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Analysis of Particle Formation under Monomer-Starved Conditions in Emulsion Polymerization Reactors

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Summary: An important characteristic of monomer-starved nucleation in semibatch reactors is that the rate of growth of particles is controlled by the rate of monomer addition. The reduced rate of growth of particles prolongs the nucleation interval by slowing down the rate of emulsifier micelle depletion and forms a larger number of particles (N_p). Model calculations show how N_p varies with the formulation parameters as the monomer-flooded nucleation shifts into monomer-starved one. Particle formation in the intermediate conversion of interval III of the styrene batch emulsion polymerization also showed an enhancement because of a low rate of growth of newly formed particles. However, at a higher conversion, the rate of particle formation decreased significantly. Modeling results show that the reduction in the rate of particle formation at high conversions could not be simply explained by existing theories which rely on the decrease in monomer concentration in the aqueous phase as a means to explain the decrease in the rate of radical capture.

Keywords: emulsion polymerization; micelles; monomer-starved, particle nucleation; semibatch reactors

Introduction

Emulsion polymerization is perhaps the most important process for manufacturing polymer colloids. The particle nucleation stage of emulsion polymerizations is of crucial importance because it significantly affects the final properties of latexes. The mechanisms of particle birth and growth were described by Smith and Ewart (SE)[1] long ago for an *ab initio* batch emulsion polymerization. In the SE scheme particle formation occurs in the presence of monomer droplets (monomer-flooded conditions). For many industrial emulsion polymerization reactors, such as semibatch and continuous stirred tank reactors and even batch reactors with a high emulsifier/monomer ratio, particle formation is not confined to interval I and may occur in interval III where monomer droplets do not exist (monomer-starved conditions).

Research work on particle nucleation under monomer-starved conditions is scarce, even for semibatch polymerization reactors which are usually operated under such conditions. This is

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perhaps because semibatch processes are usually proceeded by a seeding batch stage during which particle formation occurs under monomer-flooded conditions. It is not surprising that batch and semibatch emulsion polymerization processes have been considered to be similar in terms of particle formation according to some sources[2]. If the monomer concentration used in the initial charge of a typical semibatch process is not sufficient to consume all emulsifier micelles, nucleation will continue into the feeding stage where both monomer-flooded and -starved conditions may predominate[3-6]. In this article, we present and analyze some of the results obtained with the semibatch and batch emulsion polymerization of styrene and methyl methacrylate (MMA) under such conditions.

Monomer-starved conditions

In conventional emulsion polymerization reaction under monomer-flooded conditions, monomer droplets serve to supply monomer to the growing polymer particles and also keep the phases saturated with monomer. The amount of monomer that a polymer particle takes is a result of the minimization of the free energy of the system. Morton's equation[7] predicts that the monomer concentration in polymer particles ($[M]_p$) is a strong function of size below a radius of 20 nm. A similar equation by Vanzo[8] predicts variation in $[M]_p$ with particle size for starved conditions.

$$[M]_p = [M]^{\infty}_{p,sat}\, tanh\left(\frac{r}{r_f}\right) \qquad (1)$$

$$w_p = \frac{[M]_p MW_m - \rho_m}{[M]_p MW_m\left(1-\frac{\rho_m}{\rho_p}\right) - \rho_m} \qquad (2)$$

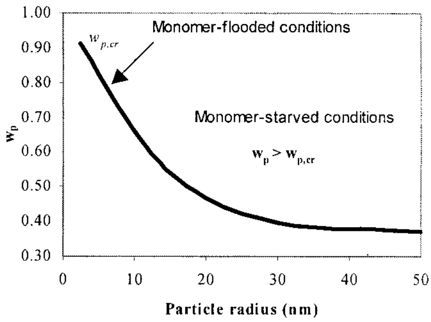

Figure 1. Boundary of starved conditions for polystyrene particles with different size. $[M]^{\infty}_{p,sat}$ = 5.80 mol/L is $[M]_p$ for large particles, r is the radius of particles and r_f = 8 nm is a constant, MW_m is the molecular weight of monomer, and ρ_m (0.878 g/cm^3) and ρ_p (1.044 g/cm^3) are densities of monomer and polymer, respectively. w_p is the polymer weight ratio in the polymer particles.

