

# Miniemulsion and Macroemulsion Copolymerization of Vinyl Acetate with Vinyl Versatate

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**ABSTRACT:** The miniemulsion and macroemulsion polymerization of vinyl acetate with vinyl versatate in batch and semibatch systems was investigated. Vinyl versatate was added either as an emulsion with the vinyl acetate, or as a neat liquid stream. In the batch runs, there is a poor dispersion of vinyl versatate during the nucleation period for the runs in which the vinyl versatate was added neat at the beginning of the polymerization. This led to smaller particles, lower polymerization rate, and different polymer composition evolution when compared with runs in which the vinyl versatate was emulsified with the vinyl acetate. In seeded semibatch runs, residual surfactant in the seed latex, along with the propensity for homogeneous nucleation in vinyl acetate emulsions, resulted in continuing nucleation during the entire semibatch interval. The polymerization rate was primarily affected by monomer feed rate rather than the feeding mode. The effect of monomer feeding mode on copolymer composition was weak when the semibatch feed rate was low, indicating some level of vinyl versatate mass transfer resistance. In all runs, only one glass transition temperature was observed, indicating effective copolymerization. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2219–2229, 2002

**Key words:** emulsion polymerization; copolymerization; micelles

## INTRODUCTION

Issues of monomer mass transfer can be important in emulsion and miniemulsion copolymerization, particularly when one of the monomers has very low water solubility. Since the bulk of the mass transfer resistance is from the monomer droplets into the aqueous phase, miniemulsion

polymerization may provide some advantages over conventional emulsion (macroemulsion) polymerization, since the monomer droplets are smaller by at least one order of magnitude, and therefore provide a very large area for interfacial mass transfer. The following study was undertaken to explore issues of mass monomer mass transfer in mini- and macroemulsion polymerization. The system of vinyl acetate (VAc) and vinyl versatate was used in this because of its commercial importance, and because the water solubilities of the two monomers vary substantially. VAc/vinyl versatate polymers exhibit excellent hydrophobicity, hydrolytic stability, and ultraviolet

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(UV) resistance. These properties ensure long-lasting good performance when used in interior and exterior latex paints. There is extensive data concerning the performance properties and applications of VAc/vinyl versatate copolymers.<sup>1,2</sup> However, little work has been done on the polymerization aspects. Balic<sup>3</sup> investigated the kinetics of homopolymerization of neodecanoate. Araujo et al.<sup>4</sup> studied VAc/vinyl versatate copolymerization in a loop reactor. Unzue et al.<sup>5</sup> have used a mathematical model of this system to optimize polymerization rate and thus minimize kettle time. Since vinyl versatate has the same reactive group as VAc, its reactivity is close to that of VAc in free radical polymerization.<sup>6</sup> This feature benefits synthesizing random copolymers of VAc/vinyl versatate, which is highly desired to enhance the performance of resulted coatings.

At room temperature, the water solubility of VAc is 2.58 wt %, and neodecanoate (one of the isomers in Veova-10) is  $7.5 \times 10^{-4}$  wt %.<sup>3</sup> The extreme difference in water solubility between the two comonomers may impact copolymer composition and the properties of final polymer, due to the mass transfer of monomers.<sup>7</sup> In this work, mini- and macroemulsion polymerizations of VAc/vinyl versatate, were designed to investigate the effects of monomer transport and feeding strategies (for semibatch runs) on the reaction rate, particles size distribution, molecular weight distribution, copolymer composition, and glass transition temperature ( $T_g$ ) of the resultant polymer.

## EXPERIMENTAL

### Materials

Reagent grade VAc was supplied by Aldrich Co., vinyl versatate (Veova-10, >99%) was supplied by Shell Chemical Co. The inhibitors in both monomers were removed by using inhibitor remover (disposable column, for removing hydroquinone and hydroquinone monomethyl ether). The treated monomers were stored at  $-2^\circ\text{C}$  until used. Potassium persulfate (KPS, 99% Aldrich), sodium lauryl sulfate (SLS, 98% Aldrich), hexadecane (HD, 99% Aldrich), and hydroquinone (HQ, 98% Fisher) were used as supplied. The water used was deionized.

### Polymerization

The experimental modes and recipes are listed in Table I. For all runs, polymerization temperature

was  $55^\circ\text{C}$ , and impeller speed was 300 rpm. Semibatch runs utilized seed obtained via the mode of *mibat*. For each semibatch mode, three runs were carried out, at feed rates of 0.6 and 0.15 ml/min respectively. For example, mis6 refers to the feed rate set at 0.6 mL/min. For batch miniemulsion polymerizations, the cosurfactant (HD) was dissolved in the monomer mixture. A part of total recipe water (20%) was taken for the preparation of initiator solution. The surfactant (SLS) was dissolved in the remaining of water. The monomer solution was dispersed into the water solution, creating a course emulsion. The course emulsion was pumped through the flow cell on a Fisher 300W Sonic Dismembrator to form the miniemulsion.

Then the miniemulsion was flowed into a 250 mL reactor, which was equipped with nitrogen purging tube, condenser, temperature controller, and stirrer. With nitrogen purging, the reaction materials were heated to  $55^\circ\text{C}$  for 20 min. The initiator solution was then injected into the reactor to start the polymerization. At intervals, samples of 5–6 g were removed from reactor with a syringe for gravimetric conversion analysis. Samples were injected into vials containing 0.5 wt % HQ solution to quench the polymerization. In batch macroemulsion polymerization, the preparation was the same with the exception that there was no sonication (and, of course, no HD).

