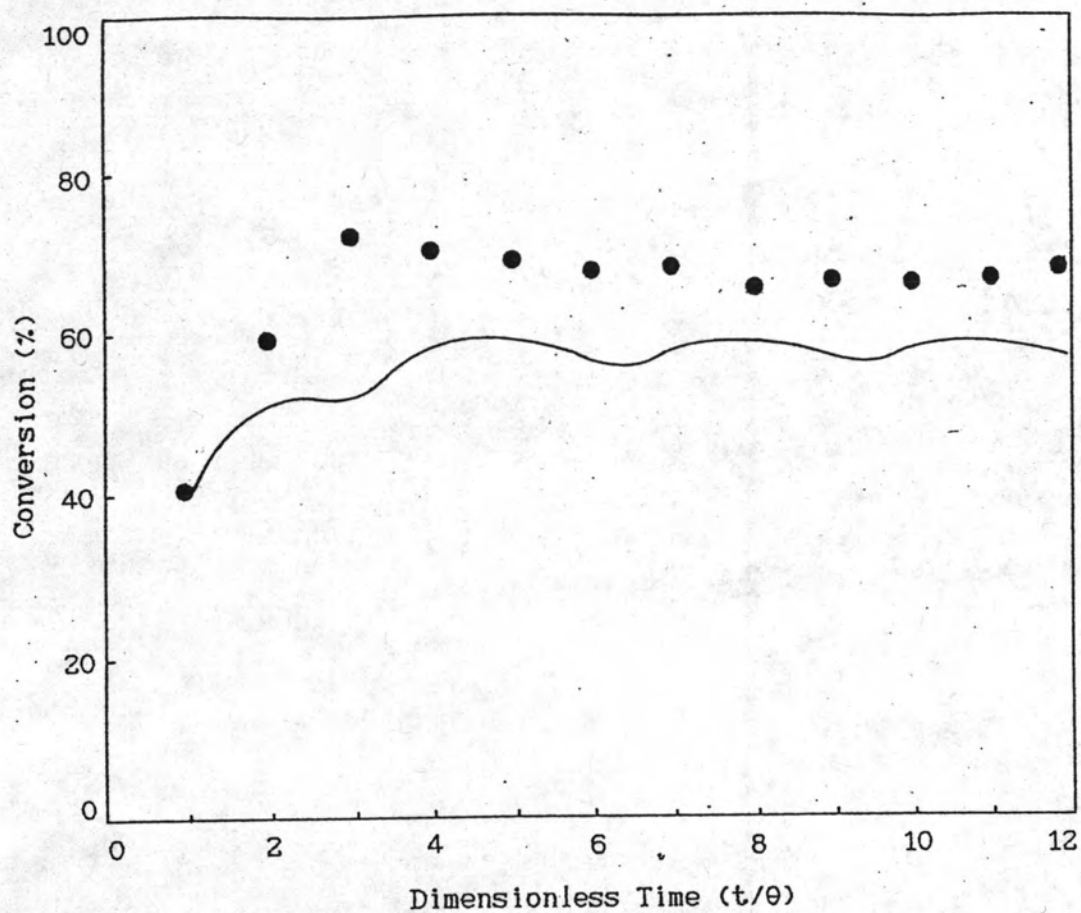


Figure 4.3 Comparison between experimental result and model result of conversion.

$T = 60\text{ }^{\circ}\text{C}$, $\theta = 30\text{ min}$, $V_{\text{Ac}}/V_{\text{Water}} = 4/10$, $[I] = 0.01\text{ mol/dm}^3$
 $[S] = 0.05\text{ mol/dm}^3$, ● Exp, — Model.