Figure 1, prepared by using an empirical correlation[9], depicts the boundary of starved conditions with size for the polystyrene-styrene particles. For the smaller sized polymer particles the monomer-starved condition is established at a lower monomer concentration (higher w_p). In order to maintain starved conditions for small particles usually encountered during nucleation, therefore, the amount of monomer in the reacting latex should be minimum and/or the rate of monomer addition should be kept at a very low level.

Rate of particle growth

The volumetric growth rate of a polymer particle containing one growing radical (μ) is given by Eq. (3)[10]. In intervals I and II of conventional batch emulsion polymerizations, μ is thermodynamically controlled at a constant level by monomer diffusion from the monomer droplets to the polymer particles; $\varphi_p = \varphi_{p,sat}$. If $\mu = k_1 (1-\varphi_p)/\varphi_p$ is drawn against φ_p, a curve similar to that shown in Figure 2 is obtained. The abscissa of this figure was normalized by dividing μ over that of imaginary monomer-swollen particles containing 1.0 vol % polymer ($\varphi_p = 0.01$). The symbols on Figure 2 show the relative growth rate of polymer particles in the equilibrium state ($\varphi_p = \varphi_{p,sat}$). For any point beyond these symbols ($\varphi_p > \varphi_{p,sat}$), the corresponding polymer-monomer system is under monomer-starved conditions and μ is depressed. Values of φ_p smaller than $\varphi_{p,sat}$ can be obtained only if a swelling agent is used. Polymer particles with a higher $[M]_{p,sat}$ (vinyl acetate;VA) provide a greater flexibility in the control of μ. If a policy is adopted, for example by using a semibatch process, so that φ_p can be kept constant at 0.97 during monomer feeding, almost two orders of magnitude decrease in μ is obtained, in comparison with the flooded conditions. This policy provides an efficient tool to depress μ and enhance nucleation.

$$\mu = \frac{k_p \rho_m}{N_A \rho_p} \frac{1-\varphi_p}{\varphi_p} = k_1 \frac{1-\varphi_p}{\varphi_p} \qquad (3)$$

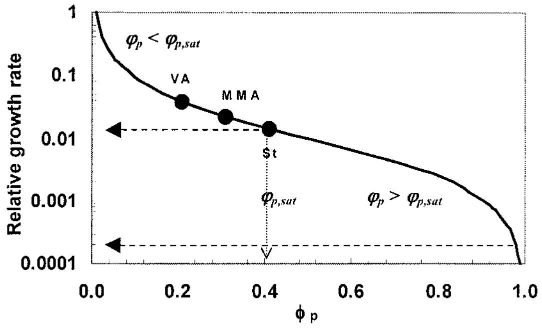

Figure 2. Relative growth rate of polymer particles with φ_p (k_p is propagation rate constant, and φ_p is volume fraction of polymer in the polymer particles and k_i (i = 1, 2, ...) is a constant.

Monomer partitioning

Monomer partitions among the three sites available in a monomer-starved semibatch emulsion polymerization: polymer particles, micelles, and water phase. The number of molecules of a monomer solubilized in a micelle (N_{mm}) decreases with the monomer concentration in the water phase ($[M]_w$)[11]. Because of continuous variation in the state of system, the aggregation number of micelles is also subject to variation in the course of reactions[12]. The size variation of micelles is conformed to a constant surface coverage ratio of emulsifier molecules. The variations in the number of micelles during nucleation does not seem to affect nucleation. However, the amount of monomer solubilized in the micelles could be important if little monomer is present in the reactor. The importance of the monomer solubilized in the micelles on the kinetic features of polymerization becomes more significant as emulsifier concentration $[S]$ is increased.