In the polymerization of VAc miniemulsions (or macroemulsions) plus neat vinyl versatate, the VAc miniemulsion (or macroemulsion) was made up as above. The neat vinyl versatate was injected into the polymerization system at the same time as the injection of initiator solution.

For the semibatch processes, 20 wt % of the polymer solids was in the form of seed and the remaining 80% was fresh monomer emulsion. The seed latex was prepared as a miniemulsion polymerization (using the *mibat* recipe). To prepare fresh monomer emulsion, the monomer solution was added into the surfactant aqueous solution under stirring, so that a uniform emulsified mixture was obtained. Before being added into the reactor, the emulsion passed through the sonication cell to form the miniemulsion (for the preparation of macroemulsions, this step was eliminated). Thus, the miniemulsion was made (sonicated) in-line, immediately prior to feeding into the reactor. The first shot of initiator solution was introduced when the feed of monomer emulsion started. A subsequent shot followed the removal

**Table I** Experimental Modes and Recipes for Batch and Semibatch Runs

Exp. Code	Modes of Batch Experiments
<b>mibat</b>	Miniemulsion polymerization of VAc/Veova-10
<b>mabat</b>	Macroemulsion polymerization of VAc/Veova-10
<b>minbat</b>	Polymerization of (VAc miniemulsion + neat Veova-10)
<b>manbat</b>	Polymerization of (VAc macroemulsion + neat Veova-10)
Recipes	
VAc/(VAc + VeoVa) = 0.8 wt/wt = 0.9 mol/mol Oil/(Oil + Water) = 0.3 wt Oil + Water = 300 g SLS = 0.02 mol/L-water KPS = 0.03 mol/L-water HD = 1.5% wt in monomer (only for mibat and minbat)	
Exp. Code	Modes of Semibatch Experiments
<b>mis6, mis15</b>	Seed + feeding miniemulsion of VAc/Veova-10
<b>mas6, mas15</b>	Seed + feeding macroemulsion of VAc/Veova-10
<b>min6, min15</b>	Seed + feeding (VAc miniemulsion + neat Veova-10)
<b>man6, man15</b>	Seed + feeding (VAc macroemulsion + neat Veova-10)
Recipes for Feeds	
(Seed: Feed = 1:4) VAc/(VAc + Veova) = 0.8 wt/wt = 0.9 mol/mol Oil/(Oil + water) = 0.3 wt Oil + Water = 220 g SLS = 0.005 mol/L-water KPS = 0.03 mol/L-water HD = 1.5% wt in monomer (only for mis6, 3, 15, and min6, 3, 15)	

of each latex sample. Samples of 5–6 g were removed at intervals from reactor with a syringe for gravimetric conversion analysis. Samples were injected into vials containing 0.5 wt % HQ solution to quench the polymerization. The reactor system was continuously purged with nitrogen during polymerization.

In the semibatch runs of VAc miniemulsion (or macroemulsion) plus neat vinyl versatate, with simultaneous feeding of VAc miniemulsion (or macroemulsion), the neat vinyl versatate was injected into the polymerization system two (for the feed rate of 0.6 mL/min) or three (for 0.3 mL/min) times during each sampling interval.

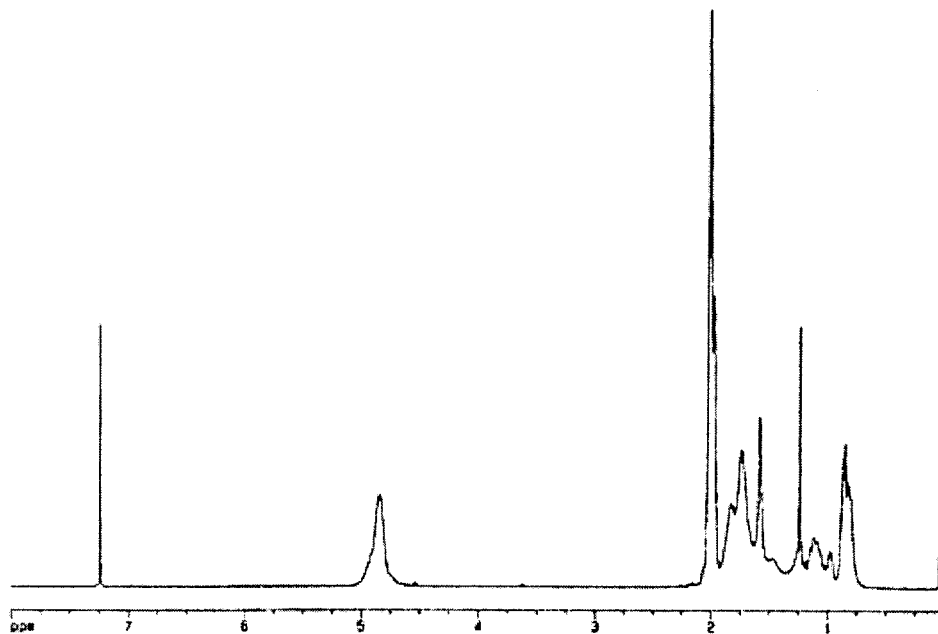
### Particle Size

Polymer particle sizes were measured by light scattering with a ProteinSolution LSR-TC instrument. To measure polymer particle size, the latex was diluted in a 0.2 wt % SLS aqueous solution. The diluted solution was heated at 50°C for 4 h to drive off the residual volatile monomer. The

treated particle suspension was diluted again with DI water then placed in a plastic curette for analysis.