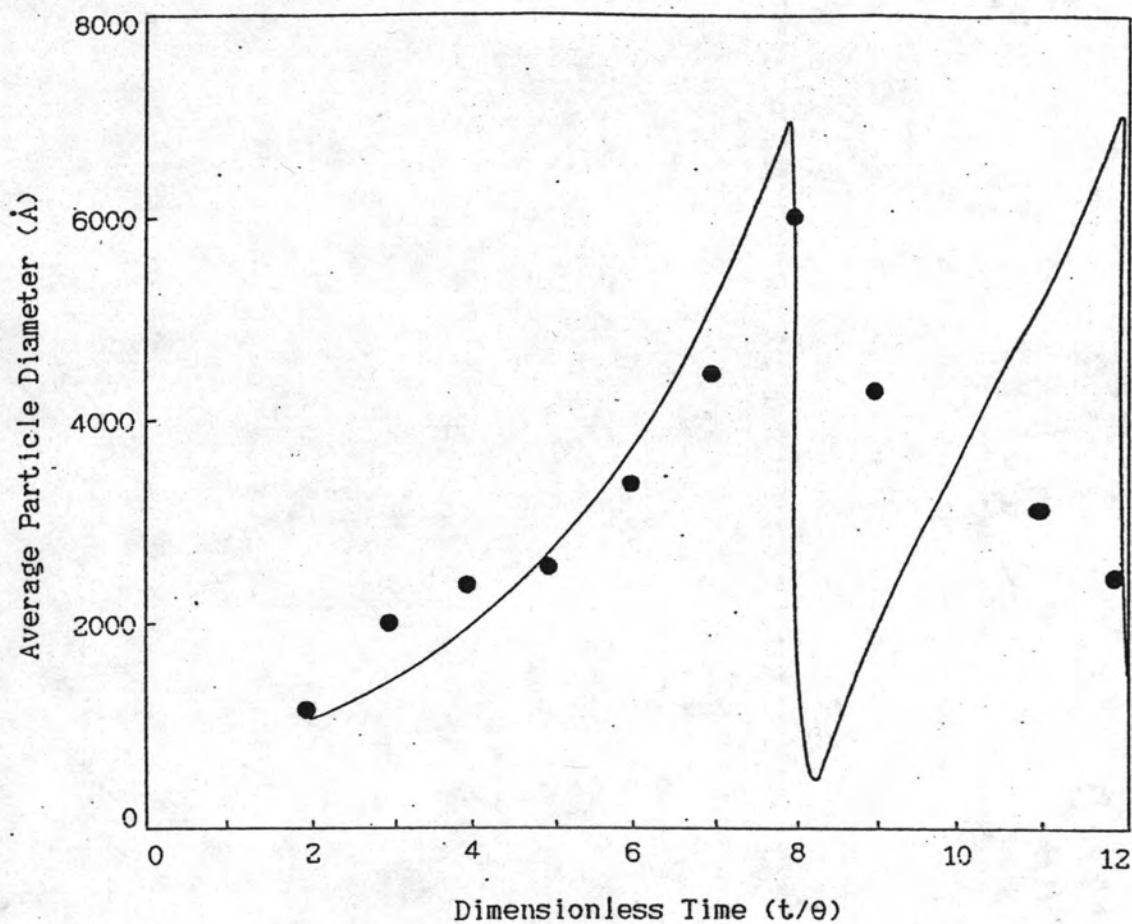


Figure 4.4 The comparison between experimental result and model result of average particle diameter.

$T = 60^\circ\text{C}$, $\theta = 30\text{ min}$, $V_{\text{Ac}}/V_{\text{Water}} = 4/10$, $[I] = 0.01\text{ mole/dm}^3$
 $[S] = 0.01\text{ mole/dm}^3$, ● Exp. — Model.

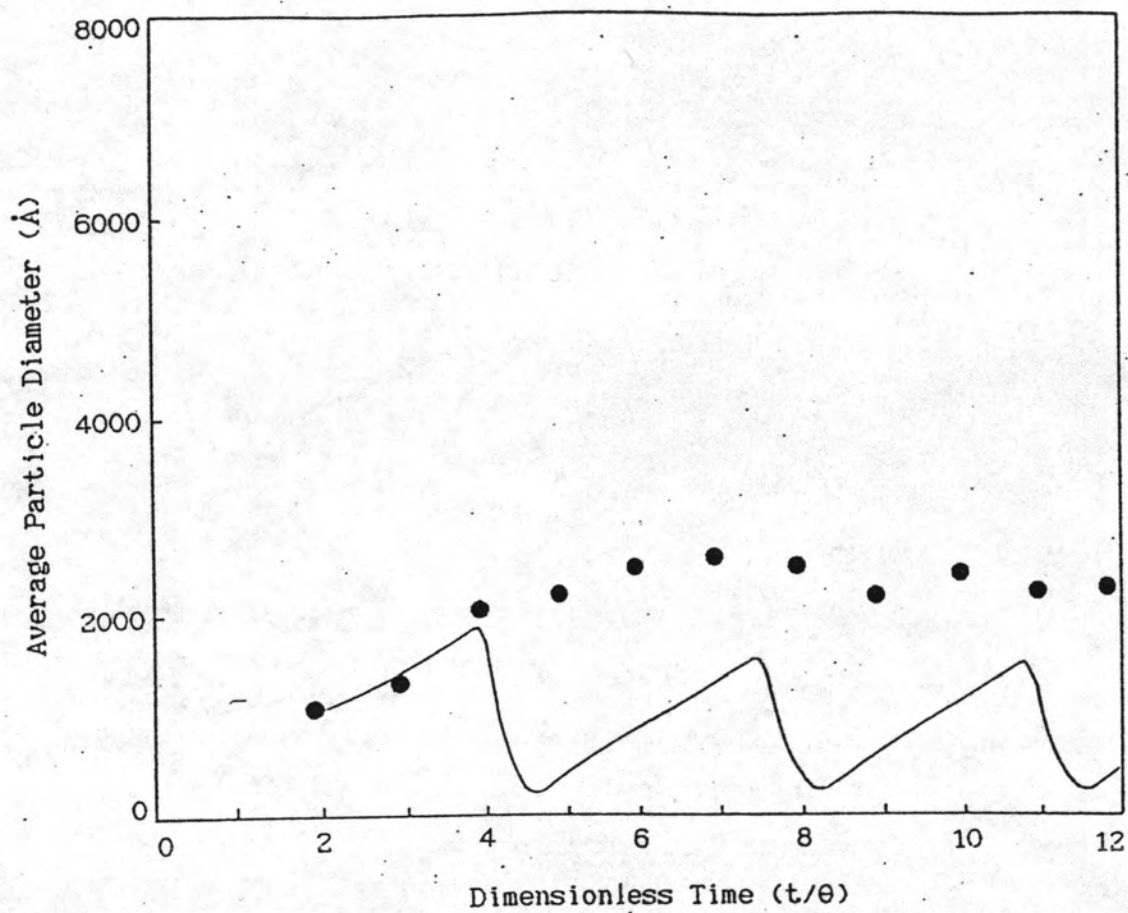


Figure 4.5 The comparison between experimental result and model result of average particle diameter.

$T = 60^\circ\text{C}$, $\theta = 30$ min, $V_{\text{Ac}}/\text{Water} = 4/10$, $[I] = 0.01$ mole/dm³
 $[S] = 0.03$ mole/dm³, ● Exp, — Model.