$$[M]_p = \left(\frac{(1-w_p)\rho_m / MW_m}{1-w_p+w_p\rho_m/\rho_p} \right) \qquad (4)$$

$$[M]_w = [M]_{w,sat} \left(\frac{[M]_p}{[M]_{p,sat}} \right)^{0.60} \qquad (5)$$

$$N_{mm} = K_{eq}[M]_w \qquad (6)$$

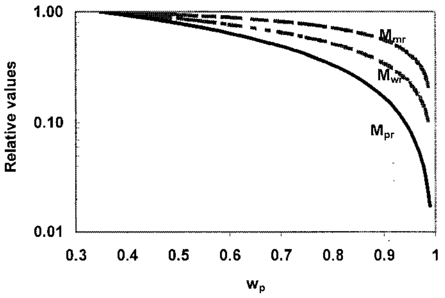

Figure 3. Variations in the relative styrene concentration, with respect to the corresponding saturation value, in the polystyrene particle (M_{pr}), in the water phase (M_{wr}) and in the SLS micelles (M_{mr}) with w_p at 70 °C ($[M]_{p,sat} = 5.8$ and $[M]_{w,sat} = 5.6\times10^{-3}$ mol/L, $K_{eq} = 1.68\times10^4$ L/mol). The correlations used for the conversion of N_{mm} to $[M]_m$ are given in ref [6].

Figure 3 shows the variation of the styrene monomer concentrations in the polymer phase ($[M]_p$), water phase ($[M]_w$) and sodium lauryl sulfate (SLS) micelles ($[M]_m$) with increasing polymer weight ratio in polymer particles (w_p) in relative terms. Note that $[M]_m$ here is defined as the concentration of the styrene monomer in micelles, the hydrophobic volume of the surfactant tail was taken into consideration[6]. The fall in $[M]_p$ with w_p starts earlier than the others. $[M]_w$ and $[M]_m$ are closer to the saturation values at medium w_p but start to decrease drastically at higher values of w_p. A significant drop in $[M]_w$ and consequently in $[M]_m$ is observed at $w_p > 0.90$.

Particle formation in semi-batch reactors under starved conditions

In semi-batch processes the rate of particle growth can be controlled by the rate of monomer addition as[12]:

$$\mu(t) = \frac{R_a}{N_p} \qquad w_p > w_{pcr} \qquad (7)$$

where R_a is the rate of monomer addition in L/sec.L(aq) and N_p is the number of polymer particles. In the above equation, the difference between monomer and polymer densities and the monomer solubilized in the micelles and dissolved in the water phase have been neglected for simplicity. The above equation predicts a linear relation between the instantaneous rate of particle growth ($\mu(t)$) and the rate of monomer addition. Using the above equation and similar to the treatment of SE, it is possible to show that the nucleation time is given by:

$$t_f = k_2\,(a_s N_A[S])\, R_I^{-1/3}\, R_a^{-2/3} \qquad (8)$$

where R_I the rate of radical generation in the water phase, a_s the adsorption area occupied by a molecule of emulsifier on the surface of polymer particles and $[S]$ the concentration of emulsifier per unit volume of water. The following equation is obtained for the final number of polymer particles[12]:

$$N_p = k_3\,(a_s N_A[S])\, R_I^{2/3} R_a^{-2/3} \qquad (9)$$

The suppressed growth rate of particles under monomer-starved conditions prolongs the nucleation period (see Eq.(8)) and thus results in formation of a larger number of polymer particles. It should be noted that because μ is controlled by R_a, therefore, all kinetic events which could affect the rate of particle growth (and monomer/polymer composition) under flooded conditions such as radical loss due to desorption from polymer particles and termination in the polymer particles are irrelevant. Eq. (9), however, neglects particle formation via radical re-entry into micelles. This is not a serious matter for the styrene monomer because the rate of radical desorption from polystyrene particles is not appreciable and furthermore the fate of radical is believed to be re-entering particles. However for more water-soluble monomer such as methyl methacrylate a large deviation is expected.

While the above model includes kinetic events occuring in the polymer phase, it does not account for those occuring in the water phase. Monomer concentration in the water phase plays an important role in the rate of entry of radicals into polymer particles and micelles under starved conditions. Radicals with a longer chain, have more of a chance for entry into micelles and particles[13,14]. The concentration of such radicals depends on $[M]_w$ as shown below.

$$[IM_i^\circ] = \frac{k_{pw}^{i-1}[IM_{i-1}^\circ][M]_w}{k_{pw}^{i}[M]_w + k_{tw}[R^\circ] + k_{ap}^{i}N_p + k_{am}^{i}N_m} \qquad i = z, \ldots, j_{cr}\text{-}1 \qquad (10)$$

The probability of reaching the chain length of i for a growing radical strongly depends on $[M]_w$. z is the critical chain length for entry of a radical into particles and/or micelles[15]. With a higher $[M]_w$, a faster propagation rate for radicals would allow for more radical entry into micelles (and particles) compared with termination in the water phase. Perhaps the most important feature of the entry model adopted in this research is that it can reflect the effects of variations in $[M]_w$ on the whole nucleation process. A numerical model that included kinetic events occuring in the polymer and water phases and also monomer and emulsifier partitioning in the three phases was developed. The details of this model have been given elsewhere[12].

