Kinetics of seeded emulsion polymerization of vinyl acetate with no added emulsifier

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Kinetics of emulsion polymerization of vinyl acetate have been studied in the absence of emulsifiers using potassium persulphate as the radical generator. Uniformity of particle sizes, in batch operation, indicated that nucleation of stable particles occurs early in the polymerization. The polymerization rate was proportional to the 0.69 power of the initial monomer concentration. Particle sizes were consistent with the suggestion that particles are stabilized by initiator fragments. When polymerization was carried out in the presence of a dialysed seed latex, with no added emulsifier, the polymerization rate was found to depend on the initiator concentration raised to the power 0.60 ± 0.05 but was independent of the monomer-to-polymer ratio. New stable particles could be produced when the monomer-to-polymer ratio was high. The production of these new particles did not affect the polymerization rate significantly. Polymerization rate was insensitive to the stirrer speed unless the speed was very high. At high speed the polymerization rate was reduced.

(Keywords: emulsion polymerization; vinyl acetate; seed latex; particle nucleation; kinetics; emulsifier-free)

INTRODUCTION

The kinetics of emulsion polymerization of vinyl acetate have been studied by a number of workers in recent years[1-7]. From these studies, it is clear that Smith–Ewart kinetics[8] are not observed and there is a wide variety of experimental results. Some of the apparent contradictions may arise from differences in experimental conditions. Some workers[1,4,5] postulated that much of the polymerization occurs in the aqueous phase. However, many other workers[2,3,6] have indicated that, after the particle nucleation period, most polymerization takes place in the monomer-swollen polymer particles. Chang et al.[7] concluded that polymerization rate is approximately zero-order with respect to monomer concentration and that the number of particles is roughly independent of conversion after 30% conversion (in unseeded polymerization).

When sodium dodecyl sulphate is the emulsifier and persulphate is used as an initiator, the order of polymerization with respect to initiator has been found to vary between 0.5 and 1.0 depending on circumstances[7]. Few workers considered the formation of particles beyond interval 1 (the conventional particle nucleation period) or during seeded polymerization. However, Hayashi et al.[9] have identified the formation of new particles in the seeded polymerization of vinyl acetate.

When no separate monomer phase was present, Dunn and Taylor[3] found that the maximum polymerization rate depended on the 0.64 power of the initiator (persulphate) concentration. Dunn and Chong[10] drew attention to the importance of ionic strength. When the ionic strength was constant, these workers found that the maximum polymerization rate could become proportional to the persulphate concentration in both the presence and absence of emulsifier. Priest[11] also found that the number of particles (in either the presence or absence of emulsifier) depended on the concentration of added salt. The summary table of results given by Chang et al.[7] does not distinguish between those cases where ionic strength varied and cases where ionic strength was constant.

Previous workers have considered four possible loci for particle nucleation. These are (a) monomer-swollen micelles[10,12], (b) adsorbed emulsifier layers[13] (on any two-phase interface), (c) the aqueous phase[1,14,15] and (d) the monomer droplets[16,17]. Mechanistically (b) is difficult to distinguish from (a), and (c) is usually applied to relatively water-soluble monomers. With aqueous nucleation, precipitated oligomeric radicals are thought to adsorb emulsifier to become primary particles, which then flocculate to form stable particles. Locus (d) becomes significant when small monomer drops are generated. The most important distinction between (a) and (c) is the duration of the particle nucleation period. With (a) particles can form only when the emulsifier concentration exceeds the critical micelle concentration (CMC).

Stability of the latex particles depends on the nature of the particle surfaces[18]. The condition of these surfaces can be influenced strongly by the presence of

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adsorbed emulsifier. Stabilizing functional groups can exist on particle surfaces without emulsifier being present. Emulsifier-free emulsion polymerization of styrene has received much attention[19,20].

The purpose of the present study is to investigate the kinetics of seeded and non-seeded emulsion polymerization of vinyl acetate in the absence of emulsifier. Conditions for the formation of new particles in seeded emulsion polymerization will be examined also.