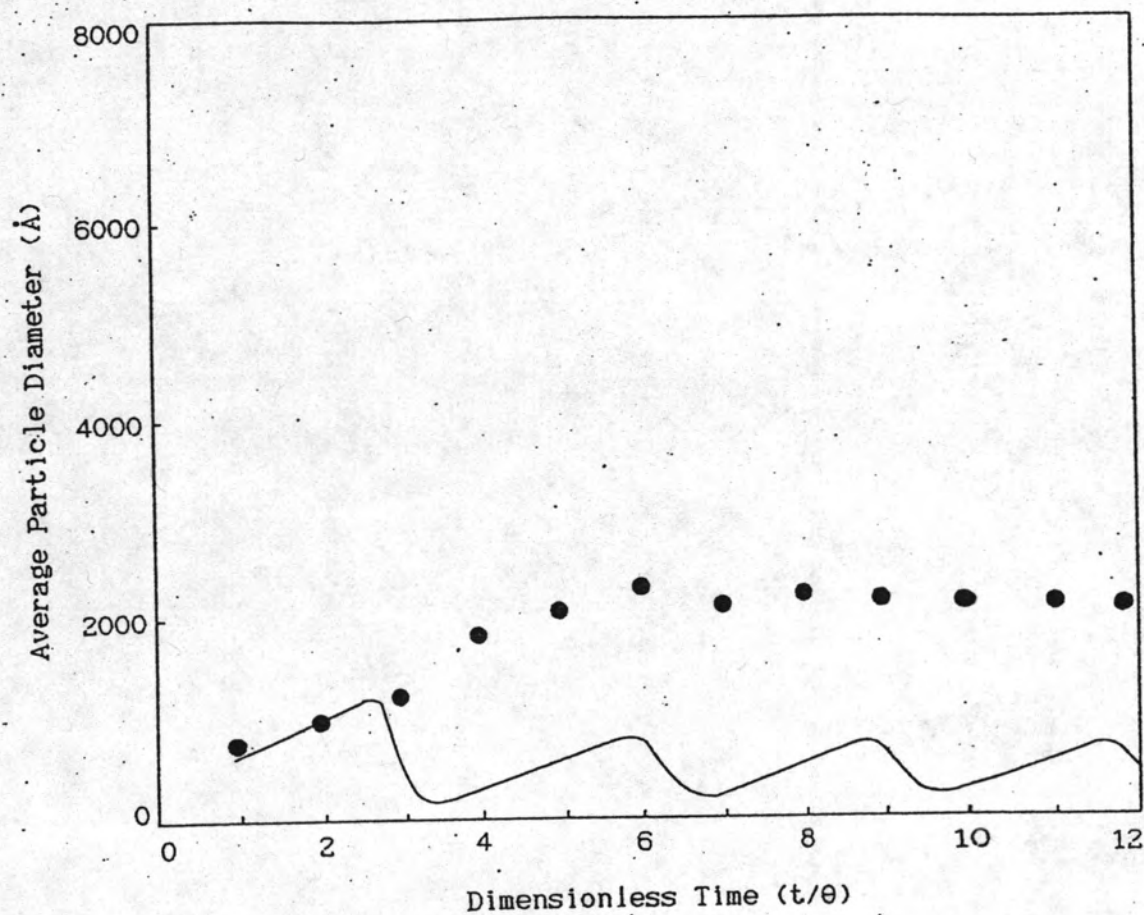


Figure 4.6 The comparison between experimental result and model result of average particle diameter.

$T = 60\text{ }^{\circ}\text{C}$, $\theta = 30\text{ min}$, $V_{\text{Ac}}/V_{\text{Water}} = 4/10$, $[I] = 0.01\text{ mole/dm}^3$
 $[S] = 0.05\text{ mole/dm}^3$, ● Exp. — Model.

