

# Some Comparative Aspects of Particle Formation and Rate of Reaction in Emulsion Polymerization of Vinyl Acetate and Butyl Acrylate

Fatemeh Jahanzad

*Division of Chemical and Petroleum Engineering, London South Bank University,  
London SE1 0AA, United Kingdom*

Received 15 July 2008; accepted 21 September 2009

DOI 10.1002/app.31517

Published online 2 March 2010 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The comparative study of monomers, in terms of particle formation and rate of polymerization, facilitates the interpretation of the results from the corresponding copolymerization runs and can be considered as a preliminary step toward formulation of copolymerization reactions. Batch emulsion homopolymerization of vinyl acetate (VA) and butyl acrylate (BA), as model monomers with a wide water solubility disparity, were carried out to investigate the effects of variations in the monomer concentration, electrolyte concentration, reaction volume, and surfactant type on the kinetics of polymerization. With sodium lauryl sulfate as surfactant, VA emulsion polymerization produced more particles than BA at a lower monomer concentration, but fewer particles at a higher monomer concentration. At a lower VA concentration, a

depressed growth for newly formed particles during interval III contributed to the formation of a large number of particles. The application of aerosol MA and OT surfactants improved the stability of polyvinyl acetate (PVA) particles so that a larger number of polymer particles was obtained for VA, in comparison with BA. BA emulsion polymerization showed little sensitivity to electrolyte concentrations and reaction volumes within the range studied. The colloidal stability of PVA particles was found to be quite sensitive toward the aforementioned variables. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 84–90, 2010

**Key words:** emulsion polymerization; colloids; particle nucleation; vinyl acetate; butyl acrylate

## INTRODUCTION

Emulsion polymerization is widely used as a technique to produce latexes with a wide variety of properties. In an emulsion polymerization, the main variables that determine the kinetic features of the reaction are usually initiator and surfactant concentrations and the reaction temperature. The effects of these variables on the kinetics of emulsion polymerization have been extensively studied and well documented in the literature.<sup>1,2</sup> However, there are other variables that may play an important role in the polymerization reactions. These are, for example, monomer concentration, surfactant type, inhibition effects, agitation speed, electrolyte concentration, etc. Some of these parameters have been often ignored in the early literatures on emulsion polymerization simply because most attempts at the time were focused on the understanding of the roles of the main parameters. With achievements of considerably good understanding of underlying mechanisms occurring in emulsion polymerization reaction, now

attempts are directed toward the effects of the secondary parameters. These parameters have shown to severely affect the polymerization kinetics under some circumstances. One might argue that such parameters are of prime importance. Although we cannot refute such an argument, we can state that the effects of these variables are usually limited to a certain range of conditions. For examples, the stirring speed<sup>3–5</sup> and monomer concentration<sup>6–8</sup> are known to have little effect on the emulsion polymerization within certain ranges. The secondary variables become of paramount importance in studying copolymerization of monomers with widely different properties. For a copolymerization reaction, it is quite useful that the behavior of the individual monomers is known at the polymerization conditions. In this research, the preliminary results from the batch and semibatch emulsion polymerization of vinyl acetate (VA) and butyl acrylate (BA) are presented. These are monomers with widely different polarities or water solubilities. The polarity of the monomer–water interfaces influences the surfactant adsorption on the growing polymer particles, thus affects the transition from interval I to II, and also affects monomer swelling of growing polymer particles, which marks the transition from interval II to III. We study the effect of monomer concentration,

Correspondence to: F. Jahanzad (jahanzaf@lsbu.ac.uk).

**TABLE I**  
**Base Recipe for VA and BA Emulsion Polymerizations**

Formulation parameter	Quantity
Monomer, VA or BA (g)	250
Distilled water (g)	500
Surfactant, SLS (g)	5
Initiator, KPS (g)	0.27
Electrolyte, SBc (g)	0.27
Impeller speed (rpm)	325
Temperature (°C)	50

electrolyte concentration, surfactant type, and reaction volume in the VA and BA homopolymerizations.

### EXPERIMENTAL

Both monomers, VA and BA, were obtained from Aldrich (VA, 99+%, inhibited with 3–5 ppm of hydroquinone, and BA, 99+%, inhibited with 10–15 ppm hydroquinone mono methyl ether). Both monomers were distilled under vacuum and then stored at  $-18^{\circ}\text{C}$ . The initiator, potassium persulfate (KPS), the electrolyte, sodium bicarbonate (SBc), and surfactant, sodium lauryl sulfate (SLS) were obtained from Aldrich and used as received. Aerosol MA-80 (sodium dihexyl sulfosuccinate, 80% active) and aerosol OT-10 (sodium dioctyl sulfosuccinate, 10% active) were obtained from Cytec Industries and were used without any further purification.