EXPERIMENTAL

Materials

Vinyl acetate (Aldrich) was distilled under reduced pressure and stored at 280 K. Potassium persulphate (BDH), potassium sulphate (Fisons) and hydroquinone (Fisons) were used as received. Cellophane tube, for dialysis, was supplied by Medicell International Ltd.

Procedures

Polymerization was carried out using agitated, one-litre, glass flange-topped vessels. An atmosphere of oxygen-free nitrogen was maintained throughout.

Seed latices were prepared by purging mixtures of vinyl acetate and water with nitrogen and then adding a solution of initiator (potassium persulphate), which had also been purged with nitrogen. Polymerization was then continued until almost 100% conversion of monomer. The seed was then transferred to a dialysis bag to remove excess initiator and its by-products. The distilled water surrounding the bag was changed each day for 20 days. Dialysed latex was stored at 280 K.

Monomer conversion in seeded and unseeded polymerization was determined gravimetrically. Small amounts of hydroquinone were added to latex samples before evaporation and drying. Particle size was determined by using a transmission electron microscope.

Polymerization rates were obtained from the slope of the linear regions in the plots of conversion against time.

For seeded polymerization, monomer, water, seed latex and initiator solution were flushed separately with nitrogen for 20 min. All materials (including potassium sulphate, where necessary), except the initiator, were then mixed in the reactor and nitrogen purging continued at reaction temperature before adding the initiator.
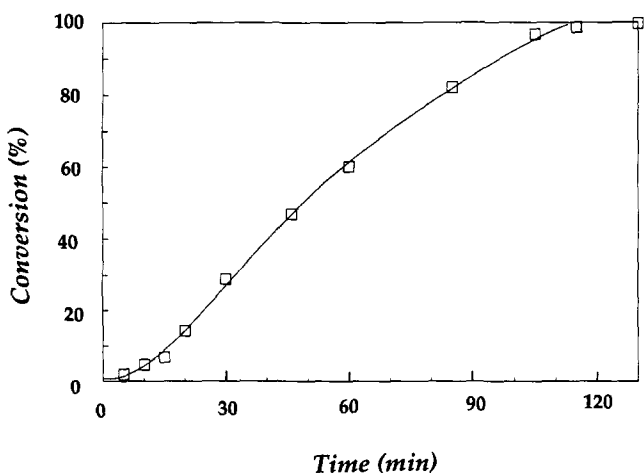
Table 1 Effect of initial monomer concentration on R_p and D_p[a]

M_0 (mol dm^{-3})[b]	1.165	1.446	2.908	4.357
D_p (μm)	0.48	0.58	0.78	0.88
Particle number, N (10^{14} dm^{-3})	14.54	10.24	8.47	8.37
R_p (10^{-4} mol s^{-1} dm^{-3})	2.40	2.64	3.81	6.23

[a] Reaction conditions: [I] = 0.037 mol dm^{-3}; T = 45°C; stirring speed 150 rev min^{-1}

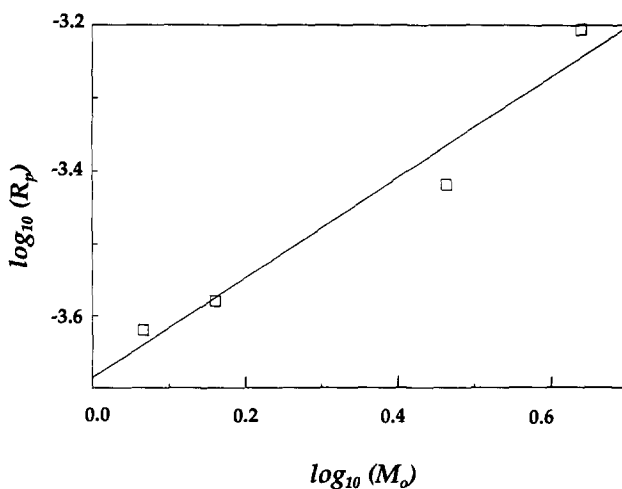[b] Overall concentration in the initial dispersion