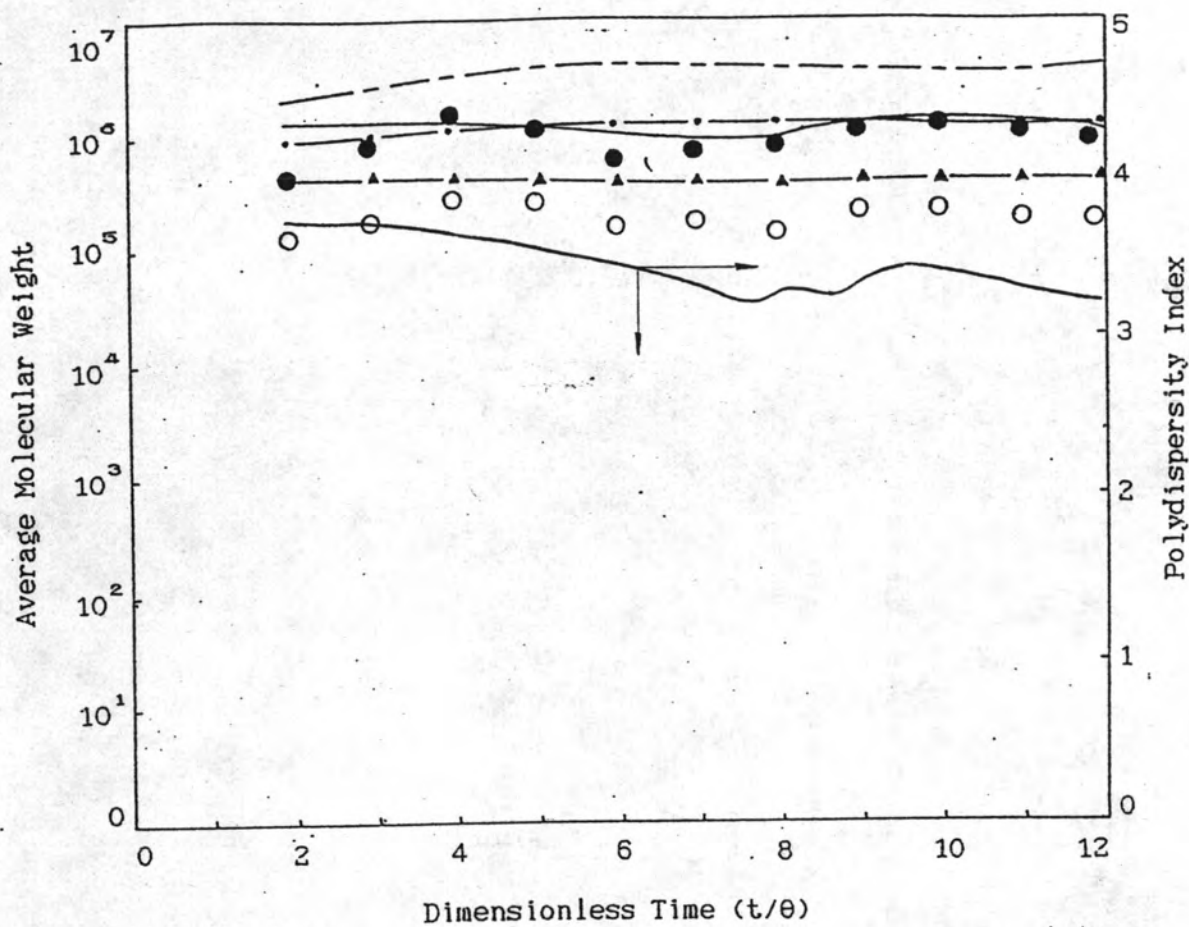


Figure 4.7 Comparison between experimental result and model result of average molecular weight.

$T = 60\text{ }^{\circ}\text{C}$, $\theta = 30\text{ min}$, $\text{Vac/Water} = 4/10$, $[\text{I}] = 0.01\text{ mol/dm}^3$

$[\text{S}] = 0.01\text{ mol/dm}^3$, $\circ M_n, \text{Exp}$, $\bullet M_w, \text{Exp}$,

--- $M_n, \text{Lee's Model}$, --- $M_w, \text{Lee's Model}$,

— \triangle — $M_n, \text{Proposed Model}$, — \bullet — $M_w, \text{Proposed Model}$.

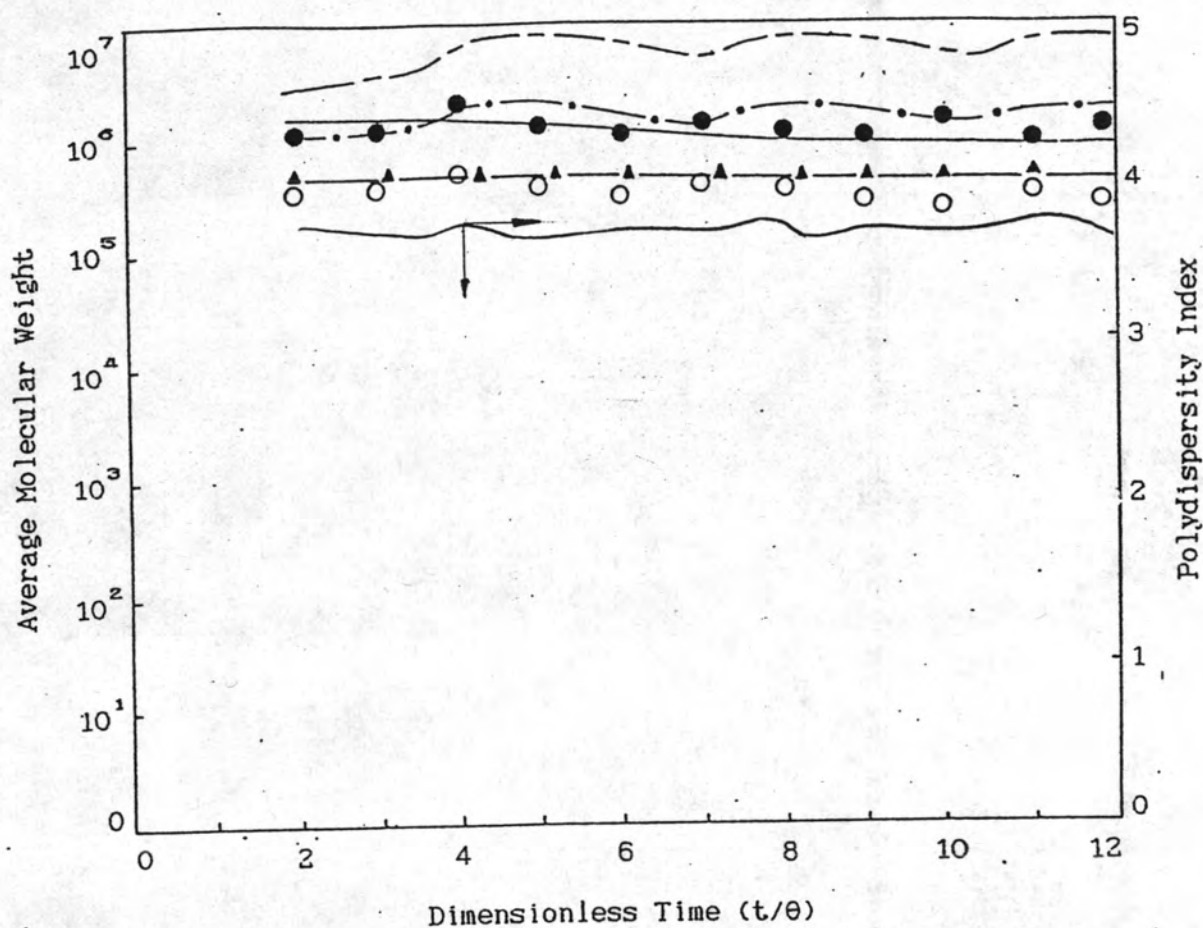


Figure 4.8 Comparison between experimental result and model result of average molecular weight.

