Exit in the Emulsion Polymerization of Vinyl Acetate

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ABSTRACT: The following model is proposed to explain the independence of polymerization rate on monomer concentration which is often observed in the emulsion polymerization of vinyl acetate: that radical loss is by transfer to a monomeric species which is very slow to propagate and whose radical activity is lost by exit and termination, either in the aqueous phase or when it enters a particle containing a growing radical. Since the transfer step is rate-determining, the rate of this process is proportional to monomer concentration, which cancels the dependence on monomer concentration in the overall polymerization rate expression; this model also predicts that the radical loss rate coefficient should be either $k_{tr}C_P$ or $2k_{tr}C_P$, depending on which is the actual fate of the desorbed radical (where k_{tr} is the rate coefficient for transfer to monomer and C_P is the concentration of monomer in the particles). Experimental radical loss rates, determined directly by γ-radiolysis relaxation studies, are quantitatively in accord with the hypothesis.

1. Introduction

Where the gel effect is not operating in emulsion polymerizations, the exhaustion of the separate monomer phase (i.e., the onset of Interval III) is usually followed by a decrease in conversion rate due to the decrease in monomer concentration in the particles (C_P). The unusual feature of the emulsion polymerization of vinyl acetate (VAc) is that the rate remains constant throughout most of Interval III,[1] even though the average number of radicals per particle is so low that the gel effect cannot operate to counteract the decrease in monomer concentration.

It is widely believed that, in the case of VAc, termination in the particle phase is transfer-dominated.[2,3] If transfer is nearly always followed by exit and termination, a simple explanation of the observed independence of conversion rate on monomer concentration becomes available, as follows. The polymerization rate is proportional to C_P; so too is the transfer rate and hence the termination rate (since transfer is assumed to lead nearly always to exit and exit is assumed to lead nearly always to termination). Thus as C_P decreases, growing polymer molecules grow more slowly but live proportionately longer, and the overall conversion rate remains constant. This explanation is quantified in the next section.

This explanation can be quantitatively tested, since it will be seen that it implies that the rate coefficient for radical *loss* should be given by a simple expression involving the transfer constant, which in turn can be obtained from independent experiments. The test of our hypothesis is therefore performed by directly observing the radical loss process using initiation by γ-radiolysis, removing the emulsion polymerization reactor from the radical source, and observing the rate at which polymerization slows down; this should be the same (within experimental uncertainty) as the value predicted using literature transfer constants.

2. Model for Vinyl Acetate Kinetics

One explanation for the observed kinetics in VAc has been put forward by Chern and Poehlein,[3] who proposed that exit of the monomeric free radicals formed by transfer to monomer ($M^•$) in VAc emulsion polymerization is rapid. However, their model relies on changes in the desorption rate during Interval III to explain the independence of conversion rate on monomer concentration. This is ascribed to an increase in viscosity with conversion which is proposed to fortuitously cancel the effect of decreasing C_P during Interval III. Another shortcoming of this approach is that as particle size increases through growth in Interval II, the desorption rate should decrease, thereby increasing the conversion rate; this does not seem to be the case.

We now quantify our explanation for the observed effect. It will be seen that there are two mechanisms for emulsion polymerization kinetics consistent with the observed behavior, denoted Limits 1 and 2b.[4] Both limits require that most $M^•$ exit the particle and do not reinitiate. In Limit 1, the $M^•$ exit the particle and terminate in the aqueous phase, while in Limit 2b they re-enter and exit dead particles until they enter a live particle and terminate. The time evolution of the average number of radicals per particle, $\bar{n}$, is in these cases given by

$$\frac{d\bar{n}}{dt} = \rho(1 - 2\bar{n}) - k\bar{n} \qquad (1)$$

(for Limit 1, this requires that desorption of monomeric radicals be more rapid than their propagation within the particles). Here ρ is the rate coefficient for free-radical entry into the particles (the number of radicals per unit time entering a particle) for radicals arising both from initiator and from thermal entry (but excluding re-entry of exited radicals, this being taken into account in the exit term), and k is the rate coefficient for radical exit (desorption) from the particle, i.e., the number of loss events by desorption, per radical-containing particle per unit time. One has

$$k = k_{tr}C_P \text{ (Limit 1)}; \qquad k = 2k_{tr}C_P \text{ (Limit 2b)} \qquad (2)$$

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where k_{tr} is the rate coefficient for transfer (e.g., to a monomer) to give a species which can exit. The steady-state value of eq 1 is

$$\bar{n}_{ss} = \frac{\rho}{2\rho + k} \tag{3}$$

If, as is usually the case for VAc, $\bar{n}$ is small, then $\rho \ll k$ (basically because of the high transfer constant) and one has

$$\bar{n}_{ss} \approx \frac{\rho}{k} \tag{4}$$

Given eq 2, one has

$$\bar{n}_{ss} \approx \frac{\rho}{a k_{tr} C_P} \tag{5}$$

where $a = 1$ for Limit 1 and $a = 2$ for Limit 2b.