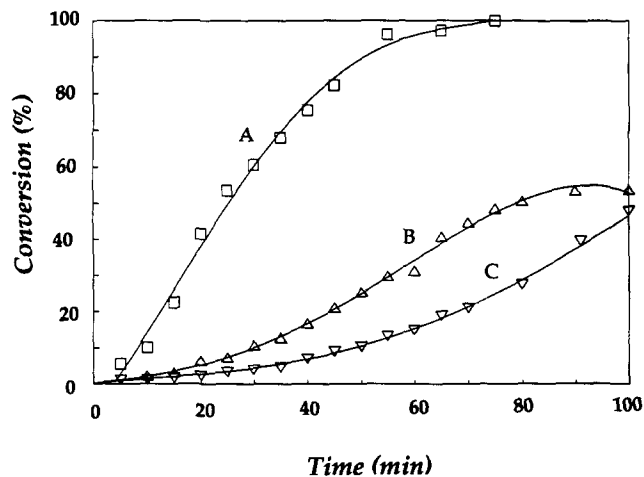**Figure 2** Plot of $\log_{10} R_p$ against $\log_{10} M_0$. Conditions given in *Table 1*

Figure 3 Conversion against time in presence of seed latex. Initial D_p = 0.25 μm, organic content 10%, monomer-to-polymer ratio = 10, T = 50°C, ionic strength = 0.05. Initiator concentrations: A, 0.0170 mol dm^{-3}; B, 3.28 × 10^{-3} mol dm^{-3}; C, 1.73 × 10^{-3} mol dm^{-3}

RESULTS

Figure 1 shows a typical plot of conversion against time for the emulsifier-free emulsion polymerization of vinyl acetate. *Table 1* shows polymerization rate (R_p) and particle characteristics for the unseeded emulsion polymerization at different monomer concentrations, M_0. The final polymer particles had virtually uniform sizes in each experiment. Variation of R_p with M_0 is shown in *Figure 2*. The effect of varying initiator concentration in seeded emulsion polymerization is shown in *Figures 3-5*. Here, ionic strength is adjusted to a constant value by addition of potassium sulphate and 'organic content' means total monomer plus polymer.
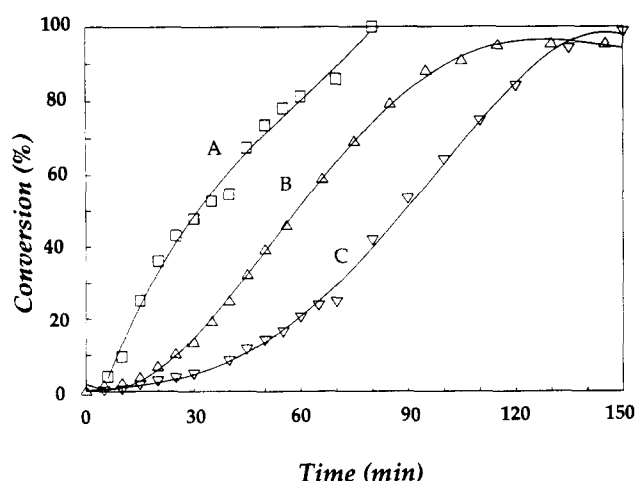

Figure 1 Typical plot of monomer conversion against time. M_0 = 1.16 mol dm^{-3}, [I] = 0.037 mol dm^{-3}, T = 70°C, stirrer speed = 100 rev min^{-1}