$T = 60\text{ }^{\circ}\text{C}$, $\theta = 30\text{ min}$, $V_{Ac}/Water = 4/10$, $[I] = 0.01\text{ mol/dm}^3$

$[S] = 0.03\text{ mol/dm}^3$, $\circ M_n, \text{Exp}$, $\bullet M_w, \text{Exp}$,

—•— $M_n, \text{Lee's Model}$, ——— $M_w, \text{Lee's Model}$,

—▲— $M_n, \text{Proposed Model}$, ——— $M_w, \text{Proposed Model}$.

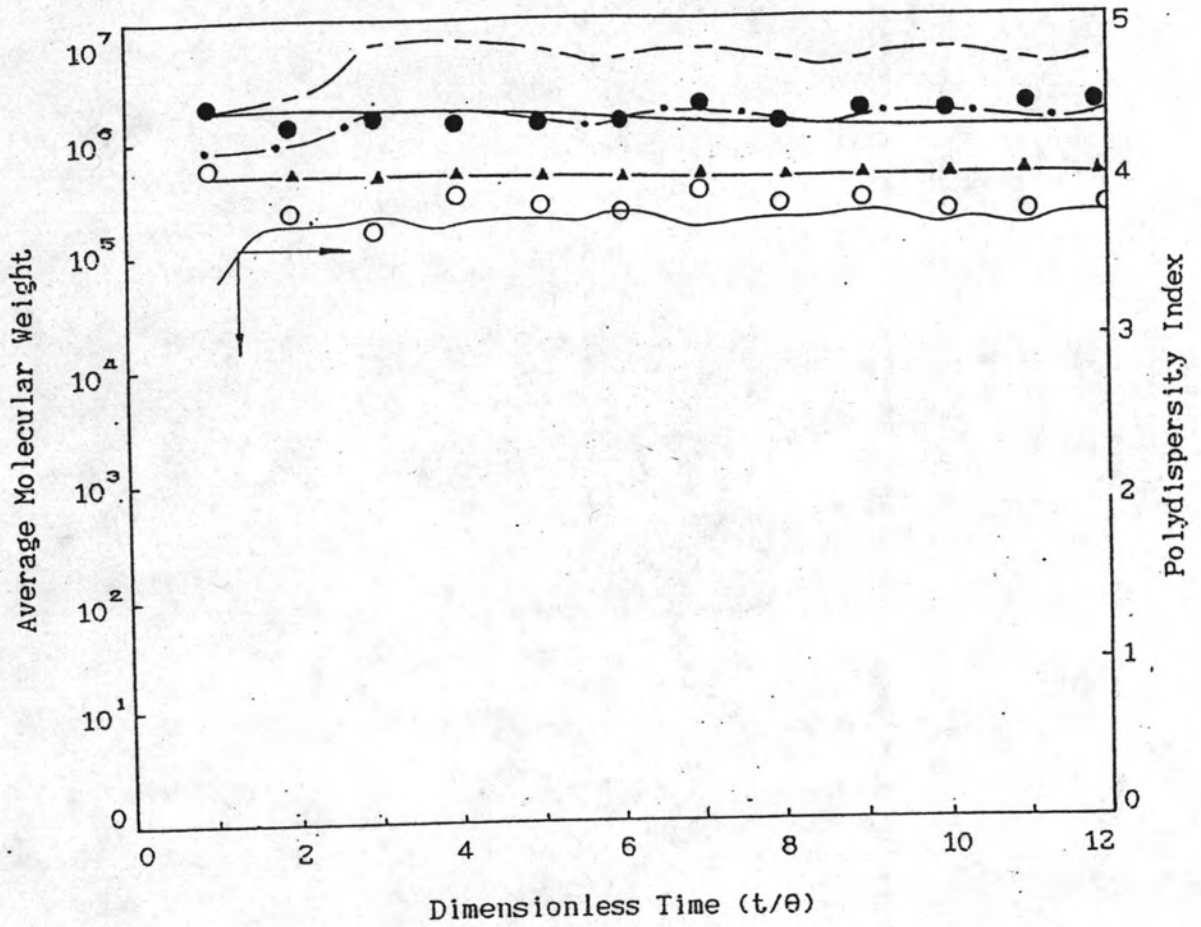


Figure 4.9 Comparison between experimental result and model result of average molecular weight.

$T = 60\text{ }^{\circ}\text{C}$, $\theta = 30\text{ min}$, $\text{Vac/Water} = 4/10$, $[\text{I}] = 0.01\text{ mol/dm}^3$

$[\text{S}] = 0.05\text{ mol/dm}^3$, \circ $M_n, \text{Exp.}$ \bullet $M_w, \text{Exp.}$

--- $M_n, \text{Lee's Model}$, --- $M_w, \text{Lee's Model}$,

—▲— $M_n, \text{Proposed Model}$, —●— $M_w, \text{Proposed Model}$.

molecular weight. According to the experimental results, the increase in emulsifier concentration increase polydispersity index.

Friis and Hamielec(1975) suggested that transfer to dead polymer lead to branching and cause a shift to higher molecular weight. Transfer to polymer does not change the total numbers of polymer molecule and therefore number average molecular weight is unaffected but weight average molecular weight is increased. Terminal double bond reaction reduce numbers of dead polymer molecules and increase both number and weight average molecular weight.

Figure 4.7 - 4.9 show that the proposed model give better agreement to experimental results than that of Lee and Mallinson's model. This is due to the fact that the proposed model determines the difference between terminal and non-terminal double bond species and treats them separately. According to Lee and Mallinson(1988), they mentioned that the neglecting in the difference of terminal and non-terminal double bond tends to over emphasize the terminal double bond reaction and give rise in simulated polymer molecular weights. In addition, Lee and Mallinson assumed that all radicals can diffuse out of particle, then there is small number of radicals in the particle and give rise in polymer molecular weights. Lee and Mallinson's model always give high simulated average molecular weights. Due to both stated different assumptions, the proposed model should gives better simulation results than those of Lee and Mallinson's model.

