Seeded emulsion polymerization of vinyl acetate: order of reaction with respect to initiator

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The emulsion polymerization of vinyl acetate has been studied using carefully prepared seed lattices. Experiments were carried out in which temperature, particle size and the monomer–polymer ratio could be varied independently. In all cases the polymerization rate was proportional to the initiator concentration raised to the 0.7 power. No new particles were formed. The importance of polymerization in the aqueous phase and changes in the propagation rate coefficient are discussed.

Keywords Polymerization; emulsion; vinyl acetate; initiator; aqueous phase; propagation

INTRODUCTION

No unique and acceptable mechanism has been proposed for the emulsion polymerization of vinyl acetate. The two main uncertainties are: (a) reaction rate order with respect to the initiator and (b) role of the aqueous phase during polymerization. Dunn and Taylor[1] and Dunn and Chong[2] obtained respectively rate orders of 0.64 and 0.6–0.9. Friis and Nyhagen[3] and Normura *et al.*[4] obtained a value of 0.5. Litt *et al.*[5] obtained the value of 1.0 while Gershberg[6] obtained a value of 0.6. The foregoing shows clearly that, from the literature, no single rate order can be assigned to vinyl acetate emulsion polymerization. Experimental conditions were not always the same in these previous studies.

Patsiga *et al.*[11] and Friis and Nyhagen[3] proposed two different reaction models which can be considered to assume extreme conditions. Patsiga *et al.* assumed that most polymerization and termination occurred in the aqueous phase while Friis and Nyhagen assumed polymer phase termination. It is significant that both models predict a reaction rate order of 0.5.

In the work presented here, the effect of initiator concentration on polymerization rate in seeded systems of vinyl acetate has been studied. The experiments were designed so that the effect of monomer–polymer ratio, particle size and temperature on the reaction rate order could be investigated.

EXPERIMENTAL

Materials

Vinyl acetate was freed from inhibitor by washing with 1% aqueous solution of sodium hydroxide and distilled water. Reagent grade sodium dodecyl sulphate (SDS) was used as emulsifier. Analytical grades of the following chemicals were used directly: ammonium and potassium persulphate, aluminium sulphate, ammonium ceric nitrate, sodium bromide and ferrous ammonium sulphate.

Experimental procedure

Details of the experimental technique used in this study for preparing seed lattices and swelling the polymer particles with monomer can be found in recent publications[7,8]. The polymerizations were conducted in a 1 litre well-mixed batch glass reactor. Temperature inside the reactor was monitored by the glass bulb thermometer and samples were withdrawn at appropriate intervals with a syringe and a hypodermic needle.

In preparing the seed lattices, vinyl acetate was polymerized until complete conversion was achieved. Remaining salts in the aqueous phase were removed by dialysis. The latex was placed in a bag made from Visking tubing and the bag was placed in 10 litres of distilled water at 303 K. The water was changed daily and after 5 days the residual persulphate concentration (estimated by the ferrometric method of Kolthoff and Carr) was low.

To carry out a seeded polymerization, a given weight of a prepared seed was introduced into the reactor; this was then swollen with a known weight of vinyl acetate. No separate monomer phase existed after the swelling stage. Additional amounts of distilled water and persulphate were usually introduced to bring the solid and persulphate contents to desired concentrations. Before the start of any seeded reaction the initial concentration of persulphate in emulsion was determined as described above. During polymerization, samples were withdrawn at intervals and their polymer content was determined gravimetrically.

By the use of electron microscopy it was possible to show that the particle population remained essentially constant during the seeded polymerizations. The number of particles in the seeds ranged between 5×10^{16} and 3×10^{17} per dm^3. (A list of symbols and units is given below.)