The experiments were carried out in 1 L jacketed glass reactor with a diameter of 10 cm equipped with a four-bladed flat turbine type impeller with a width of 4/10 of vessel diameter and four baffle plates with the width of 1/10 of vessel diameter located at  $90^{\circ}$  interval. The stirrer rate was kept constant at 325 rpm. The temperature of the reactor contents was controlled at  $50^{\circ}\text{C} \pm 1^{\circ}\text{C}$  by pumping water with appropriate temperature through the jacket.

Overall monomer conversion was determined gravimetrically. The rate of polymerization ( $R_p$ ) was obtained from the linear part of conversion-time curves taking into account the mass of initial monomer. Laser light scattering was used for particle size measurements (Malvern Zetamaster). The measurements were carried out at  $90^{\circ}$  angle. Ten measurements were made and the average was assigned as the mean average size of particles. The number of particles,  $N_p$ , is given by:

$$N_p = (6 m_0 x / \pi \rho_p D_v^3) \quad (1)$$

where  $m_0$  is the initial monomer mass per liter of the aqueous phase,  $x$  conversion,  $\rho_p$  polymer density, and  $D_v$  is the volume average diameter of particles.

The methodology for conversion of z-average diameter, obtained by laser light scattering, to volume average diameter is similar to that explained elsewhere.<sup>6</sup>

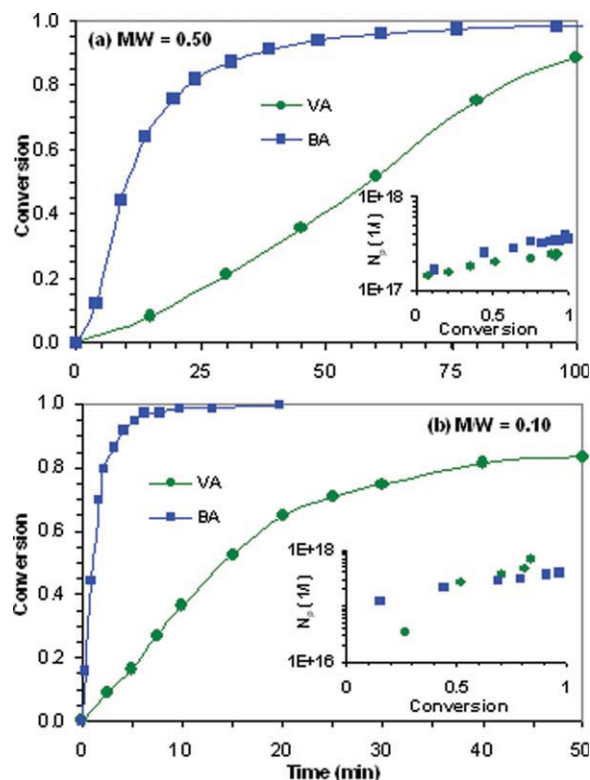
The base recipe used to study the batch emulsion polymerization of VA and BA is given in Table I. The variations from the base formulation are mentioned where appropriate.

### RESULTS AND DISCUSSION

At the start of the polymerization reactions induction periods were observed for both monomers. An induction period of 5–30 min for VA emulsion polymerization has been reported by many research groups.<sup>9,10</sup> In these experiments, an induction period of 1–15 min for both VA and BA monomers was observed. To do a comparative study, induction periods were eliminated from all conversion-times curves.

#### Effect of monomer concentration

Figure 1 shows the conversion-time trajectories for VA and BA emulsion homopolymerization with SLS



**Figure 1** Conversion versus time and number of particles versus conversion (insets) for VA and BA emulsion polymerizations with (a)  $M/W = 0.50$  (base formulation) and (b)  $M/W = 0.10$  (See Table I for the formulation). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

as surfactant and monomer-to-water ratio ( $M/W$ ) of 0.50 (the base formulation) and 0.10. The number of particles ( $N_p$ ) is also shown in the insets. For BA, the rate of polymerization is very fast with a short period of steady state and decays quickly. For VA, the rate of polymerization remains almost constant for most of the reaction time.<sup>10,11</sup> The initial rate of polymerization ( $R_p$ ) did not change significantly with  $M/W$  ratio for both monomers (note that  $R_p = m_0 dx/dt$ ). Generally, the rate of polymerization is much higher for BA than VA.