Figure E1 - E3 show the simulated effect of emulsifier concentration on polymer properties.

Figure E1, E2 and E3 show that the total number of polymer particles, the total particle surface area and conversion increase with emulsifier concentration.

Figure E4 shows the calculated average number of radicals per particle from Normura's model. The figure shows that average number of radicals per particle is decrease with increasing in emulsifier concentrations.

Figure E5 shows the free emulsifier concentrations during the reaction period, higher emulsifier concentrations give higher free emulsifier concentration. The figure shows that the first generation of particles are produced exclusively by homogeneous nucleation, because there is no free emulsifier concentration at the beginning of the reaction period. Figure E5 contribute to figure E1 that higher free emulsifier concentration give higher generated number of polymer particles.

Figure E6 shows rate of reaction which increase with emulsifier concentration. Higher emulsifier concentration give rise in number of polymer particles and particle surface area, then rate of reaction is increased.

Figure E7 shows that monomer concentration in particle decrease with increasing in emulsifier concentration. Higher emulsifier concentrations give higher rate of reaction, then decrease monomer concentration in polymer particle.

Figure E8 shows that average molecular weights increase slightly when emulsifier concentration is increased. As mention in the theoretical aspects, an increase in emulsifier concentration increase the mean polymerizing lifetime of radical then high molecular weight is obtained. The figure shows that the proposed model has less sensitivity to the change in emulsifier concentration.

Figure E1 - E7 show that increasing in emulsifier concentration increase both frequency and magnitude of oscillation.

4.2 Effect of initiator concentration.

Three concentrations of initiator, 0.01, 0.03 and 0.05 mole/dm³, with 0.01 mole/dm³ emulsifier concentration and 30 minute mean residence time are considered.

Figure E9 - E11 show that changing in initiator concentration have no effects on number of polymer particles, total particle surface area and average particle diameter. This is due to initiator has no role in particle generation process.

Figure E12 - E13 show that conversion and rate of reaction increase with initiator concentration. The increasing in initiator concentration leads to an increase in water phase radical concentration then average number of free radicals per particle is increased, thus rate of reaction and conversion are also increased.

Figure E14 shows monomer concentration in particle during the reaction period which decrease with increasing in initiator concentration. This is due to the rising in rate of reaction and conversion at high initiator concentration.

Figure E15 shows simulated results of average molecular weight which decrease with increasing in initiator concentration. This is due to the fact that high initiator concentration produces high water phase radical, thus mean polymerizing life time is decreased, then average molecular weights are decreased.

Figure E9 - E14 show that increasing in initiator concentration has no effect on the oscillation frequency but increase the magnitude of oscillation of conversion, rate of reaction, monomer concentration in particle. This is due to initiator has no effect on particle generation process but increase the rate of reaction.

4.3 Effect of mean residence time.

Three mean residence time, 20, 30 and 40 minute, with 0.01 mole/dm^3 emulsifier concentration and 0.01 mole/dm^3 initiator concentration are considered.

Figure E16 shows that number of polymer particles of the first generation of different mean residence time are the same but decrease with different rate. Mean residence time of 20 minute has the fastest decreasing rate due to its highest wash out rate thus it has the most frequent oscillation.

Figure E17 and E18 show the total particle surface area and average particle diameter which decrease in oscillating frequency with increasing in mean residence time due to low mean residence time gives high wash out rate.

Figure E19 shows conversions which increase with mean residence time. This is due to the fact that high mean residence time provides long polymerizing lifetime for radicals.

Figure E20 shows rate of reactions which decrease with increasing in mean residence time.

Figure E21 shows monomer concentrations in polymer particle which decrease with increasing in mean residence time. This is due to high mean residence time give high polymerizing lifetime thus the reaction consumes more monomer than the lower one.

Figure 22 shows average molecular weight. The significant differences of the average molecular weights due to the effects of mean residence time can not be determined during the reaction period because the reactions are in the transient states, but their trends show that higher mean residence time gives higher average molecular weight.

Figure E16 - E21 show that the increase in mean residence time provide decreasing in oscillating frequency but have no effect on the magnitude of oscillation. This is due to higher mean residence time gives lower wash out rate but it has no effect on particle generation process. Thus low and high mean residence time give the same number of particles and the same maximum peaks are generated.

Kisparissides et al.(1980) and Rawling and Ray(1987) suggested that the oscillation in transient state of continuous emulsion polymerization is due to the following mechanisms.

- 1 Particles are initiated by radicals enter into micelles.
- 2 The particles polymerize and grow, requiring more free emulsifier to stabilize their increased surface area. Eventually all the free emulsifier is adsorbed on the particle surface and there are no micelles. Particle initiation then ceases.
3. The large particles eventually wash out of the reactor and micelles reappear due to the emulsifier entering in the feed. The process then repeats itself indefinitely.

Frequency of oscillation depends on the feed rate of emulsifier, the wash out rate and the growth rate of polymer particles.

The oscillation behavior in a single continuous stirred tank reactor can be stopped, according to Kisparsissied et al.(1980), Framojaney(1982) and Rawling and Ray(1987), (i) by using an excessive quantity of emulsifier to promote continuous generation of particles and/or (ii) by feeding continuous stirred tank reactor with a seeded latex or an exit stream of a tubular pre-reactor. The former leads to large number of particles with small size.

4.4 Comparison between Lee and Mallinson's model and the proposed model.

Although both models are develops in the same way, the proposed model has some advantages over Lee and Mallinson's model. The comprehensive comparisons between both models are shown in table 4.1.