Figure 4 Conversion against time in presence of seed latex. Initial $D_p = 0.25 \mu m$, organic content 10%, monomer-to-polymer ratio = 20, $T = 50°C$, ionic strength = 0.05. Initiator concentrations: A, 0.0170 mol dm^{-3}; B, 3.70×10^{-3} mol dm^{-3}; C, 1.90×10^{-3} mol dm^{-3}
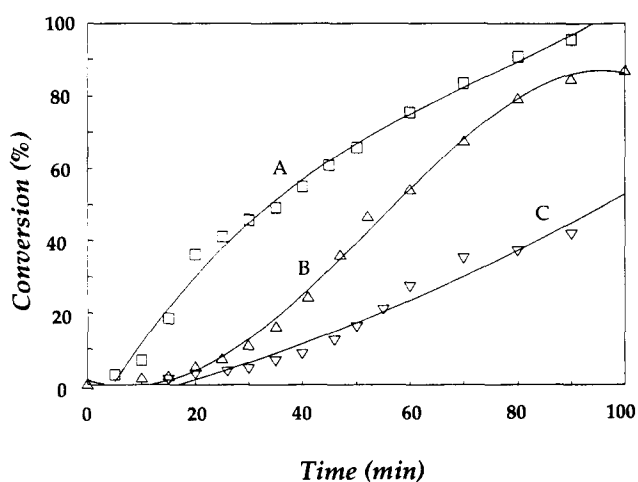

Figure 5 Conversion against time in presence of seed latex. Initial $D_p = 0.34 \mu m$, organic content 10%, monomer-to-polymer ratio = 40, $T = 50°C$, ionic strength = 0.05. Initiator concentrations: A, 0.0168 mol dm^{-3}; B, 3.79×10^{-3} mol dm^{-3}; C, 1.92×10^{-3} mol dm^{-3}

The effect of monomer-to-polymer ratio in the seeded polymerization of vinyl acetate is shown in *Tables 2–4*. When this ratio was less than about 10, the final sizes of the polymer particles remained uniform. At higher ratios, two groups of polymer particles, each with narrow size distributions, could be observed. The particles with the smaller size are described as 'newly formed' in *Tables 2–4*.

Table 5 shows the effect of stirring rate on the unseeded polymerization.

DISCUSSION

From *Figure 1* it can be seen that, in the absence of emulsifier, polymerization rate for unseeded emulsion polymerization remains almost constant over a wide range of conversion. In 'conventional' emulsion polymerization the uniformity of particle size is sometimes attributed to nucleation restrictions arising from the presence of finite amounts of emulsifier. Clearly, the uniformity of particle sizes observed in the present experiments arises for other reasons because no emulsifier was present. Although primary particle nuclei may be

generated throughout the polymerization process, the final narrow particle size distribution indicates that new stable particles do not form after the early stages. Presumably heterocoagulation between mature latex particles and small-particle nuclei (or aqueous oligomers) occurs.

Figure 2 shows that R_p is proportional to the 0.69 power of initial monomer concentration. This result is different from that obtained by Litt et al.[4] in which no significant change in rate was observed. However, Litt's results were obtained from their early experiments, and were not repeated, and also the change of initial monomer concentration in their experiment was very small. The monomer concentrations shown in *Table 1* are 'global' concentrations. Although most of the monomer existed as a separate phase, some monomer will have dissolved in the aqueous phase. If it is assumed that the aqueous phase is saturated with monomer, an apparent dependence of R_p on volume fraction of monomer phase can be estimated. Calculations show that R_p is proportional to approximately the 0.59 power of the initial phase ratio (monomer phase to aqueous phase).

Table 1 shows that final particle diameter increases as initial monomer concentration increases. From *Table 1*, it can be seen that higher monomer concentration results in fewer particles. This can be explained as follows.

Polymer particles in emulsifier-free emulsion polymerization, in which ionic initiator is used, are stabilized by ionic end-groups from the initiator. Low initiator concentration provides fewer ionic end-groups to stabilize polymer particles. In these experiments, initiator concentration was kept constant with increasing monomer concentration, and therefore the concentration of ionic end-groups at the particle surface decreased at any given monomer conversion. Therefore, the particle stability decreased with increasing monomer concentration and

Table 2 Effect of monomer–polymer ratio on particle growth[a]