### Composition of Copolymer

The composition of the copolymer was obtained by <sup>1</sup>H nuclear magnetic resonance (NMR) analysis. The samples were dried and washed before analysis. The <sup>1</sup>H-NMR spectra of samples were recorded at 24°C with a Bruker AMX 400 system and Xwinnmr software. Deuterated chloroform (CDCl<sub>3</sub>) was used as reference and solvent. A typical spectrum was shown in Figure 1. The peak at 7.24 ppm is from the deuterated chloroform. The resonance peak around 1.98 ppm corresponds to the shift of the —CH<sub>3</sub> group in the vinyl acetate unit. The peak around 0.90 ppm is the resonance of the —CH<sub>3</sub> group in the vinyl versatate unit. The copolymer composition was calculated from the relative intensities (integral value) of the peaks at 1.98 and 0.90 ppm. Thus, the percentage



**Figure 1** Typical NMR spectrum for copolymer of Vac/vinyl versate.

of vinyl acetate was calculated by using the following equation:

$$\text{VAc}\% = \frac{S_{1.98}/3}{S_{1.98}/3 + S_{0.90}/9} \times 100\% \quad (1)$$

where  $S_{1.98}$  and  $S_{0.90}$  are integral areas of the peaks at 1.98 and 0.90 ppm respectively.

### Glass Transition Temperature and Molecular Weight

The glass transition temperature,  $T_g$ , of polymer in the final latexes was measured with a differential scanning calorimetry, DSC-7 (Perkin-Elmer). The scanning was set from  $-30.0$  to  $+100.0^\circ\text{C}$  at a rate of  $10.0^\circ\text{C}/\text{min}$ .

A Waters Gel Permeation Chromatography (GPC) system was used to measure the molecular weight of the synthesized polymers. The GPC system included a Waters 510 HPLC (high performance liquid chromatography) Pump, Waters 410 Refractive Index Detector, and three columns ( $300 \times 7.8$  mm, in series, gel pore sizes of  $10^3$ ,  $10^4$ , and  $10^6$  Å). The TriSec GPC Software (ViscoTek) was used to calculate the molecular weight via conventional calibration related to polystyrene standards. The samples were prepared by dissolving the dried latex in tetrahydrofuran (THF) at a

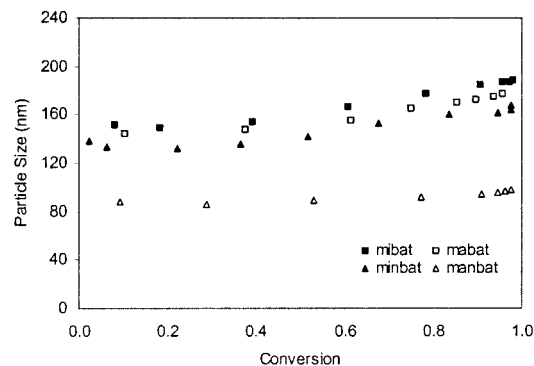
concentration of 5 mg/mL THF. The GPC was operated at room temperature and a flow rate of mobile phase (inhibitor-free HPLC-grade THF) of 1.0 mL/min.

## RESULTS AND DISCUSSION

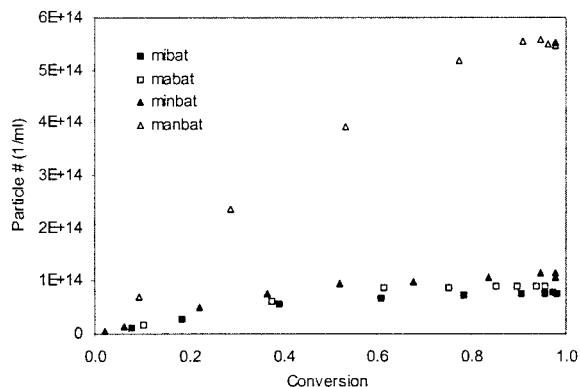
### Part I: Batch Experiments

#### Particle Size

The evolution of polymer particle size and number with monomer conversion for all batch runs is