Lee and Mallinson(1988) treated teminal and non-terminal double bond as the same specie but the proposed model treated them separatedly. Thus, it can be said that the proposed model provides better representation to the actual situation than Lee and Mallinson's model.

Although the value of the propagation and transfer rate have strong effect on the molecular weights, they do not effect the polydispersity index as the terminal double bond reaction does. Generally, the monomeric radical concentration in particle is very small and variation of this value create large deviation in the moments and cause the deviation in average molecular weights and polydispersity index. Lee and Mallinson stated that the oscillation in average molecular weights and polydispersity index are due to the varaition in the total radical concentration in particle. In the proposed model, the model for radical desorption of Nomura et al.(1981) is used. Chern and Poehlein(1987) developed a model for radical desorption rate constant by taking the nonuniform radical distribution in praticle into consideration. Inorder to achive the simulation result, a systematic analysis would be advantageous to determine the most appropriate parameter values.

Table 4.1 Comparison between Lee and Mallinson's model and the proposed model.

The proposed model	Lee and Mallinson's model
<p>The differences of terminal and non-terminal double bond species in the kinetic point of view are taken into consideration and are treated separately.</p>	<p>The differences of terminal and non-terminal double bond species are neglected, which lead to over emphasize in the terminal double bond reaction then high calculated molecular weight are obtained.</p>
<p>Only monomeric radicals can desorbed from the particles due to high viscosity in the particle and low solubility in the water phase of long chain polymeric radicals, suggested by Nomura et al.(1981) and Rawling and Ray (1987). The proposed model use Nomura et al.'s model for average number of radical per particle to calculate that property although they stated that average number of radicals per particle calculated from their model is some what lower than the actual system but it gives good agreement to the experimental data.</p>	<p>They suggested that all radical can desorb from the particle, which lead to the period that monomeric radical concentration in particle equals to zero. This phenomena does not occur in the actual system because monomeric radical is produced by adsorbed water phase radical and transfer to monomer reaction. During the reaction period, water phase radical and monomer concentration in particle exist then monomeric radical will never be equaled to zero. Due to this assumption, very low value of monomeric radical will lead to high simulated value of average molecular weight.</p>
<p>Determine the effect of branching points.</p>	<p>Do not determine the effect of branching points.</p>

4.5 Summary

According to above discussions, some trends of the stated effects are noted below.

1 The increasing in emulsifier concentration increases the frequency and magnitude of oscillation.

2 The increasing in initiator concentration increases the magnitude of oscillation but has no effect on oscillating frequency.

3 The increasing in mean residence time decreases the oscillating frequency but the magnitude of oscillation is unaffected.

4 High polydispersity index and low number average molecular weight values of the experiment are produced by the solubilized sodium dodecyl sulphate which give rise in polymer disintegration.

5 High observed particle size is due to the swelling of solubilized sodium dodecyl sulphate and the flocculation of hetero-disperse particle size.

6. Transfer to dead polymer and terminal double bond reaction are the major reaction that control polydispersity index.

The experience from the model simulation show that the system is quite sensitive to variation in parameters. The predictive utility of this model will be much greater when values of the constants are known for various emulsion polymerization system.

4.6 Conclusion

Mathematical model to predict molecular weights of poly-(vinyl acetate) from continuous stirred tank reactor has been developed by moment method. Special consideration has been given on the differences between terminal and non-terminal double bond species, the effect of branching points, initiation and termination mechanism. The molecular weight oscillation, which are often observed in continuous emulsion polymerization, are associated with a heterogeneous initiation mechanism that involve radical adsorption and desorption processes.

The model provides the correct trend for the corresponding experimental data. However, it fails to account for the prediction of number average molecular weight. The appropriate parameters would be accompanied by sensitive study.

4.7 Recommendation for the further study.

Due to the comparison experimental data and the model results, some additional works and suggestions for further studies are

- 1 Run experiments with other types of emulsifier to determine the effect of solubilized emulsifier.
- 2 Try to fit this model with other systems of emulsion polymerization.
- 3 Try to develop the model of emulsion copolymerization.
- 4 Run an extensive experiment and develop the extensive model to predict the effect of other parameters such as agitation rate, impurities.

NOTATION

$A_m, A_m(t)$	total micelle surface area, dm^2/dm^3
$A_n(t, t)dt$	total surface area of a $n(t, t)dt$ type particles, dm^2/dm^3
$A_p, A_p(t)$	total surface area of polymer particles, dm^2/dm^3
a	interfacial surface area of a polymer particle, dm^2
$a_p(t, t)$	surface area of a $n(t, t)dt$ type particles, dm^2
$a_p(t, t)$	surface area of a micelle, dm^2
a_s	specific surface per unit of micelle
C_w	radical concentration in water phase, mole/dm^3
$D(t)$	total polymer particle diameter, dm/dm^3
$D_p(t)$	diameter of a $n(t, t)dt$ type particles, dm
$D_p(t, t)$	micelle size, dm
D_w	diffusion coefficient of radical in water, dm^2/s
D_p	diffusion coefficient of radical in particle, dm^2/s
d_m	density of monomer, g/dm^3
d_p	density polymer, g/dm^3
F	reactant feed rate
f	initiator decomposition efficiency
fk_d	effective initiator decomposition rate constant, $1/\text{s}$
$f(t)$	particle nucleation rate, $\text{particles}/\text{dm}^3 \cdot \text{s}$
$[I]_{\text{feed}}$	initiator concentration in feed, mole/dm^3
k_0	coefficient for radical enter into particle, dm/s
k_1	radical adsorption rate constant to micelle, dm^3/s
k_2	radical adsorption rate constant to particle, dm^3/s
k_d	rate coefficient of initiator decomposition, s^{-1}
k_{de}	free radical desorption rate constant, s^{-1}
k_{fm}	rate coefficient of chain transfer to monomer, $\text{dm}^3/\text{mole} \cdot \text{s}$
k_{fp}	rate coefficient of chain transfer to polymer, $\text{dm}^3/\text{mole} \cdot \text{s}$
k_h	rate coefficient of homogeneous nucleation, s^{-1}
k_m	rate coefficient of micellar nucleation, $\text{dm}^3/\text{mole} \cdot \text{s}$
k_p	rate coefficient of propagation reaction, $\text{dm}^3/\text{mole} \cdot \text{s}$