It can be seen from the insets in Figure 1 that for  $M/W = 0.5$ , a higher final  $N_p$  is obtained for BA emulsion polymerization in comparison with VA. But as  $M/W$  is reduced to 0.10, VA emulsion polymerization produces more particles. Note that for BA emulsion polymerization, particle nucleation was almost complete in the mid of reaction. In opposite,  $N_p$  for VA emulsion polymerization continues to increase above the critical conversion (0.23), and into interval III (the conversion at which the transition from interval II to III occurs, is called critical conversion,  $x_{cr}$ ). This is in accord with the data reported by Zollars.<sup>9</sup> However, Friis and Nyhagen reported that  $N_p$  reached a constant value after the critical conversion.<sup>10</sup> These works have been conducted under very similar conditions (in terms of monomer, surfactant, and initiator concentrations and the reaction temperature) with our study. The reason for this discrepancy is not clear.

The increase in  $N_p$  in the course of VA emulsion polymerization using  $M/W = 0.10$  is obvious from Figure 1. The area occupied by a molecule of SLS on polybutyl acrylate (PBA) and polyvinyl acetate (PVA) particles ( $a_s$ ) is 0.63 and 1.1 nm<sup>2</sup>, respectively.<sup>6,12</sup> The calculation of particle surface converge ratio by the surfactant indicates that micelles exist in a large number till the end of polymerization for both  $M/W$  ratios used, and in particular for  $M/W = 0.10$ , in VA polymerization. This implies that nucleation has occurred under monomer-starved conditions in interval III (note that nucleation continues above  $x = 0.23$  and into interval III). Sajjadi has shown that particle nucleation in interval III of emulsion polymerization can lead to formation of a larger number of particles due to the reduced growth of particles.<sup>13</sup> In interval III, the growth of freshly formed particles occurs at the cost of shrinkage of existing particles. It was also shown that particle number may even increase as the system becomes more starved with monomer. Note that the solubility of VA monomer in the water phase is around 2.5 wt %. Therefore, for  $M/W = 0.10$ , the start of interval III is further advanced, in terms of conversion, so that most of nucleation occurs under highly monomer-starved conditions. Another possible reason for an increase in  $N_p$  with decreasing

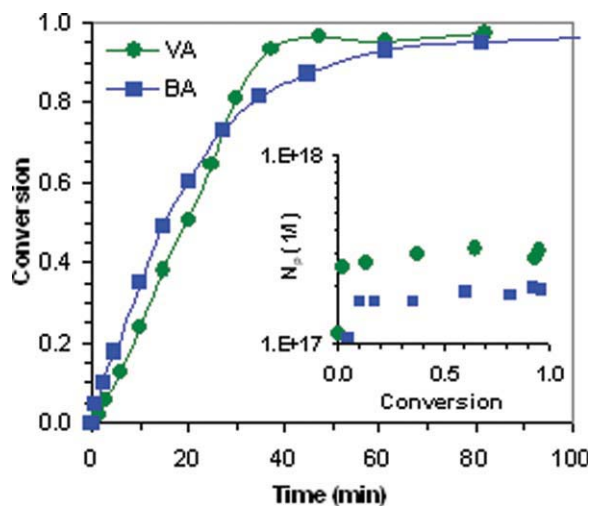
$M/W$  is the reduced particle coagulation at low solids content. Interestingly, the change in the trend in  $N_p$  with monomer concentration (as shown in Fig. 5) is consistent with that observed for the same monomers in the monomer-starved semibatch emulsion polymerization.<sup>14</sup> It has been shown that when BA monomer produces more particles than VA at a high rate of monomer addition, the reverse becomes true at a low monomer feed rate.<sup>14</sup>

It should be noted that the variation in  $N_p$  with  $M/W$  ratio for VA monomer may not occur at a low surfactant concentration, which allows for a short nucleation period. It can be stated that the relative number of particles in VA and BA emulsion polymerization is in fact a function of monomer/surfactant ratio. It also follows from this discussion that in the copolymerization of VA and BA monomers, the effect of feed composition on the nucleation pattern should not be generalized based on a single formulation. Core-shell particles with PBA-rich core and PVA-rich shell are formed in VA/BA copolymerization due to large differences in VA and BA reactivity ratios. It has been reported that the average particle size is almost independent of copolymer feed composition.<sup>15</sup> However, if the monomer concentration is so low that BA content in the copolymerization feed is depleted before the completion of nucleation, the particle nucleation continues into the region where VA plays a dominant role. In such a case the average particle size may show more sensitivity toward copolymer feed composition.