Monomer–polymer ratio	Diameter of large particles after polymerization (μm)	Theoretical diameter (μm)	Newly formed small-particle diameter (μm)	Polymerization rate (10^{-4} mol s^{-1} dm^{-3})
4.22	0.84	0.79	–	1.97
12.97	1.17	1.05	0.62	2.39

[a] Reaction conditions: [I] = 0.017 mol dm^{-3}; $T = 45°C$; initial diameter of unswollen particles = 0.42 μm

Table 3 Effect of monomer–polymer ratio on particle growth[a]

Monomer–polymer ratio	Diameter of large particles after polymerization (μm)	Theoretical diameter (μm)	Newly formed small-particle diameter (μm)	Polymerization rate (10^{-4} mol s^{-1} dm^{-3})
6.81	0.71	0.56	–	1.94
7.04	0.76	0.64	–	2.11
10.77	0.64	0.73	0.35	1.90
21.84	0.68	0.91	0.38	2.02

[a] Reaction conditions: [I] = 0.028 mol dm^{-3}; $T = 70°C$; initial diameter of unswollen particles = 0.32 μm

Table 4 Effect of monomer–polymer ratio on particle growth[a]

Monomer–polymer ratio	Diameter of large particles after polymerization (μm)	Theoretical diameter (μm)	Newly formed small-particle diameter (μm)	Polymerization rate (10^{-4} mol s^{-1} dm^{-3})
8.65	0.55	0.54	–	4.84
14.38	0.58	0.62	–	5.60
19.80	0.69	0.70	–	3.71
25.00	0.74	0.74	–	5.18
39.00	0.62	0.87	0.42	4.42

[a] Reaction conditions: $[I] = 0.017$ mol dm^{-3}; $T = 50°C$; initial diameter of unswollen particles $= 0.25\,\mu$m

Table 5 Effect of stirring[a]

Agitation speed (rev min^{-1})	50	100	150	300
Conversion (%)	86.17	100	81.99	95.01
Final particle diameter (μm)	0.52	0.56	0.56	–
D_{theory} (μm)	0.57	0.57	0.57	0.57
R_p (10^{-4} mol s^{-1} dm^{-3})	4.25	4.12	4.29	1.16

[a] Reaction conditions: $[I] = 0.017$ mol dm^{-3}; monomer-to-polymer ratio $= 10$; organic content 10%; $T = 50°C$; initial diameter of unswollen particles $= 0.25\,\mu$m

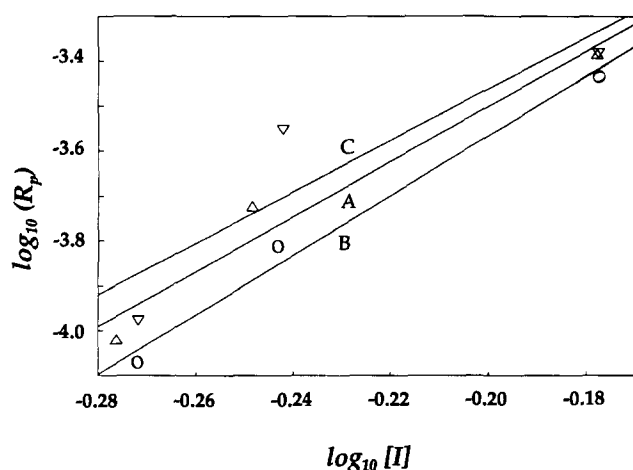**Figure 6** Plot of $\log_{10} R_p$ against $\log_{10} [I]$. Monomer-to-polymer ratios: A ($\triangle$), 10; B($\bigcirc$), 20; C ($\triangledown$), 40

more particles tended to coalesce to form a large particle. This results in fewer particles (but an increase in total particle surface area) with increasing amount of monomer as shown in *Table 1*. At high monomer concentrations some of the initial monomer will be in aqueous solution with the remainder dispersed as drops. A dependence of polymerization rate on particle surface area could imply that polymerization occurred in the outer regions of the particles. The particle sizes (shown in *Table 1*) are relatively large and monomer diffusion from the surface to the interior of the particles may not be rapid.