The rate equation for emulsion polymerizations is

$$R_p = C_P \bar{n} \frac{k_p N_c}{N_A} \tag{6}$$

where R_p is the conversion rate, k_p the propagation rate coefficient, N_c the number concentration of particles, and N_A Avogadro's constant. Hence combining eqs 5 and 6, one has for the steady-state rate

$$R_p \approx \frac{\rho}{a k_{tr}} \frac{k_p N_c}{N_A} \tag{7}$$

Thus the independence of conversion rate on monomer concentration can be explained if either of these limiting cases applies to the emulsion polymerization of VAc. The key point is that most transfer to monomer must lead to exit and subsequent termination, to satisfy eq 2.

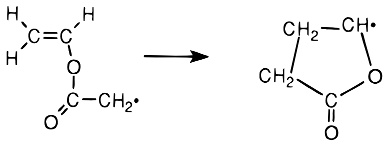
This can be tested with a relaxation experiment. When the external source of initiating radicals is switched off, ρ becomes negligible and eq 1 can be integrated and rearranged to yield k directly:

$$k \approx \frac{\ln(\bar{n}_0/\bar{n})}{t} \tag{8}$$

(where $\bar{n}_0$ is the average number of radicals per particle before the initiating source is switched off and t is time elapsed after the initiating source is switched off). The means of carrying out such a relaxation experiment is to use initiation by γ-rays.[5]

There is still some debate about the nature of the monomeric free radical formed by transfer in VAc polymerization. Chang *et al.*[6] argue for abstraction of a vinylic hydrogen to produce a vinylic free radical, while others[2,7] argue for the chemically more reasonable abstraction of an acetyl hydrogen. Both sets of authors conducted similar deuterium isotope experiments but obtained contradictory results. Starnes' NMR and MWD data support the proposition that transfer is primarily by abstraction of a methyl hydrogen from the monomer. However, the assertion that $M^\bullet$ re-initiates polymerization in bulk systems is not proven unequivocally by the data presented: the tabulated ^{13}C shifts and the 1:1 ratio of the concentration of end groups could be ascribed to the bimolecular termination product of the poly(vinyl acetate) radical (pVAc$^\bullet$) and Starnes' $M^\bullet$. In any case, under the kinetic regime of emulsion polymerizations, the fate of $M^\bullet$ could be quite different from its fate in a bulk system.

Another complication is introduced by the proposed rapid cyclization of the acetyl radical to form a butyrolactonyl radical:[2]



This is claimed[2] to partition almost exclusively into the aqueous phase, where it may terminate. Starnes *et al.*[7] failed to detect butyrolactone end groups in the NMR studies and concluded that they were not involved significantly in re-initiation.

VAc is a relatively unreactive monomer for addition to most radicals. This is borne out by its reactivity ratios with other common monomers[8] (styrene: 0.05, 50; acrylamide: 0.004, 8.25; butyl acrylate: 0.018, 3.48; acrylic acid: 0.021, 8.66; acrylonitrile: 0.06, 5.51; 2-chlorobutadiene: 0.0, 33.52; butyl methacrylate: 0.0, 30.18; MMA: 0.0, 30). Despite this relatively low reactivity of the monomer to most other radicals, it has a high k_p,[9,10] i.e., a high reactivity toward pVAc$^\bullet$, and, as shown by the above reactivity ratios, pVAc$^\bullet$ is highly reactive toward other monomers as well. This reactivity is also seen in the high transfer constant to its own monomer. Indeed, based on reactivity rates toward a range of transfer agents, it has been claimed that pVAc$^\bullet$ is 1500−2000 times as reactive in transfer as the polystyrene free radical.[11]

Whichever of the three proposed radicals (acetyl, butyrolactonyl, or vinylic) is actually formed by transfer, the important thing for the present purpose is that the radical site is chemically completely different from that on pVAc$^\bullet$ and is probably very much less reactive than the extraordinarily reactive pVAc$^\bullet$. Since VAc is not a very reactive monomer and $M^\bullet$ has a relatively high water solubility, the chances of $M^\bullet$ escaping from the particle before it can re-initiate are very much greater in the VAc system than is the case, for example, with styrene emulsion (homo)polymerizations.