k_{pdb}	rate coefficient for terminal double bond reaction, $\text{dm}^3/\text{mole}\cdot\text{s}$
k_{tc}	rate coefficient for termination by combination, $\text{dm}^3/\text{mole}\cdot\text{s}$
k_{td}	rate coefficient for termination by disproportionation, $\text{dm}^3/\text{mole}\cdot\text{s}$
k_{tw}	rate coefficient of termination in water phase, $\text{dm}^3/\text{mole}\cdot\text{s}$
k_t	termination rate constant, $\text{dm}^3/\text{mole}\cdot\text{s}$
k_v	volume ratio of polymer to aqueous phase
L	critical diffusion length, dm
$M_{1,0}^*$	monomeric radical in water phase without terminal double bond
$\underline{M}_{1,0}^*$	monomeric radical in water phase with a terminal double bond
$M_F, M(t)$	feed and effluent monomer concentration, mole/dm^3
M_w	molecular weight of monomer, g/mole
M_w	weight average molecular weight
M_n	number average molecular weight
$[M_p]$	monomer concentration in particle
$[M_0]$	zero moment for dead polymer without terminal double bond, mole/dm^3
$[M_1]$	first moment for dead polymer without terminal double bond, mole/dm^3
$[M_2]$	second moment for dead polymer without terminal double bond, mole/dm^3
$[M_0^*]$	zero moment for living polymer without terminal double bond, mole/dm^3
$[M_1^*]$	first moment for living polymer without terminal double bond, mole/dm^3
$[M_2^*]$	second moment for living polymer without terminal double bond, mole/dm^3
$[\underline{M}_0]$	zero moment for dead polymer with terminal double bond, mole/dm^3
$[\underline{M}_1]$	first moment for dead polymer with terminal double bond, mole/dm^3
$[\underline{M}_2]$	second moment for dead polymer with terminal double bond, mole/dm^3

$[M_o^*]$	zero moment for living polymer with terminal double bond, mole/dm ³
$[M_1^*]$	first moment for living polymer with terminal double bond, mole/dm ³
$[M_2^*]$	second moment for living polymer with terminal double bond, mole/dm ³
$m, m(t)$	partition coefficient of monomeric radicals between water and particle
N_a	Avogadro's number
N_n	number of polymer particles with n radicals
N_p	number of polymer particles
$N(t)$	total number of particles at time t, particles/dm ³
$[N_o]$	dead particle concentration, particles/dm ³
$[N_t]$	total particle concentration, particles/dm ³
$[N^*]$	active particle concentration, particles/dm ³
$n(t, t)dt$	number of particles at time t born within time interval t to t+dt, particles/dm ³
$P_{j,b}$	dead polymer with j monomer units, b branch points without terminal double bond
$P_{j,b}^*$	living polymer with j monomer units, b branch points without terminal double bond
$\underline{P}_{j,b}$	dead polymer with j monomer units, b branch points with a terminal double bond
$\underline{P}_{j,b}^*$	living polymer with j monomer units, b branch points with a terminal double bond
$P_{1,0}^*$	monomeric radical in particle without terminal double bond
$\underline{P}_{1,0}^*$	monomeric radical in particle with a terminal double bond
$p(t)$	property of polymer at time t
$P(t)$	total property of polymer at time t
q	average number of radicals per particle
$q(t, t)$	average number of radicals per particle for $n(t, t)dt$ type particle
R_a	rate of radical enter into particle

$R_i, R_i(t)$	radical initiation rate, mole/dm ³
R_p	total rate of polymerization
R_{pp}	rate of polymerization per particle
$[R_w]$	water phase radical concentration
$[R^*]$	primary radical concentration in water phase
$[R^*]_p$	adsorbed primary radical concentration in micelle and polymer particle
S_F	emulsifier concentration in feed, mole/dm ³
S_{cmc}	critical micelle concentration, mole/dm ³
S_m	emulsifier concentration on micelle surface
S_p	emulsifier concentration on particle surface
s_d	area cover by one molecule of emulsifier
t	time, s
t_f	time where all micelle are used up, s
u	constant equal to k_{ho}/k_m
u_p	particle volume growth rate, dm ³ /s
V	reactor volume, dm ³
V_p	total polymer particle volume, dm ³
$v_p(t,t)$	volume of a $n(t,t)dt$ type particles, dm ³
$v_p(t,t)$	volume of micelle, dm ³
X_c	critical monomer conversion
$X, X(t)$	total monomer conversion

Greek letters

δ	$(1 + D_w/mD_p)^{-1}$
ε	constant equal to k_{ab}/k_m
$\zeta(t)$	time dependent function = $\frac{(1 - e^{-t/\theta})\phi(t)}{(1 - \phi(t))A^{1/2}(t)}$
$P(t)$	free radical nucleation rate, particle/s
θ	mean residence time, s
$\phi(t)$	volume fraction of monomer in polymer particle
ϕ_{sat}	saturation monomer volume fraction in polymer particles
λ	constant = $\frac{k_p d_m}{N_A d_p} \left[\frac{k_p f k_d [I]_{feed} m_0}{12 \uparrow D_w \delta k_{fm}} \right]^{1/2}$
τ_p	mean polymerizing lifetime of radical

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