Figures 4 and 5 compare the experimental N_p with the model predictions for z values of 2 and 3. The experiments started with almost no styrene monomer in the initial charge. The styrene monomer was added at a low rate to the reaction vessel containing an aqueous solution of an emulsifier (SLS) and an initiator (potassium persulfate; KPS) at the reaction temperature of 70 °C[6]. The N_p exponents together with the experimental data are given in Table 1.

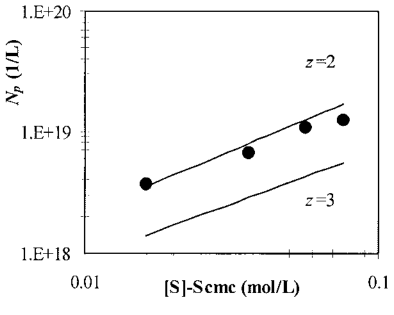

Figure 4. Variation in N_p with $[S]$ ($[I]$ = 2 mmol/L, $R_a = 2.6\times10^{-5}$ L/L.s.).[12]

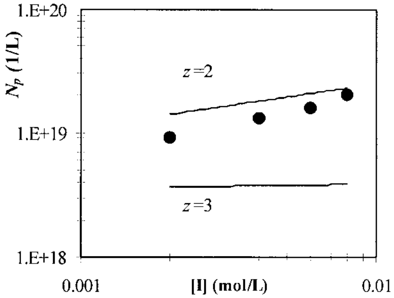

Figure 5. Variation in N_p with $[I]$ ($[S]$ = 40 mmol/L, $R_a = 1.1\times10^{-5}$ L/L.s.).[12]

Table 1. Comparison of the exponents obtained from experimental data and model predictions[12].

	Analytical model	Numerical model		Experimental
		$z=2$	$z=3$	
N_p versus $[S]-S_{CMC}$	1.00	1.00	0.87	0.80
N_p versus $[I]$	0.67	0.34	0.04	0.55
N_p versus R_a	-0.67	-0.63	-0.32	-0.65

Figure 6 shows a typical N_p-R_a for the monomer-starved semibatch emulsion polymerization of MMA. The exponent of N_p versus R_a (-1.98) was found to be much greater, in the absolute value, than that found and predicted for the styrene monomer. Such a difference is not surprising as radical desorption plays an important role in the MMA emulsion polymerization.

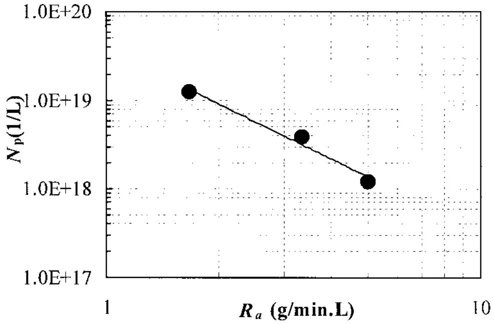

Figure 6. Variations in the experimental N_p with R_a for MMA semibatch emulsion polymerization under monomer-starved conditions ($[S]$ = 5 g/L; $[I]$ = 1.25 g/L; T = 50 °C)[16].

Transition from monomer-starved to monomer-flooded nucleation

Particle nucleation in a semibatch emulsion polymerization may occur under flooded-conditions if the requirements for maintaining starved conditions, as previously mentioned, are not met. Figure 7 depicts the variation in final N_p with R_a for the semibatch emulsion polymerization of styrene at 70 °C with almost no initial monomer charge. The experimental data are from ref [6]. At a high R_a, the initial rate of polymerization (R_p) is lower than R_a ($R_p << R_a$) so that monomer droplets accumulate in the reactor. Note that R_p is the instantaneous rate of polymerization which usually increases with time during nucleation as more particles are formed. In the flooded region

N_p is independent of R_a, similar to a batch polymerization (F region). With a further decrease in R_a, the condition of $R_p < R_a$ can be only maintained for a short period of time so that nucleation starts under monomer-flooded condition but later extends into monomer-starved condition as R_p increases so that $R_p > R_a$ (F-S region). As a result, a slight rise in N_p is obtained. With a further decline in R_a, eventually a point is reached where $R_p >> R_a$. This is the region which applies to monomer-starved nucleation with an exponent of −2/3 for N_p verusu R_a (S region)[12].