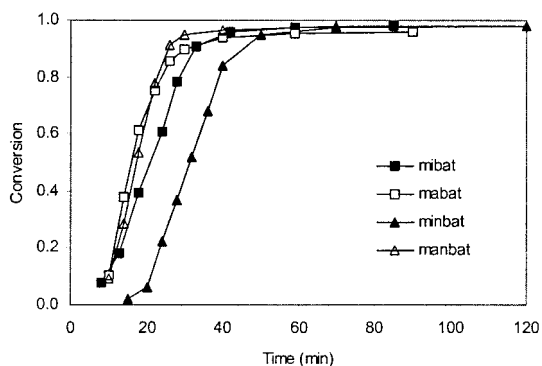


**Figure 2** Particle size changes with conversion in batch runs.

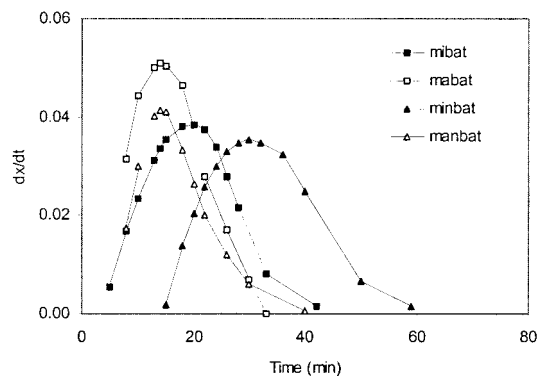


**Figure 3** Particle number changes with conversion in batch runs.

shown in Figures 2 and 3. As expected, the polymer particle sizes in the macroemulsion (*mabat*) [or macroemulsion + neat vinyl versatate (*manbat*)] polymerization are smaller than that in the miniemulsion (*mibat*) [or miniemulsion + neat vinyl versatate (*minbat*)] process. Adding neat vinyl versatate led to smaller particle sizes and higher particle numbers. This can be ascribed to the effect of monomer concentration. In the *minbat* and *manbat* experiments the same recipe was used as in the *mibat* and *mabat* experiments, but with only VAc was used to prepare the emulsion, while the vinyl versatate was added neat at the beginning of the polymerization. With neat vinyl versatate, the monomer concentration in the emulsion was relatively low, so that the droplet size was lower in miniemulsion (for *minbat*), or the number of micelles were higher in macroemulsion (for *manbat*). As soon as the neat vinyl versatate was added, the polymerization was initiated. At this point, nucleation was primarily caused by droplet nucleation (miniemulsion) or



**Figure 4** Conversion-time curves for the batch runs.

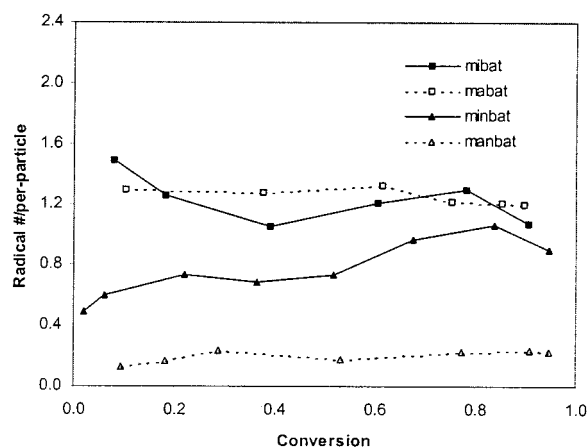


**Figure 5** Reaction rate curves for the batch runs.

micellar nucleation (macroemulsion). Because of the poor dispersion of vinyl versatate, it did not participate in the nucleation. The effects caused by insufficient dispersion of vinyl versatate during initial period is further discussed in following sections.

### Polymerization Rate

Figure 4 shows the conversion-time curves of the batch runs. From conversion-time curves, the rates of polymerization (first derivative of the conversion-time curves) were estimated and are shown in Figure 5. One can see that the rate of macroemulsion polymerization is faster than that of the miniemulsion polymerization. Interestingly, the polymerization rates for **minbat** and **manbat** are lower than that of their counterparts, **mibat** and **mabat**. However, as shown above, the particle numbers in **minbat** and **manbat** are much higher than in their counterparts.



**Figure 6** The  $\bar{n}$  vs conversion for all batch runs.



The average radical number in per particle, ( $\bar{n}$ , calculated from the rate of polymerization, and the particle number) vs conversion is plotted in Figure 6. One may see that, in the nucleation period (conversion less than 0.2), the  $\bar{n}$  values for **minbat** and **manbat** show very different trends compared with their counterparts, increasing slowly from relatively low levels. These phenomena may be explained by considering the transport of free radicals into and out of monomer-swollen particles.

During the nucleation period, primary radicals formed from initiator decomposition in the aqueous phase grow into oligomeric radicals. Only when the oligomers have grown to a critical length can they be captured by monomer droplets, surfactant micelles, or monomer-swollen particles. The critical chain length varies widely with monomer. If vinyl versatate is well incorporated into the oligomer radical chain, the efficiency of capture will be enhanced due to the high hydrophobicity of vinyl versatate. On the other hand, reinitiation inside the monomer-swollen particles may occur due to chain transfer to monomer. The monomeric radical formed may desorb from the particle. Desorption of pure VAc oligomers is favored over vinyl versatate-containing radicals due to the same considerations of hydrophobicity. When Chern and Poehlein considered the monomer-unit radical transport out of particles, they noted that there was a relationship among the rate constant for desorption of a monomeric radical,  $k_{dm}$ , the diffusion coefficient of the monomeric radical,  $D_m$ , and the particle size,  $d$ , shown as below<sup>8</sup>:

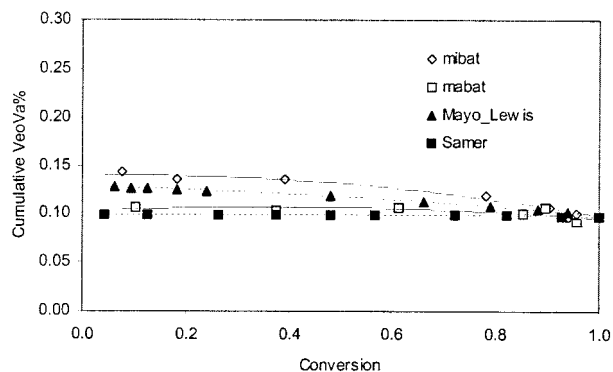
$$k_{dm} \propto D_m d^{-2} \quad (2)$$

Since the concentration of monomeric radicals in monomer-swollen particles is extremely low, the system inside particles can be taken as a dilute solution in the nucleation period. Thus, the diffusion of monomer-unit radical in the particle phase follows the theory of molecular diffusion in dilute solution.<sup>9</sup>

$$D_m \propto r_m^{-1} \quad (3)$$

where  $r_m$  refers to the radius of monomeric radical. Thus,

$$k_{dm} \propto r_m^{-1} d^{-2} \quad (4)$$



**Figure 7** Cumulative composition vs conversion in bath macro/mini-emulsion copolymerization of VAc/vinyl versatate.

Thus, the VAc radical will tend to leave the particle more easily than a vinyl versatate radical, due to its smaller radius.

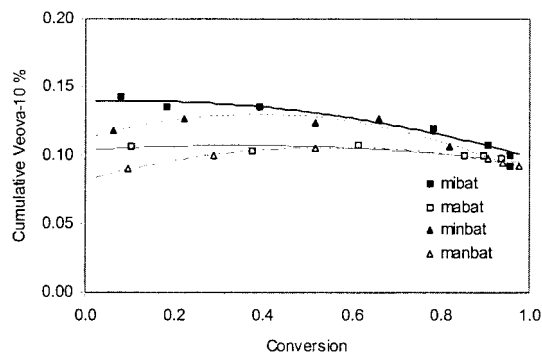
Because of the poor dispersion of vinyl versatate during the period of nucleation in the *minbat* and *manbat* experiments, vinyl versatate was not effectively present to enhance the capture of oligomer radicals from aqueous phase or retard the loss of monomeric radicals from particles. Therefore, the polymerization rate of these two runs was depressed even though the particle numbers were higher than that in **mibat** and **mabat**.

### Composition of Copolymers

The composition of copolymers was analyzed with proton NMR. The profiles of cumulative polymer composition versus conversion for **mibat** and **mabat** were plotted in Figure 7. The vinyl versatate molar content with respect to the total monomer in the recipe is 0.098. The curve calculated by integrating the Mayo–Lewis equation,<sup>9</sup> eq. (5), represents theoretical comonomer incorporation under conditions where the mole fraction of each monomer at the locus of polymerization is equal to its mole fraction in the recipe.

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1] r_1 [M_1] + [M_2]}{[M_2] [M_1] + r_2 [M_2]} \quad (5)$$

Here  $[M_i]$  is the monomer molar concentration at the polymerizing site. The reactivity ratios (for homogeneous copolymerization),  $r_1$  and  $r_2$ , used here were estimated based on the Q-e values<sup>6</sup> as 0.744 for VAc and 1.382 for vinyl versatate. The



**Figure 8** Cumulative composition vs conversion profiles in all batch runs.

curves for the mini/macroemulsion polymerization are above and below the curve of the ideal case respectively, deviating slightly from the ideal case.

For the macroemulsion polymerization of VAc/vinyl versatate, since the water solubility of vinyl versatate is significantly low compared with Vac [similar to Wu and Schork's work on VAc/DOM (dioctyl maleate) monomer system<sup>6</sup>], the evolution of polymer composition can be estimated via the following approximation. According to the method proposed by Samer<sup>11</sup> for extremely water-insoluble monomer, a pseudo-partition coefficient,  $\kappa$ , was used to replace the monomer partition coefficient,  $K$ , in Schuller's equation<sup>12</sup> (a modification of the Mayo-Lewis equation for emulsion polymerization), shown as below:

$$r'_1 = r_1 \frac{1 + (1/K_2\varphi)}{1 + (1/K_1\varphi)}$$

(6)

and

$$r'_2 = r_2 \frac{1 + (1/K_1\varphi)}{1 + (1/K_2\varphi)}$$

where  $K_i = [M_i]_p/[M_i]_a$  and  $\varphi = \text{organic volume}/\text{aqueous volume}$ .  $[M_i]_p$  and  $[M_i]_a$  are the monomer concentrations in the polymerizing particle and aqueous phases, respectively. Here, the partition coefficient of VAc,  $K_1$ , and pseudo-partition coefficient of vinyl versatate,  $\kappa_2$ , can be assumed as  $K_1 \rightarrow \infty$  and  $\kappa_1 \leftarrow 1$ . Thus the composition trend for the macroemulsion process was also estimated and plotted in the figure. The result is close to the experimental data.

In Figure 8, the copolymer composition evolu-

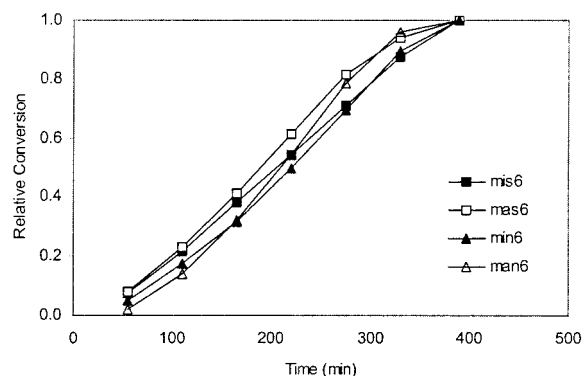
**Table II** Glass Transition Temperature and Molecular Weight for Final Latexes