3. Materials and Methods

The kinetic scheme resulting in eq 7 was tested by monitoring the γ-radiolysis relaxation behavior of a seeded VAc emulsion polymerization, where polymerization is initiated with γ-rays, the reactor vessel then removed from the radiation source, and the polymerization rate accurately monitored. Any decrease in rate so observed must be due entirely to radical-loss events, which yields a direct measure of the exit rate coefficient of eq 1 (see, for example, ref 4, for a summary of the method and data treatment). An automatic tracking device measures the meniscus height in a dilatometer every 3 s. When the dilatometer is removed from the γ source, initiation by radiolysis drops immediately to zero, and the only kinetic events remaining are exit (and possibly re-entry) of monomeric free radicals and thermal initiation.

One technical aspect of these relaxation experiments which needs to be taken into account is the effect of the heat of reaction on the temperature of the reaction mixture.[12] While there is no need to take this into account in most experiments using dilatometry in emulsion polymerization systems, it will be seen that this is not the case in relaxation studies in VAc. Normally, the reactor temperature in a jacketed vessel will be that of the heating/cooling liquid, but this is not necessarily the case as there will always be some time lag in heat transfer from the reactor to the jacket. In the experiments outlined below, the temperature was found to increase by as much as

2 deg when the dilatometer was placed in the γ source and the polymerization recommenced; a blank dilatometer and temperature probe placed in the γ source exhibited no change. This means that on removal from the source the reaction temperature decreases, the reaction mixture contracts. If this contraction is not taken properly into account, it appears as more conversion than there actually is. In other words, the relaxation appears to take longer than it should and entirely spurious interpretations may result. The reason that this effect is significant in VAc is the high reaction rate and exothermicity of this polymerization. In order to compensate for this effect, the temperature and contraction of the reaction mixture were monitored (out of source) while the temperature of the water jacket was lowered through the range appropriate to the particular experiment. These data were used to construct a calibration curve which, together with a sensitive temperature probe in the dilatometer, were then used to correct the conversion/time data obtained during the relaxation experiment.

Hydroquinone inhibitor (3−5 ppm HQ) was removed from VAc monomer (Aldrich) by adsorption onto basic alumina and a reflux distillation, discarding the first and last 20% of distillate. The monomer was either used immediately or stored overnight at 4 °C. Emulsifiers Aerosol MA-80 and Aerosol OT-75 were used as supplied by Cyanamid. The buffer used was sodium hydrogen carbonate (Merck) and the initiator used to prepare the seed was potassium persulfate (Merck), both being used without further purification.

The seed latex was prepared at 60 °C under nitrogen as a starved-feed batch. An initial charge of monomer (30 g) was solubilized in Milli-Q water (472 g) in which emulsifiers (Aerosol OT-75, 3.767 g, and Aerosol MA-80, 3.762 g) and buffer (0.75 g) had been dissolved previously. Potassium persulfate (0.675 g) was dissolved in water (26 mL) and an initial charge of 6 mL added to commence the reaction. The remaining monomer (165 g) and initiator were added at rates of 0.7 g min^{-1} and 0.1 mL min^{-1}, respectively. The seed so produced had a number-average particle diameter of 74 nm with a polydispersity of 1.15 (measurement being by capillary hydrodynamic fractionation: Matec Instruments) and solids content of 18.67% after dialysis.

In a typical γ-relaxation experiment, monomer (4 g) was solubilized in water (15 g) in which emulsifier (AMA-80: 0.14 g) and buffer (0.060 g) had been previously dissolved. Next the seed (40 g) was added to the dilatometer and allowed to swell for 1 h. After the calibration step outlined above, the dilatometer was lowered into the γ source (87.5 Gy h^{-1}) where, after an inhibition period, polymerization commenced. When the reaction had reached a steady state, the dilatometer was removed from the source (the time required to be removed completely from the radiation field being about 3 s), and the meniscus height and reactor temperature monitored until a new (thermal) steady state was reached. This procedure was repeated several times per run.

The rate of change of density with temperature for VAc is different from that of pVAc so the heat correction factor varies with conversion. For this reason a calibration had to be done before each relaxation.