The presence of monomer in the initial reactor charge is similar to the case that a high R_a is used with no initial monomer charge. In both cases the nucleation may occur fully under flooded conditions, but may also extend into starved conditions if a low concentration of monomer and/or a low monomer feed rate is used. In such a case polymerizations are always limited to the regions of F or F-S and so an exponent less than −2/3 is expected.

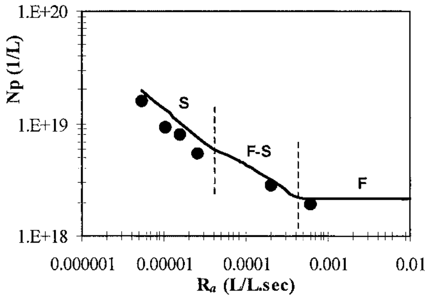

Figure 7. Variation in N_p with R_a (z =2, [S] = 40 and [I] = 2 mmol/L, T = 70 °C).

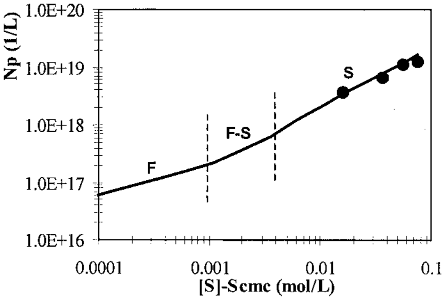

Figure 8. Variation in N_p with [S] (z = 2, see caption of Figure 4).

Figure 8 depicts the variation in N_p with emulsifier concentration at a constant R_a. At a low emulsifier concentration, R_p is rather low because particle formation occurs very briefly and a small number of particles is formed. In this region $R_a > R_p$, therefore, nucleation occurs under flooded condition and an exponent close to that predicted by SE, 0.60, is obtained. With further rise in [S], a region is reached where nucleation initially occurs under flooded conditions, but later continues into starved conditions. An exponent greater than 0.60 is obtained for this region. Eventually, with increasing [S] a point is reached where nucleation fully occurrs under starved conditions with a theoretical exponent close to 1.0.

Smith and Ewarts[1] derived the following equation for the prediction of number of polymer particles (N_p) formed in conventional batch reactors with the case II kinetics:

$$N_p = k_4 \, (a_s \, N_A [S])^{3/5} (R_I/\mu)^{2/5} \tag{11}$$

From the comparison of Eqs. (9) and (11) it is apparent that for semibatch emulsion polymerizations under monomer-starved conditions, the number of particles is more sensitive to formulation variables than that under the monomer-flooded conditions. The number of particles formed in the semibatch emulsion polymerization under monomer-starved conditions over that in the corresponding conventional monomer-flooded emulsion polymerization is obtained as:

$$\frac{N_{p,semibatch}}{N_{p,batch}} = k_5 [S]^{6/15} R_I^{4/15} R_a^{-10/15} \tag{12}$$

As a general statement, monomer-starved semibatch emulsion polymerization reactions produce more particles than the corresponding batch polymerization reactions. Eq.(12) reveals that if all the formulation variables are multiplied by a factor, the ratio of $N_{p,semibatch}/N_{p,batch}$ remains constant.

Drop stability and monomer transport

Semibatch emulsion polymerization requires that monomer diffuses from the fed-in monomer droplets to the water phase, diffuses through the water phase and eventually penetrates into growing polymer particles[17]. The stability (lifetime) of droplets under monomer-starved conditions, in which the water phase is under-saturated with monomer, can play an important role in the kinetics of semibatch polymerization. At a low agitation speed, the monomer diffusion is improved if monomer is added to the reaction vessel as a pre-emulsified emulsion, in comparison with a neat monomer[18]. The monomer diffusion does not seem to affect the rate of polymerization at a conventional (moderate) agitation speed[18,19]. The presence of dissolved oxygen in the pre-emulsified feed, however, may inhibit polymerization and leads to accumulation of monomer[19].