RESULTS

At the start of all the polymerization reactions induction periods were observed. The length of an induction period appeared to depend on intensity of nitrogen purge and

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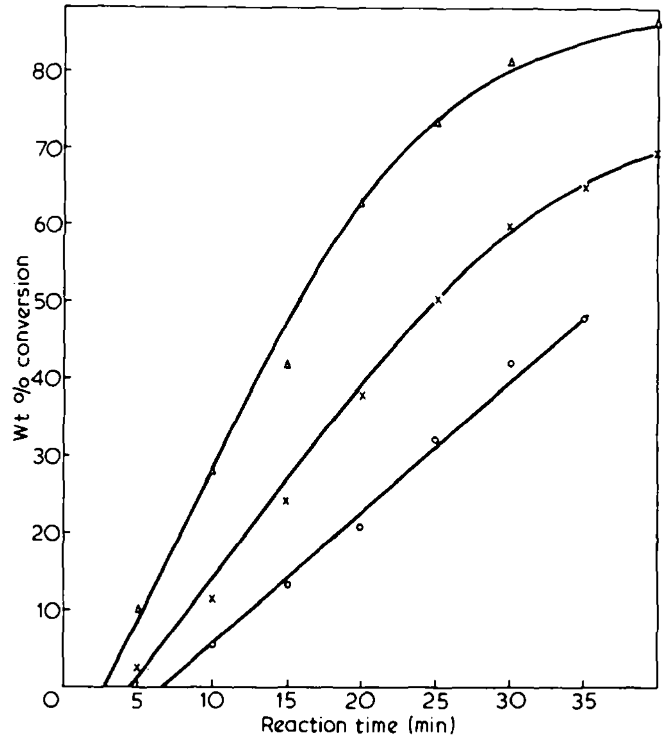

Figure 1 Typical conversion–time curves from seeded polymerizations. Conditions as for experiment c in *Table 2*. Initiator concentrations for (○), (X) and (△) are 4.62×10^{-3}, 8.07×10^{-3} and 1.41×10^{-2} mol dm^{-3} water respectively

Table 1 Recipes for seed preparation

	I	II
Vinyl acetate	64.64 g	60.00 g
Ammonium persulphate	2.01 g	–
Potassium persulphate	–	0.04 g
Sodium dodecyl sulphate	3.08 g	1.20 g
Water	300 g	180 g
Reaction temperature	40°C	60°C
Average particle diameter ($\pm 5.0 \times 10^{-9}$ m)	1.243×10^{-7} m	0.885×10^{-7} m

initial concentration of persulphate. This observation was also made by Zollars[9]. No induction period was observed when an identical procedure was used in the emulsion polymerization of styrene or methylmethacrylate[7,8].

Typical conversion time curves obtained from the seeded polymerizations are shown in *Figure 1*. It will be noticed from the curves that polymerization rates remained fairly constant until very high conversions had been attained (in contrast with the styrene and methyl methacrylate seeded systems[8]). This behaviour is very similar to that observed in conventional batch polymerization of vinyl acetate where the reaction rate remains constant long after the disappearance of monomer droplets[3,5].

Effects of monomer–polymer ratio on polymerization rate

The seed used in this set of experiments was prepared from recipe I (in *Table 1*). For a given initial monomer–polymer ratio (X), two or three seeded polymerizations were carried out at different initial initiator concentrations, $[I]$ at 60°C. The four monomer–polymer ratios used were 1.70, 0.98, 0.72 and 0.52. A summary of the results from these experiments is presented in *Table 2*.

Logarithmic values of R_p and $[I]$ in *Table 2* are plotted in *Figure 2* (lines corresponding to the various monomer–polymer ratios are labelled A, B, C and D). From the gradients of the straight lines through the plotted points it was deduced that the relationship below holds for the four sets of experiments:

$$R_p \propto [I]^n \qquad (1)$$

where $n = 0.7 \pm 0.05$.