### Effect of surfactant type

SLS is perhaps the most widely used surfactant in emulsion polymerizations, at least in academia. There are many other anionic surfactants with appropriate properties that are often used in emulsion polymerization. Mixture of aerosols has been reported as a good surfactant system for VA/BA copolymer latexes.<sup>15,16</sup> A couple of runs were performed using a mixture of aerosol MA-80 (sodium dihexyl sulfosuccinate) and aerosol OT-10 (sodium dioctyl sulfosuccinate). The ratio of active aerosols in the mixture was OT/MA = 5/95. The initiator concentration for this particular set was 1.08 g/L twice that used for polymerization with SLS. The results for the rate of polymerization and number of particles are shown in Figure 2. The application of aerosols leads to the formation of a larger number of particles for VA, but a smaller number of particles for BA, in comparison with those with SLS. The overall concentration of SLS or active aerosols used was 10.0 g/L. The critical micellar concentration (CMC) of SLS and aerosol MA are 1.12 and 3.88 g/L (or  $3.9 \times 10^{-3}$  and  $1.0 \times 10^{-2}$  mol/L), respectively.





**Figure 2** Conversion versus time and number of particles versus conversion (inset) for VA and BA emulsion polymerizations with a mixture of aerosol MA-80 and OT-10 as the surfactant ( $W = 500$  g, monomer = 250 g, KPS = 0.27 g, SBc = 0.27 g, MA-80 = 5 g, and OT-10 = 10 g). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

So nucleation occurred in the presence of micelles, probably via micellar nucleation mechanism, for both polymerizations with SLS and aerosols. The reason for this discrepancy in  $N_p$  can be attributed to the surfactants properties. A high CMC value for aerosols probably means a better availability of emulsifier molecules for adsorption onto growing particles and better particle stability during the growth stage. However, adsorption of anionic surfactants, such as, SLS at the fairly polar vinyl acetate latex surface is generally weak and shows complex adsorption isotherms. It has been shown that SLS molecules adsorb on the surface of PVA particles and then slowly penetrate into the particles taking water with it causing swelling and gradual dissolution of the disintegrated polymer chains.<sup>17</sup> Vijayendran et al. demonstrated that bulkier anionic surfactants, such as, aerosols, adsorb only at the latex interface and are unable to penetrate into particles.<sup>18</sup> These surfactants showed a normal saturation type adsorption behavior. We also noted that PVA latexes obtained using SLS transformed to a clear gel-like material after a few weeks. This did not happen when aerosols were used as surfactant. The gradual penetration of SLS molecules into polymer particles could contribute to particle instability/coagulation in the course of nucleation. Note that the area occupied by a molecule of surfactant on polar polymers, such as, PVA is much greater than that on hydrophobic polymers, such as, PBA. This may indicate that a larger number of particles can be expected in the course of polymerization, if the surfactant is appropriate. The results obtained confirm that SLS may

not be a proper surfactant for VA emulsion polymerization due to its solubilization in the polymer phase.

Generally, polymerizations of VA and BA became rather similar, in terms of  $R_p$ , when the aerosol mixture was used as surfactant, as indicated in Figure 2 (note that the rate is larger for BA in terms of g/L min but equal in terms of g mol/L min). Kong et al. showed that VA and BA homopolymerize at very similar rates in the presence of aerosol MA.<sup>16</sup> In comparison with SLS, application of aerosols accelerated the rate of polymerization for VA monomer, but depressed that for BA monomer. This may indicate that the rate of polymerization for both monomers varied according to their change in  $N_p$ . For Case I polymerization systems such as VA, however, only a slight change in  $R_p$  is expected with variations in  $N_p$ .<sup>3,10</sup> Table II compares the rate of polymerization ( $R_p$ ) and number of particles for the runs with SLS and aerosols at  $M/W = 0.50$ . The average number of radical number ( $\bar{n}$ ) is calculated from the following equation.

$$\bar{n} = \frac{R_p N_A}{k_p M_p N_p} \quad (2)$$

where  $k_p$  is the rate coefficient of propagation,  $M_p$  is monomer concentration in the polymer particles, and  $N_A$  is Avogadro's number. The  $\bar{n}$  values are also listed in Table II. One should note that the radical number is a model-based quantity whose magnitude is highly dependent on the  $k_p$  value assumed.<sup>6</sup> Literature values of  $k_p$  for BA monomer are widely spread. In this work,  $k_p = 2.94 \times 10^5$  L/mol min was used. The  $\bar{n}$  values calculated are consistent with those published elsewhere using the same  $k_p$  value.<sup>6</sup> An interesting result is that the average radical number,  $\bar{n}$ , increased significantly for VA but decreased for BA when aerosols were used as the surfactant, as indicated in Table II. For monomers confined to Case I kinetics, such as, VA and BA,  $\bar{n}$  is