In the models reported here, we assumed that monomer droplets are not stable and disappear as soon as they enter the reaction vessel. Monomer droplets could sustain in the reacting latex if the rate of monomer transport from them to growing particles is very slow. Limitation in monomer transport could also result in the underestimation of the early rate of polymerization where the amount of monomer in the reactor vessel is very low[12]. However, as polymerization proceeds, the deviation is reduced because of the trivial importance of the amount of monomer droplets in the balance of free monomer in the reactor in comparison with that in the particles.

If the stability of monomer droplets is improved, by using a water-insoluble additive, then it would be more likely to observe diffusion-controlled monomer transport occuring in a semibatch process. The seeded semibatch emulsion polymerization of styrene at 70 °C with miniemulsion feed and conventional emulsion feed (macroemulsion) was selected for this analysis[20]. The seed latex was emulsifier starved so that emulsifier micelles could not form in the reacting latex with addition of the feeds. The miniemulsion and macroemulsion feeds had similar composition, with the exception that miniemulsion feed contained 2.0 wt % hexadecane. The miniemulsion feed was exposed to sonifier disrupter before use. Figure 9*a* depicts that a higher rate of polymerization was obtained with the macroemulsion feed. This confirms that the transport of monomer from rather stable miniemulsion monomer droplets to the growing polymer particles, via water phase, is diffusion controlled.

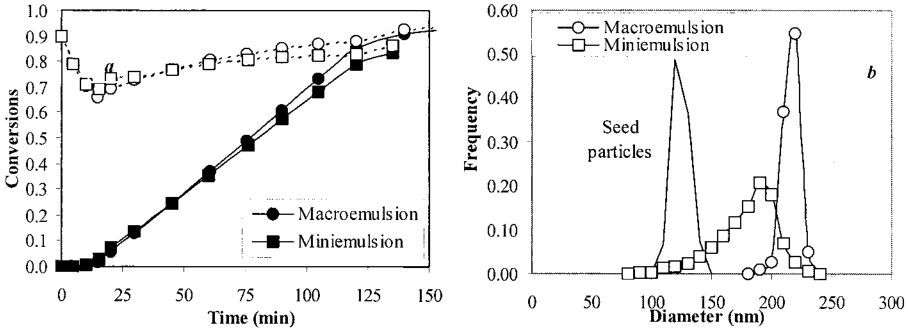

Figure 9. Comparison of macroemulsion feed and miniemulsion feed in the seeded semibatch emulsion polymerization of styrene: (*a*) Evolution of instantaneous (empty symbols) and overall (full symbols) conversions (*b*) Final particle size distributions (see ref [19] and [20] for more details).

The presence of additive in the miniemulsion droplets retards the rate of interparticle monomer transport and prolongs the lifetime of the miniemulsion droplets in the reacting latex so that they can capture radicals from the water phase and contribute effectively to particle nucleation before they disappear. Figure 9*b* depicts that a large number of polymer particles were formed through monomer droplet nucleation with the miniemulsion feed[20,21]. According to Figure 9*a* the rate of polymerization with the conventional monomer emulsion feed is higher than that with the miniemulsion feed, despite a smaller N_p for the former. This is because styrene emulsion polymerization at high conversions can be well defined by Case III kinetics in which the rate of polymerization is independent of N_p.

Particle formation at high conversions

The mechanistic information of the events governing particle formation under starved conditions can be obtained via polymerizations in interval III. The SE interval III is characterized by the disappearance of monomer droplets and by polymerization in constant number of polymer particles formed during interval I. In the SE interval III particle formation does not occur, because emulsifier micelles have depleted during interval I. However, it is possible that nucleation extends into interval III if a high concentration of emulsifier and/or a low concentration of monomer are used. In interval III, there is no monomer droplet present. So:

- Polymer particles behave as a reservoir of monomer.
- The growth of newly formed polymer particles occurs at the cost of shrinkage of existing polymer particles.
- As a result of shrinkage of the existing polymer particles, some emulsifier from the surface of existing particles might be released and contribute into nucleation.