Effect of particle size on reaction rate

From *Figure 2* it is seen that increases in monomer–polymer ratio at the start of polymerizations resulted in corresponding increases in the polymerization rate (at constant initiator concentration). This dependency of R_p on X raised the possibility that the average size of the swollen particles affects polymerization rates. Therefore a seed which contained particles of a noticeably smaller size (prepared from recipe II, *Table 1*) than that used previously was employed in a new set of experiments. The average diameter of this new seed was 0.885×10^{-7} m (unswollen). In order to eliminate X as a variable, the value of X was identical to that used in one of the experiments in *Table 2* (this made comparison of results easier). The polymerization rates from the experiments

Table 2 Results from seeded polymerization of vinyl acetate at 60°C*. (Diameter of unswollen particles 1.243×10^{-7} m)

Expt.	x	y	$\bar{v} \times 10^{18}$	$[I] \times 10^3$	$R_p \times 10^4$
A	1.70	160	3.25	8.32	4.78
				16.0	8.39
B	0.98	120	2.28	5.22	2.35
				8.39	3.05
C	0.72	130	1.94	4.62	1.78
				8.07	2.63
				14.1	4.14
D	0.52	130	1.67	5.42	1.51
				8.16	1.95
				18.1	3.54

* Symbols and units listed below

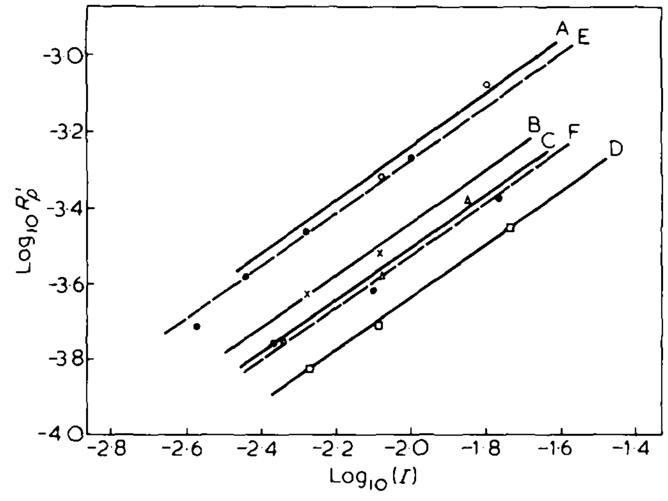

Figure 2 Plots of $\log_{10} R_p$ against $\log_{10} [I]$. (A), (B), (C), (D), (E) and (F) as in *Tables 2, 3* and *4*

Table 3 Results from seeded polymerization of vinyl acetate at 60°C*. (Diameter of unswollen particles 0.885 x 10^{-7} m)

Expt.	X	Y	$\bar{v}\times10^{19}$	$[I]\times10^3$	$R_p\times10^4$
E	0.52	180	5.97	2.68	1.44
				3.64	2.64
				5.20	3.48
				10.1	5.37

* Symbols and units listed below

Table 4 Results from seeded polymerizations of vinyl acetate at 50°C*. (Diameter of unswollen particles 0.885 x 10^{-7} m)

Expt.	X	Y	$\bar{v}\times10^{19}$	$[I]\times10^3$	$R_p\times10^4$
F	0.98	160	8.22	4.22	1.73
				7.93	2.38
				16.9	4.18

* Symbols and units listed below

with the smaller particles are presented in *Table 3*. In *Figure 2* the straight line through the plotted points is shown as the broken line labelled 'E'. The gradient of this line is also ~0.7 and this implies that equation (1) still holds, i.e. the relationship between R_p and $[I]$ is independent of average particle size.

Effect of temperature on reaction rate

Some seeded polymerizations were carried out at 50°C and a summary of the results from these experiments are presented in *Table 4*. The logarithmic plots of R_p against $[I]$ values in *Table 4* are shown in *Figure 2*. The straight line through the plotted points is shown as the broken line labelled 'F' and its gradient was also found to be 0.7. This implies that equation (1) holds both at 60°C and 50°C.

DISCUSSION

One conclusion that can be made from this study is that equation (1) is independent of particle size, temperature and initial monomer polymer ratio in seeded polymerization. Adherence to this equation in seeded systems implies that the two models proposed by Friis and Nyhagen[3] and Litt *et al.*[5] (which predict a rate order of 0.5) do not apply. Litt *et al.* obtained a rate order of about 0.8 from their seeded systems and surprisingly still proposed a model which predicts an order of 0.5. Since results from the present study appear to be at variance with the models proposed by the above-mentioned groups of workers (who separately assumed the extreme conditions of polymer phase termination and aqueous phase termination) there is a strong possibility that significant polymerization occurred in both the polymer and aqueous phases. Certainly these results imply a complicated reaction mechanism and the true rate order is different from 0.5.