**TABLE II**  
Comparison of Measured and Calculated Kinetic Parameters in VA and BA Polymerizations with SLS and Aerosols [ $M/W = 0.50$ , (S) = 10 g/L]

	SLS		Aerosols	
	VA	BA	VA	BA
$N_p$ (1/L)	$2 \times 10^{17}$	$3 \times 10^{17}$	$3 \times 10^{17}$	$2.7 \times 10^{17}$
$M_p$ (mol/L)	8.43	4.01	8.43	4.01
$R_p$ (mol/L min)	0.0545	0.252	0.134	0.133
$\bar{n}$	0.14	0.43	0.23	0.25

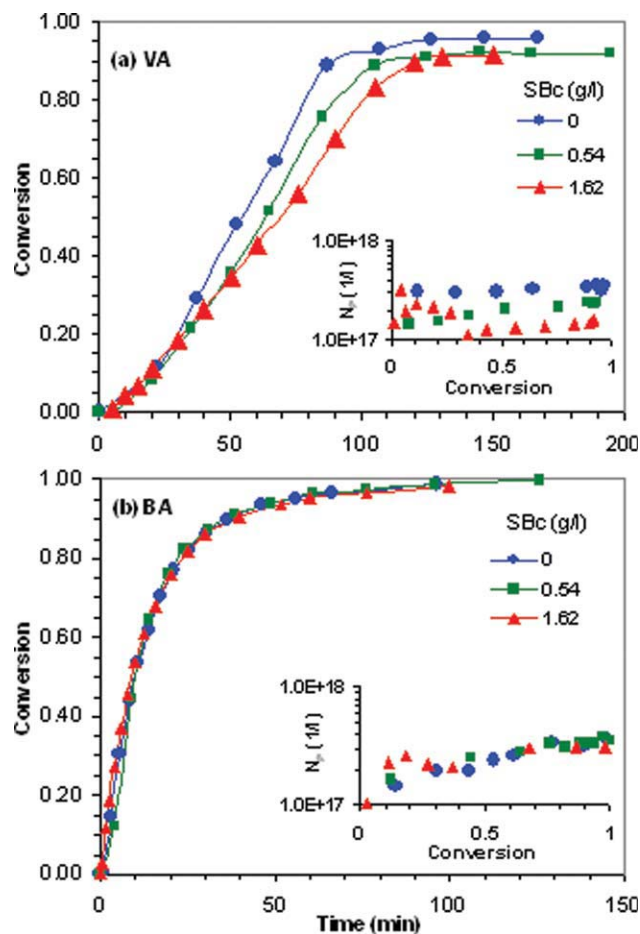
VA:  $k_p = 1.38 \times 10^5$  L/mol min;  $x_{cr} = 0.23$ .  
BA:  $k_p = 2.94 \times 10^5$  L/mol min;  $x_{cr} = 0.45$ .

proportional to  $[I]^{1/2}$  ( $[I]$  is initiator concentration). For VA polymerization, however, the increase in  $\bar{n}$  corroborates rather well with the increase in  $[I]$  in the experiment with aerosols (see Table II). Lee and Mallinson<sup>19</sup> in their study of continuous polymerization of VA, using aerosol OT (sodium dioctyl sulfosuccinate) and SLS as surfactants, found out an increase in  $R_p$  and  $N_p$  when SLS was replaced by aerosol OT, a result observed in this work too. From the experimental molecular weight, however, they concluded that aerosol OT probably acted as a chain transfer site during polymerization. This suggestion, however, cannot justify the simultaneous increase in the radical number in the presence of aerosols as observed in this work. However, the assumption of radical chain transfer to aerosols and subsequent termination in the aqueous phase is more plausible for BA polymerization, which underwent a significant radical loss. More research is required to shed light on the underlying mechanisms by which aerosol surfactants affect particle nucleation and stability. This may include the impurities contained in the aerosol surfactants. However, the results obtained in this work suggest that radical number could be affected by the type of the surfactant used. It is also concluded that kinetic events occurring in emulsion polymerizations can be influenced by the stability of particles and that can change the comparative standing of different monomers.