Exp. Code	$T_g$ ( $^{\circ}\text{C}$ )	$M_w$ (K)	$M_n$ (K)	Polydispersity Index
mibat	26.1	1315.0	254.4	5.17
mabat	27.8	1129.0	260.0	4.34
minbat	26.4	1156.0	263.2	4.39
manbat	27.5	1204.0	259.4	4.64

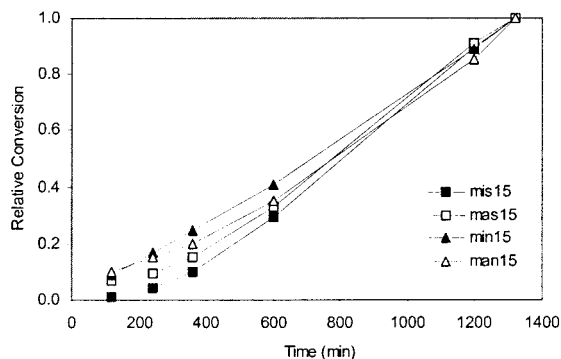
tion for all of the batch experiments is shown. During the nucleation period, the vinyl versatate content in the polymers is clearly lower for the neat addition of vinyl versatate (*manbat* and *minbat*) than for the emulsified addition (*mabat* and *mibat*) of vinyl versatate. With increasing conversion, the dispersion of vinyl versatate is improved and the deviations become smaller. This is further evidence in polymer composition to demonstrate that the insufficient dispersion of vinyl versatate can play an important role on polymerization, partly confirming the explanation above for the phenomenon of polymerization rate. It should be noted that these results are visible even though the reactivity ratios of VAc and vinyl versatate are similar, and the high water solubility of VAc helps to solubilize the vinyl versatate in the aqueous phase, two facts that would tend to minimize the evidence of copolymer composition drift caused by limited vinyl versatate transport.

### Glass Transition Temperature and Molecular Weight

The glass transition temperatures and molecular weights of the final polymers in batch runs are



**Figure 9** Relative conversion-time curves for the semibatch runs with the feed rate of 0.6 mL/min. The final overall conversions were mis6 0.553, mas6 0.561, min6 0.548, and man6 0.560.



**Figure 10** Relative conversion-time curves for the semibatch runs with the feed rate of 0.15 mL/min. The real conversions: mis15 0.6821, mas15 0.6565, min15 0.7497, and man15 0.6935.

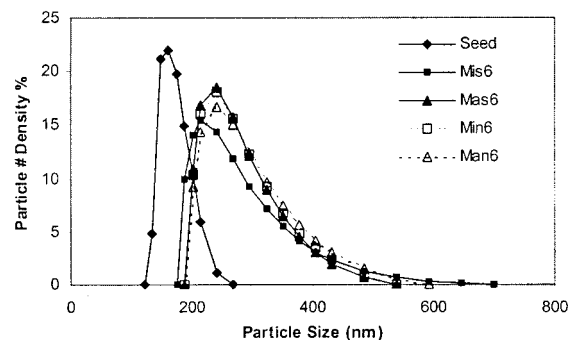
shown in Table II. For each sample, only one  $T_g$  could be seen. This indicates the absence of homopolymer. The homopolymer glass transition temperatures are 28–31°C.

For VAc, and  $-3^\circ\text{C}$  for vinyl versatate. The estimated  $T_g$  of copolymer at the recipe composition is 24–26.6°C. The experimental results are around this calculated  $T_g$ . The glass transition temperatures for the miniemulsion experiments are slightly lower compared with the macroemulsion runs. It would seem that the miniemulsion process favors the incorporation of vinyl versatate. Molecular weight determinations showed insignificant differences among the experiments.

## Part II: Semibatch Experiments

### Conversion, Particle Size, and Number

For the semibatch experiments, two monomer-addition strategies (neat or emulsified vinyl versatate) and two monomer feed rates (0.6 and 0.15 mL/min) were evaluated for both macro- and miniemulsion polymerization. For all of the semibatch runs, the overall conversion at time  $t$  is defined as follows:



**Figure 11** Particle size distribution of final latexes for seeds and semibatch runs with the feed rate of 0.6 mL/min.

$$X_t^0 = \frac{W_t}{W_f} \quad (7)$$

where  $W_t$  is the weight of the polymer produced by the time,  $t$ , and  $W_f$  is the weight of the total feeding monomers by the end. The relative conversion at time  $t$  is defined as

$$X_t^r = \frac{X_t^0}{X_e^0} \quad (8)$$

where  $X_e^0$  is the final overall conversion. The relative conversion-time curves are shown in Figures 9 and 10. It may be seen that, at constant feed rate, the monomer feed strategy does not influence the polymerization rate significantly.

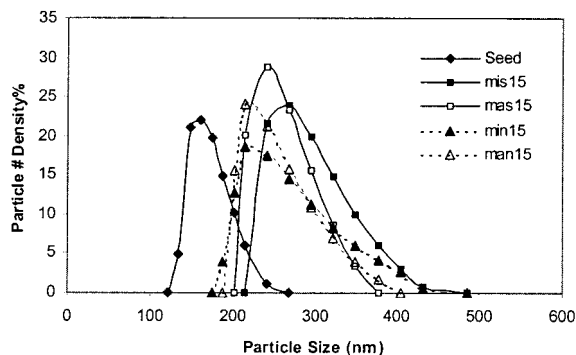
The average polymerization rate and the rate of monomer feed for each semibatch run is listed in Table III. The values for the ratio of average polymerization rate to feeding rate in all runs indicate that none of the polymerizations were run under monomer-staved condition.