Figure 2 shows that the value of R_p increases substantially with every increase in initial value of monomer polymer ratio (from a comparison of relative positions of lines A, B, C and D). These increases (which are in contrast to styrene and methyl methacrylate seeded systems[7,8]) may be accounted for by one or any combination of the following:

(1) Increase in the average radical number per particle due to bigger swollen polymer particles.

(2) Increase of monomer concentration in the particles.

(3) Viscosity decrease in the particles resulting in smaller reductions in the propagation coefficient (k_p).

(4) Increase of water phase polymerization resulting from an increase in concentration of dissolved monomer in the aqueous phase.

The first two factors above will almost certainly increase the polymerization rate but increases due to these factors may not be large enough to account for the pronounced rate increase observed. If the assumption made by earlier workers, that radical desorption rate increases with conversion[3,5] (i.e. as $1/X$), is valid then the contribution by factor (1) could be obscured. The relative positions of the lines 'E' and 'D' (both lines represent the same initial monomer–polymer ratio but different average particle sizes) appear to show that the polymerization rate decreases with particle size. However, when allowance is made for the change in particle number, it is found that the polymerization rate per particle with the smaller particles is only ~60% of that for the larger particles.

One very important factor that has received very little attention in the literature is the possibility that k_p value changes significantly during emulsion polymerization of vinyl acetate. In the study of bulk polymerization, Melville[10] showed that k_p and k_t change with conversion significantly, e.g. at 25°C, k_p at 65% was less than 5% of its value at 5% conversion. If a single polymer particle in an emulsion system can be regarded as a locus of bulk polymerization with intermittent initiation (as pointed out by Friis and Nyhagen[3]) the value of k_p will be expected to increase with increase of monomer concentration (large values for X) in the seeded polymerizations carried out in this work. There is also a likelihood that this factor plays a significant role in the observed steady polymerization rate observed in usual emulsion polymerization procedures when the separate monomer phase has disappeared. Uncertainty in the relationship between X and k_p makes it difficult to evaluate the effect of factor (2) on changes in R_p. As conversion increases the value of k_t inside the particles will decrease: this may accelerate the polymerization rate if the average number of radicals per particle exceeds 0.5.

The fourth factor is expected to be significant in the polymerization process. Even through electron microscopy did not indicate the formation of new particles during the seeded polymerizations, newly generated particles in the aqueous phase could have been swept up by the existing larger particles as suggested by Patsiga *et al.*[11]. Since vinyl acetate is relatively soluble in water[12], it will be expected that, as X increases the concentration of monomer in the aqueous phase will increase. Dunn and Taylor[1] obtained an equation for the distribution of vinyl acetate between water and poly(vinyl acetate). With the use of their equation the contribution of water phase polymerization to the overall conversion has been estimated to be ~7% (it was pointed out that this might be an underestimate[7]). If the aqueous phase polymerization is as extensive as suggested by Litt *et al.*[5,11] then factor 4 given above could have played a major role in the seeded polymerizations carried out in this study. Although polymerization in the aqueous phase may be important it will not be dominant. This is shown by comparing the group (D) esperiments with group (E).

In these cases k_p will be the same so that the apparent values for the number of radicals per particle at any given initiator concentration (neglecting aqueous polymerization) are noticeably different. This difference would not have been observed if aqueous polymerization was dominant because the aqueous monomer concentration was similar in the two cases.

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SYMBOLS AND UNITS USED

$[I]$	initiator concentration, (g mol dm^{-3} water)
k_p	propagation rate coefficient, (dm^3 s^{-1} mol^{-1})
k_t	mutual chain termination rate coefficient, (dm^3 s^{-1} mol^{-1})
R_p	overall initial rate of polymerization, (g mol s^{-1} dm^{-3} water)
X	initial weight ratio of monomer–polymer in swollen seeds
y	concentration of organic material (monomer + polymer) in emulsion, (g dm^{-3} water)
$\bar{v}$	average volume of swollen particle, (dm^3)

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