### Effect of electrolyte concentration

Variation of the electrolyte or buffer concentration inevitably changes the ionic strength of the aqueous phase. Several consequences of this have been discussed in the literature. Electrolytes reduce the surfactant solubility in the water phase and consequently decrease the CMC value of the surfactant, which in turn may increase the number of polymer particles. However, the most important effect is that the diffuse part of the electrical double layer is compressed leading to a possible increase in the rate of particle coagulation. The effect might be minor at a low electrolyte concentration, but can lead to complete destabilization of particles at sufficiently high electrolyte concentration.<sup>20</sup>

Figure 3 shows the conversion-time curves for BA and VA homopolymers using different electrolyte concentrations. For BA monomer, the rate of polymerization as well as the number of particles did not significantly change with the electrolyte concentration within a wide range. For VA monomer, the rate of polymerization decreased when a small quantity of electrolyte was used. This was associated with a significant reduction in the number of particles. Polar monomers usually produce particles



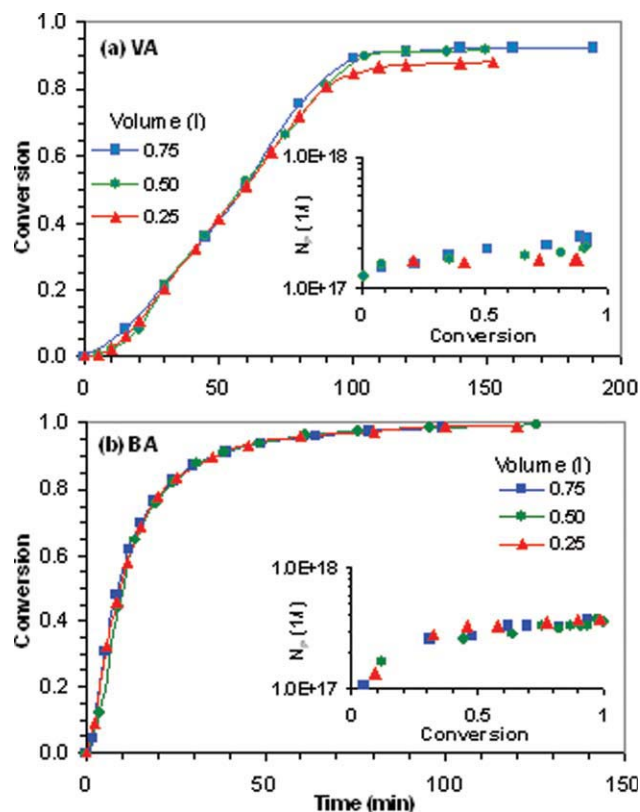
**Figure 3** Conversion versus time and number of particles versus conversion (insets) for (a) VA and (b) BA emulsion polymerizations in the presence of various electrolyte concentrations (See Table I for the formulation). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

with less stability, in comparison with nonpolar ones, because of weak adsorption of the surfactant molecules on the surface of particles. Consequently, they are more vulnerable to electrolyte-induced coagulation. The area occupied by a molecule of surfactant on polymer particles ( $a_s$ ) increases with water solubility of the monomer due to a weaker adsorption. In addition, it has been shown that  $a_s$  is not constant and increases with ionic strength resulting in further instability of polar particles with increasing electrolyte concentration.<sup>21</sup> These effects collectively result in a significant instability of primary particles against flocculation for polar polymers such as PVA particles. It is known that for any system there is a critical concentration of the electrolyte below which particles remain stable. This concentration is obviously smaller for VA monomer, due to its polar nature, than for BA monomer. It is quite likely that a drop in  $N_p$  for BA monomer will occur at a higher concentration of the electrolytes.

### Effect of the reaction volume

The effect of mixing on the kinetics of emulsion polymerization has been studied in the past.<sup>3,4</sup> An extreme mixing intensity can affect the rate of polymerization as well as particle formation. The main cause for particle coagulation in emulsion polymerization is Brownian motion. Particle coagulation, however, may also be caused by induced shear which occurs at high agitation speed.<sup>22</sup> At a low agitation speed, the rate of polymerization is controlled by the rate of monomer transport. It has been reported that at a low stirring speed and under highly diffusion-controlled conditions VA monomer produces more particles than BA monomer, whereas at a high impeller speed and under monomer-flooded conditions both monomers produced a similar number of particles.<sup>4</sup> For a typical emulsion polymerization, there is a certain range within which the kinetics of polymerizations seems to be independent of the rate of stirring. Similar effects can be expected for the reaction volume. Laboratory works on emulsion polymerization have been reported using reactors with a wide range of volumes from 0.10 to 10.0 L. At a constant stirring speed, the time frequency of particles passing through the high shear impeller zone increases as the reaction volume decreases. This might influence the rate of particle coagulation by increasing the rate of particle collisions, especially for small reactors. A large reaction volume may also depress the rate of monomer transport to polymer particles and lead to diffusion-controlled polymerization. Furthermore, polymerization reactors are not usually used by full capacity. In many occasions, the reactor content could be a small fraction of the total reactor volume. The variations in reaction volume are particularly important in semibatch emulsion polymerization reactors where a significant part of the monomer and other ingredients are added to the reactor over the time.<sup>23</sup>