The polymer particle size distributions of the final latexes for the semibatch runs are shown in Figures 11 and 12. The distribution curves in all the runs are unimodal. There is no significant difference between miniemulsion and macro-

**Table III** Average Polymerization Rate and the Rate of Feeding Monomers

Rate (g/L/min)	mis6	mas6	min6	man6	mis15	mas15	min15	man15
A poly rate, $R_p$	0.294	0.320	0.298	0.327	0.102	0.100	0.112	0.099
Feed rate, $R_f$	0.727	0.727	0.727	0.727	0.182	0.182	0.182	0.182
$R_p/R_f$	0.404	0.440	0.410	0.450	0.560	0.549	0.615	0.544





**Figure 12** Particle size distribution of final latexes for seeds and semibatch runs with the feed rate of 0.15 mL/min.

emulsion feeds. These results are quite different from those of Tang et al.<sup>13</sup> for the seeded (mini-emulsion seeds) polymerization of butyl acrylate.

In Table IV, the averages of the polymer particle size distribution, and particle number for all final latexes are listed. The difference caused by feeding mode is unclear. One may see that the particle size and polydispersity index corresponding to the feed rate 0.15 mL/min is lower slightly. The percentage of new particles nucleated in the feeding period is denoted as  $P_n$ . The runs *mis6* and *mis15* (feed of a miniemulsion of VAc/vinyl versatate), nucleated fewer new particles. Moreover,  $P_n$  is obviously higher in runs with the feed rate of 0.15 mL/min. This may be due to the fact that the residual surfactant in seed latex enhanced the homogeneous nucleation commonly found in VAc emulsion polymerization.<sup>6</sup> The runs with low feed rate were operated closer to mono-

mer starvation, and so the concentration of unreacted monomer was lower. Thus, more surfactant was available to form particles via homogeneous nucleation.

### Copolymer Composition

For the seeded polymerization process, the cumulative composition of copolymer involves two components, i.e., seed polymer, and polymer formed during the feeding process. Here, an attempt has been made to remove the effect of the seed on the copolymer composition. First, the cumulative molar fraction of monomer 1 incorporated in feeding period  $F_f$  was defined as below.

$$F_{f1} = \frac{F'_{f1}/M_{w1}}{(1 - F'_{f1})/M_{w2} + F'_{f1}/M_{w1}} \quad (9)$$

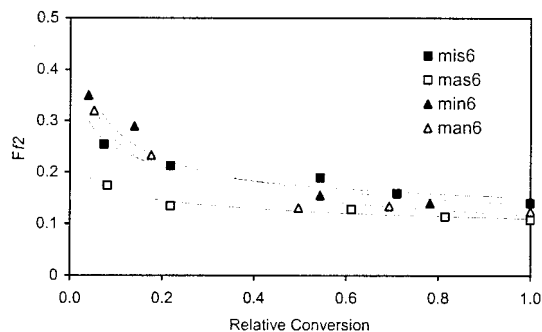
$$F'_{f1} = F'_t - \frac{(F'_s - F'_t)W_s}{W_f X'_t} \quad (10)$$

where  $W_s$  is the weight of polymer in the added seeds,  $F'$  is the mass composition of copolymer, and  $M_w$  is the molecular weight of the monomer. For the subscripts,  $e$  denotes the end of feeding stage,  $f$  denotes the feeding period,  $t$  denotes time of the feeding period, and 1 and 2 denote VAc and vinyl versatate, respectively. The relationships between  $F_f$  and  $X_f$  for the feeding period are plotted in Figures 13 and 14. The mole fraction of comonomer for the feeding recipe is 0.098. In the figures, all the trend lines are above the recipe level. This phenomenon was not seen for the mini/macroemulsion copolymerization of VAc/dioctyl

**Table IV** Polymer Particle Sizes and Distributions for Final Latexes<sup>a</sup>

Exp. Code	$D_v$ (nm)	$D_n$ (nm)	$D_w$ (nm)	Polydispersity Index	$N_p$ ( $10^{13}/\text{mL}$ )	$N_n$ ( $10^{11}/\text{mL}$ )	$P_n$ (%)
<b>Seed</b>	188.8	184.6	196.4	1.06	1.300	—	—
<b>mis6</b>	290.7	268.6	344.7	1.28	1.322	2.1	1.6
<b>mas6</b>	289.1	274.9	320.0	1.16	1.358	5.7	4.2
<b>min6</b>	288.2	272.6	320.6	1.18	1.347	4.6	3.4
<b>man6</b>	289.0	260.1	325.2	1.25	1.357	5.6	4.1
<b>mis15</b>	288.2	273.8	312.0	1.14	1.587	28.6	18.0
<b>mas15</b>	267.4	262.3	278.0	1.06	1.930	62.9	32.6
<b>min15</b>	276.6	268.0	295.0	1.10	1.933	63.2	32.7
<b>man15</b>	260.0	253.0	276.1	1.09	2.190	88.9	40.6

<sup>a</sup>  $D_v$ ,  $D_n$  and  $D_w$  are volume, number, and weight average diameters, respectively.  $N_p$  and  $N_n$  are the particle number and new particle number in the final latex.  $P_n = N_n/N_p$  %.