From *Figures 3–5* it can be seen that, in seeded mixtures, polymerization rate increases with increasing initiator concentration. A plot of log rate *versus* log initiator concentration for different monomer–polymer ratios is shown in *Figure 6*. There is some scatter of points; however, a slope of 0.60 ± 0.05 is strongly indicated. This result is similar to that obtained by Chang *et al.*[7] (where

$R_p \propto [I]^{0.60 \pm 0.03}$), but is different from that obtained by Brooks *et al.*[21] (where $R_p \propto [I]^{0.70 \pm 0.05}$). This difference may arise because the experimental conditions varied significantly in the different studies. Chang *et al.* and Brooks *et al.* used sodium lauryl sulphate as emulsifier during their studies, while there was no added emulsifier in this work. Also, the monomer–polymer ratio was changed from 0.52 to 1.70 and from 7 to 50 for Brooks' and Chang's study, respectively, while it varied from 10 to 40 in the present study. The temperature was 60°C for Brooks *et al.* and Chang *et al.*, and 50°C for the present study.

Comparison with earlier models[21] showed that, if R_p depended on $[I]$ raised to a power greater than 0.5, then it might be assumed that polymerization occurred in both the polymer particles and the aqueous phase. In the present work, evidence of polymerization in the aqueous phase was obtained by the formation of new particles in seeded polymerization experiments. These new particles could be identified in experiments where the initial monomer-to-polymer ratio was high (see *Tables 2–4*). The 'theoretical' diameter in these tables is the value that is expected if the number of particles remains unchanged during polymerization. When new particles were observed, the actual average diameter was less than this theoretical diameter. It may be that new particles form in many circumstances but are undetected because they coalesce rapidly with existing seed particles. It can be seen from the tables that an increase in monomer-to-polymer ratio (with other conditions unchanged) does not lead to appreciable changes in R_p even if new particles remain in the emulsion. The relative numbers of large and small particles were difficult to determine because the electron micrographs included an insufficient number of particles for accurate counting. There could be some uncertainty in experimental values for particle sizes if the polymer particles were distorted slightly by the electron beam in the electron microscope. If it is assumed that all the initial seed particles are preserved, then a material balance, using particle sizes in *Tables 2–4*, indicates that in some cases the number of new (small) particles can exceed the number of original (large) particles. In such circumstances, the polymerization rate is apparently not dependent on total particle number.

Table 5 shows that an increase in stirring rate does not affect R_p unless the stirring rate becomes very high. The reduction in R_p at the highest stirrer speed may result from enhanced particle coalescence. Similar results were obtained by Chiu *et al.*[20] and Song *et al.*[22] in the emulsifier-free emulsion polymerization of styrene. Particle diameter could not be measured accurately at the high speed because the particles stuck together. In *Table 5*, the theoretical diameter is calculated by assuming that all the monomer is polymerized in the seed particles.

CONCLUSIONS

The emulsion polymerization of vinyl acetate can be achieved in the absence of emulsifiers. The production of mono-sized particles indicates that the number of stable particles does not increase after the early stages of the polymerization. The polymerization rate is proportional to the 0.69 power of the initial monomer concentration. Final particle sizes are consistent with the

suggestion that particles are stabilized by initiator fragments.

In seeded emulsion polymerization, without added emulsifier, the polymerization rate depends on the initiator concentration raised to the power 0.60 ± 0.05 but is independent of the monomer-to-polymer ratio. When the monomer-to-polymer ratio is high, new stable particles can be formed. The production of these new (small) particles does not lead to a significant increase in polymerization rate.

Increases in stirring speed do not affect the polymerization rate unless the stirrer speed is very high. At high speed, polymerization rate is reduced.

ACKNOWLEDGEMENTS

NOTATION

D_p	particle diameter
D_{theory}	'theoretical' D_p
[I]	initiator concentration
M_0	initial monomer concentration
N	number of particles
R_p	polymerization rate
T	temperature

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