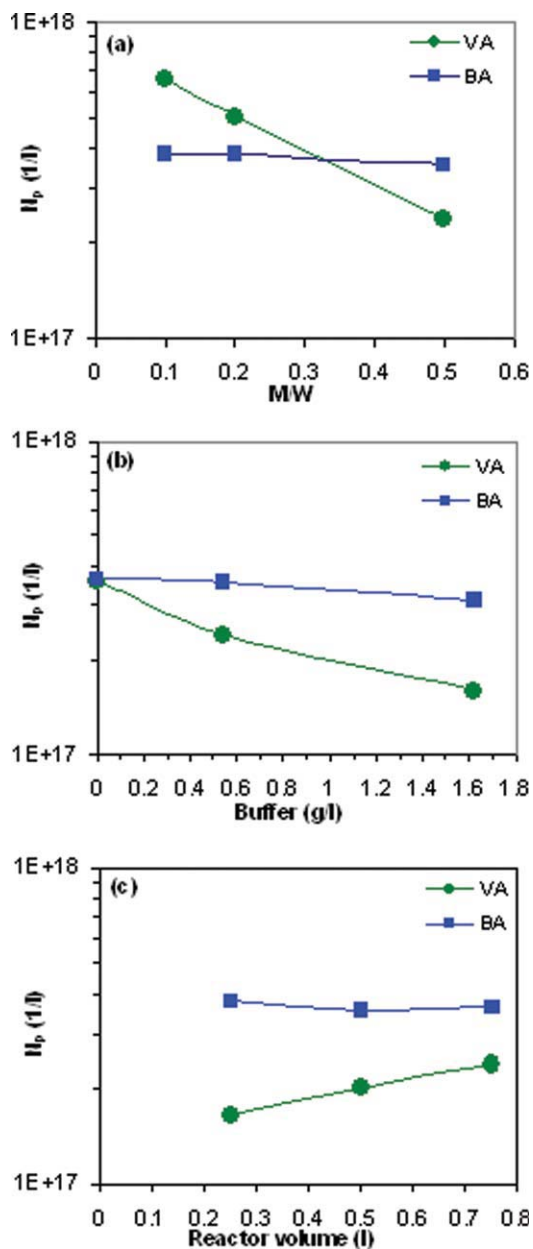
A study was performed to investigate the effect of varying reaction volume on the batch polymerization features at lab scale. It should be noted that the objective for this set of experiments is different from that for scale-up ones in which the reactor volume (size), as well as the impeller diameter and speed, are altered. Such experiments are associated with a change in characteristic features of mixing, such as, mechanical energy per unit volume, impeller tip speed, shear rate, pumping rate, etc. In the system under study, the stirring speed was maintained constant at 325 rpm. Therefore, the impeller tip speed and shear rate remained almost constant for all three reaction volumes used. The main variable in this set is in fact mechanical energy per unit volume, which inversely varies with the active reaction volume. The base formulation (with reaction volume of 0.75 L)



**Figure 4** Conversion versus time and number of particles versus conversion (insets) for (a) VA and (b) BA emulsion polymerizations for different reaction volumes (The reaction volume for the base formulation is 0.75 L as seen in Table I). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

was scaled down to lower reaction volumes of 0.50 L and 0.25 L. The conversion-time and  $N_p$ -conversion curves for VA and BA emulsion polymerizations are shown in Figure 4. No appreciable variation in the rate of polymerization and number of particles was found for BA monomer. For VA monomer, however, a small increase in the number of particles was observed but the rate of polymerization remained unaffected with increasing reaction volume. It is possible to conclude that newly formed particles in the smaller reaction volumes are lost, probably due to more frequent subjection to high shear rate region. For Case I kinetics where  $\bar{n}$  is very low, such as, VA emulsion polymerization,  $R_p$  is almost independent of  $N_p$  ( $R_p \propto N_p^{0.15}$ ). It can also be concluded that particle nucleation in semibatch emulsion polymerization reaction of VA monomer with a constant stirring might be more vulnerable to particle coagulation than corresponding batch operation if polymerization starts with a small fraction of emulsion recipe. It is thought that reaction volume plays a more critical role in unstabilized latexes, where the amount of surfactant is not enough to stabilize particles against shear-induced coagulation.