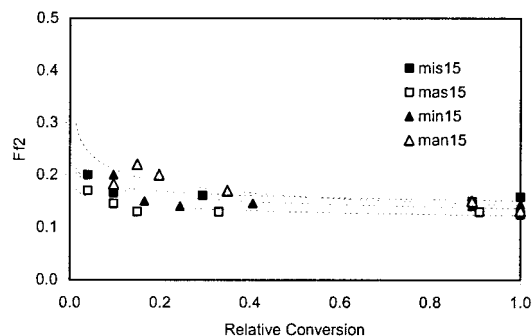
**Figure 13** Cumulative composition vs relative conversion during feeding period. Feed rate: 0.6 mL/min.

maleate.<sup>6</sup> Probably, the water solubility of vinyl versatate was enhanced by VAc in aqueous phase, and the diffusion of vinyl versatate through aqueous phase is not limiting the propagation process.

However, the composition-conversion curves for all feeding modes are closer to the recipe composition at the low feeding level than at the high one. This indicates that the composition of polymers is not affected noticeably by the mode of monomer addition at very low feeding level. The solubilization of vinyl versatate in the aqueous phase by VAc and the close reactivity ratios are eliminating any significant compositional drift caused by vinyl versatate transport limitations.

#### Glass Transition Temperature and Molecular Weight

Table V shows the glass transition temperature and molecular weight for the final polymers in the semibatch runs. As was the case with the batch runs, there is only one glass transition in each sample, indicating the absence of homopolymer. The glass transition temperatures for semibatch



**Figure 14** Cumulative composition vs relative conversion during feeding period. Feed rate: 0.15 mL/min.

**Table V** Glass Transition Temperature and Molecular Weight for the Final Latexes

Exp. Code	$T_g$ (°C)	$M_w$ (K)	$M_n$ (K)	Polyd Index
<b>Seed</b>	26.1	1315.0	254.4	5.17
<b>mis6</b>	24.1	357.0	42.2	8.46
<b>mas6</b>	25.4	433.9	88.8	4.89
<b>min6</b>	24.8	334.1	51.0	6.55
<b>man6</b>	25.8	404.3	79.7	5.07
<b>mis15</b>	23.3	345.2	37.5	9.21
<b>mas15</b>	23.9	416.3	46.8	8.90
<b>min15</b>	24.8	348.8	53.7	6.50
<b>man15</b>	25.1	388.0	80.5	4.82

runs are uniformly lower than that for batch runs, perhaps indicating slightly better vinyl versatate incorporation.

#### SUMMARY

The effect of mass transfer of vinyl versatate on the mini/macroemulsion polymerization of VAc/vinyl versatate in batch and semibatch systems was explored. For the batch experiments, the addition of neat vinyl versatate in runs of *minbat* and *manbat* formed poor dispersions of vinyl versatate, which resulted in the smaller particles, lower polymerization rates and different polymer composition tracks compared with normal mini/macroemulsion polymerization of VAc/vinyl versatate. The well-dispersed vinyl versatate seemed to help the monomer-swollen particle gaining more radicals in nucleation period.

In the semibatch experiments, the particle size distributions of the final latexes were affected by the residual surfactant in seed latex, which tended to facilitate homogeneous nucleation during the entire feeding period. The monomer feed rate determined the polymerization rate and had little effect on copolymer composition. The polymer composition for the runs with different monomer feeding modes tended to be identical at very low feed rate.

For all runs, the thermal analysis of resultant polymers showed that only one glass transition temperature could be found. This corresponded to the  $T_g$  of VAc/vinyl versatate copolymer. Lower glass transition temperatures were found for the semibatch runs, perhaps due to slightly better vinyl versatate incorporation.

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## REFERENCES

1. Veova Monomers Technical Information System, Shell Chemical Co., Houston, TX, 1999.
2. Decocq, F.; Heymans, D.; Slinckx, M.; Spanhove, S.; Nootens, C. *Paint Coatings Industry* 1998, 4, 57.
3. Balic, R. Ph.D. thesis, University of Sydney, Australia, 2000.
4. Araujo, P. H. H.; Abad, C.; de la Cal, J. C.; Pinto, J. C.; Asua, J. M. *Polym React Eng* 1999, 7, 303.
5. Unzue, M. J.; Urretabizkaia, A.; Asua, J. M. *J Appl Polym Sci* 2000, 78, 475.
6. Brandrup, J.; Immergut, E. H., Eds. *Polymer Handbook*; Wiley: New York, 1975.
7. Wu, X. Q.; Schork, F. J. *I&EC Res* 2000, 39, 2855–2865.
8. Chern, C. S.; Poehlein, G. W. *J Appl Polym Sci* 1987, 33, 2117.
9. Skelland, A. H. P. *Diffusional Mass Transfer*; Wiley: New York, 1974; Chap 3, p 54.
10. Mayo, V. R.; Lewis, F. M. *J Am Chem Soc* 1944, 66, 1594.
11. Samer, C. J. Ph.D. thesis, Georgia Institute of Technology, Atlanta, GA, July 1998.
12. Schuller, H. *Polym Reaction Eng* 1986, 137.
13. Tang, P. L.; Sudol, E. D.; Adams, M.; El-Aasser, M. S.; Asua, J. M. *J Appl Polym Sci* 1991, 42, 2019.