Polymerizations were carried with mono-sized polystyrene seed particles swollen with the styrene monomer at the amounts lower than the saturation value[22]. The reaction temperature was 70 °C. Aerosol-MA and SLS were used as emulsifiers. Figure 10 shows the final number of new or secondary polymer particles formed with aerosol-MA with initial polymer weight ratio in the polymer seed particles (w_{p0}). Two important points are worthy of attention here. First, nucleation in interval III is enhanced in comparison with interval I where free monomer droplet exists[22]. Second, N_p versus w_{p0} reveals a maximum somewhere in the medium conversion. The drop in N_p after the maximum was quite sharp. A simillar trend was also observed with SLS as an emulsifier (not shown), but the drop in N_p after the maximum was very mild.

Figure 10. N_p versus w_{p0} for the seeded styrene emulsion polymerization in interval III (with aerosol-MA). The data points are experimental[22] and the full lines are model predictions.

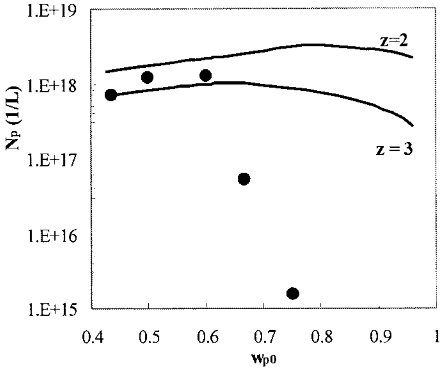

Figure 10 also shows the model predictions for z values of 2 and 3. The model used for this analysis is an extended version of that detailed in ref [12], but included allowance for seeded polymerization. The diffusion-controlled propagation was also lifted from the model for this analysis, because of ambiguity involved in nucleation at very high conversions and meaninglessly a large number of particles predicted by the model due to the cessation of polymerization in the polymer particles because of the glass effect. The model predicts increasing N_p with w_{p0} in the intermediate conversion. The experimental data fall within the model predictions up to an intermediate conversion. A large gap between the experimental and theoretical N_p develops with increasing w_{p0} indicating that particle formation is not really operative at higher conversions for aerosol-MA. The fall in N_p is more drastic for $z = 3$, in comparison with $z = 2$, as expected. At high values of w_{p0}, polymerization occurred in the seed particles, whereas no or a few new particles were formed despite the presence of micelles. The fall in the experimental N_p appears much earlier, in terms of w_p, and in a more drastic way than the model predictions. It is inferred from the pattern of monomer partitioning, as shown in Figure 3 for SLS (a similar pattern applies to aerosol-MA), that a drop in N_p could be expected at high values of w_p if the fall in $[M]_w$ was the reason. In fact $[M]_w$ and $[M]_m$ stay rather close to the corresponding saturation values up to high conversions. Note that the calculations for $[M]_m$ are not exact because monomer may reside in the shell of micelles as $[M]_w$ decreases so that a true core solubilised monomer is suppressed. The possible reasons for the fall in N_p at high conversions could be coagulation of the low molecular weight primary polymer particles formed under a restricted monomer diffusion and/or the decreased rate of radical capture of lean monomer-swollen micelles.

Conclusions

Some aspects of the kinetics of particle formation and growth under monomer-starved conditions were analyzed and quantified. The rate of monomer addition, together with the monomer concentration in the initial reactor charge, are the main important factors, which control the regime of particle formation. By reducing the rate of particle growth, the rate of emulsifier micelle depletion is reduced and nucleation time is prolonged. The particle number, N_p, was found to be proportional to $R_a^{-2/3}$. Therefore, a large number of polymer particles, in comparison with the batch operation, can be obtained by maintaining R_a at a low value. There is still a major unresolved problem in this field, that is, the slow-down of particle formation at very high conversions, which also depends on the nature of the emulsifier among the others. It can be concluded that the disagreement between the model predictions and experimental data at the higher conversions of interval III could not be simply explained by existing theories which rely on the decrease in monomer concentration in the aqueous phase as a means to explain the decrease in the rate of radical capture. The decreased rate of radical entry into partially monomer-swollen micelles can be explained by coagulation of low molecular weight primary polymer particles formed at high conversions and/or the variations in structure of micelles and subsequent reduced rate of radical capture by micelles with monomer concentration.

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