**Figure 5** Variations in  $N_p$  versus (a)  $M/W$ , (b) buffer concentration, and (c) reactor volume for VA and BA emulsions polymerization (See Table I for the formulation). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

## CONCLUSIONS

The degree of sensitivity of VA and BA monomers to variations in secondary parameters within the range studied was found to be quite different. The number of particles is plotted in terms of monomer concentration, electrolyte concentration, and reaction volume for VA and BA monomers in Figure 5. VA polymerization was found to be more vulnerable to changes in the polymerization conditions within the

range studied, whereas BA polymerization proved to be more robust. VA emulsion polymerization produced a larger number of particles at a lower monomer concentration, whereas for BA monomer the number of particles did not change significantly with monomer concentration. VA emulsion polymerization was found to be quite sensitive to particle instabilities caused by electrolyte concentration and energy input per unit volume. Figure 5(c) shows how  $N_p$  varies with reaction volume (or inverse of mechanical energy per unit volume) for VA and BA monomers. Aerosols MA and OT were found to be more effective in hindering particle coagulation for VA polymerization in comparison with BA. VA emulsion polymerization using the aerosol surfactants, proceeds practically at a similar rate of reaction with that of BA, but produced a larger number of particles. The results suggest that a careful examination of homopolymerization of monomers under a wide range of conditions can provide a better explanation for the trends observed in the copolymerization of the same monomers.

## References

- Chern, C. S. *Prog Polym Sci* 2006, 31, 443.
- Nomura, M.; Tobita, H.; Suzuki, K. *Adv Polym Sci* 2005, 175, 1.
- Nomura, M.; Harada, M.; Eguchi, W.; Nagata, S. *J Appl Polym Sci* 1972, 16, 835.
- Sajjadi, S.; Jahanzad, F. *Chem Eng Sci* 2006, 61, 3001.
- Kemmere, M. F.; Meuldijk, J.; Drinkenburg, A. A. H.; German, A. L. *J Appl Polym Sci* 1999, 74, 3225.
- Sajjadi, S.; Brooks, B. W. *J Polym Sci Part A: Polym Chem* 1999, 37, 3957.
- De la Rosa, L. V.; Sudol, E. D.; El-Aasser, M. S.; Klein, A. *J Polym Sci Part A: Polym Chem* 1999, 37, 4073.
- Nomura, M.; Harada, M. *ACS Symp Ser* 1981, 165, 121.
- Zollars, R. L. *J Appl Polym Sci* 1979, 24, 1353.
- Friis, N.; Nyhagen, L. *J Appl Polym Sci* 1973, 17, 2311.
- Nomura, M.; Harada, M.; Eguchi, W.; Nagata S. In *ACS Symposium Series*; Piirma, I., Gardon, L., Eds.; American Chemical Society, USA, 1976; Vol. 24, p. 102.
- Vijayendran, B. R. *J Appl Polym Sci* 1979, 23, 733.
- Sajjadi, S. *J Polym Sci Part A: Polym Chem* 2002, 40, 1652.
- Sajjadi, S. *Langmuir* 2006, 23, 1018.
- El-Aasser, M. S.; Makgawinata, T.; Vanderhoff, J. W.; Pichot, C. *J Polym Sci Polym Chem Ed* 1983, 21, 2363.
- Kong, X. Z.; Pichot, C.; Guillot, J. *Eur Polym J* 1988, 24, 485.
- Edelhausser, H. A. *J Polym Sci Part C: Polym Symp* 1969, 27, 291.
- Vijayendran, B. R.; Bone, T.; Gajria, C. *J Appl Polym Sci* 1981, 26, 1351.
- Lee, C. H.; Mallinson, R. G. *J Appl Polym Sci* 1990, 39, 2205.
- Dunn, A. S.; Said, Z. F. M. *Polymer* 1982, 23, 1172.
- Piirma, I.; Chen, S. R. *J Colloid Interface Sci* 1980, 74, 90.
- Chern, C. S.; Kuo, Y. N. *Chem Eng Sci* 1996, 51, 1079.
- Sajjadi, S.; Brooks, B. W. *J Appl Polym Sci* 1999, 74, 3.