4. Results and Discussion

Typical relaxation plots are shown for runs at 50 and 2 °C in Figures 1 and 2, respectively. It is of interest to note that at both temperatures, the background thermal entry rate coefficient ρ_{thermal} is negligible (to within our experimental uncertainty), which is similar to methyl methacrylate[13] but different from the styrene case.[5,14] The origin of this thermal polymerization in emulsion polymerization is unknown, although it may arise *inter alia* from peroxides formed during seed preparation.

It is clear in Figure 1 that the system relaxes very quickly at 50 °C, in fact within the 3 s interval required for complete removal from the γ source, and therefore too fast to measure with our experimental setup. However, the data are consistent within experimental uncertainty with the relaxation behavior predicted by both Limit 1 and Limit 2b models though one cannot discriminate between the two limits at this temperature.

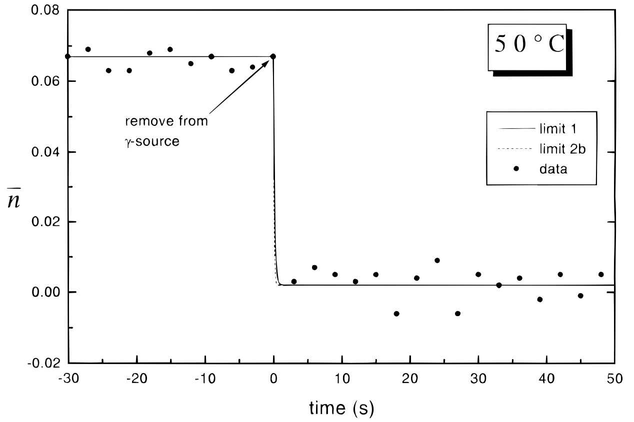


Figure 1. VAc γ-radiolysis relaxation at 50 °C. Model curves based on eqs 1 and 5, using $k_{\text{tr}} = 1.0$ dm^3 mol^{-1} s^{-1}, as estimated from the literature values for $(k_{\text{tr}}/k_{\text{p}})$[8,11] and k_{p},[9,10] and $C_{\text{P}} = 5 \pm 0.5$ mol dm^{-3}.

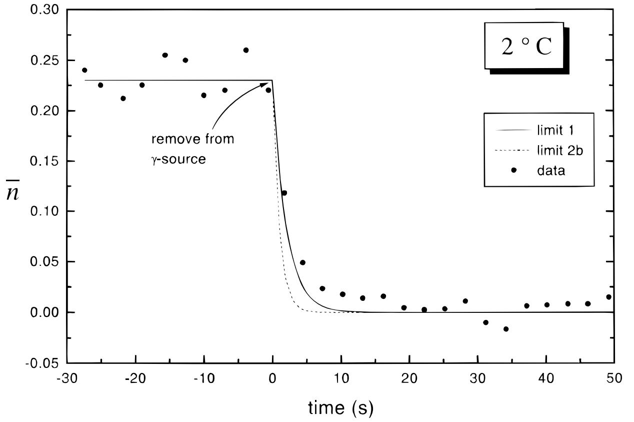


Figure 2. As in Figure 1, except for 2 °C and $k_{\text{tr}} = 0.1$ dm^3 mol^{-1} s^{-1}.

At 2 °C the relaxation takes about 10−20 s, and moderately precise measurement of k was possible, an average value of 0.4 ± 0.1 s^{-1} being obtained from four data points. As can be seen in Figure 2, the predicted Limit 1 model behavior fits the relaxation data more closely than does Limit 2b.

It should be noted here that the values used for k_{tr} are subject to significant uncertainty, and the predicted relaxation curves are very sensitive to this. Thus, although the results suggest that Limit 1 (termination of the desorbed radical in the aqueous phase) provides a better description of the kinetics than does Limit 2b (termination of the desorbed radical after it re-enters another particle containing a growing radical), the difference is only a factor of 2 in k_{tr}, which is within the experimental scatter. The uncertainty in the literature values of k_{tr} can be rectified with new experimental means of obtaining this quantity.[15,16]

Major obstacles in seeded VAc emulsion polymerization experiments are the formation of new particles and polymerization of monomer droplets. These problems were largely avoided by commencing experiments in Interval III. There was some secondary nucleation but this has very little effect on the determination of k (see eq 8). One then has to monitor conversion throughout the experiment and calculate C_{P} for each relaxation in order to compare k with $k_{\text{tr}}C_{\text{P}}$. In the two plots presented here, $C_P = 5 \pm 0.5$ mol dm^{-3}, giving a value for $k_{tr}C_P$ of 0.5 s^{-1}. No meaningful error can be assigned to this value because of the large uncertainty in the literature values of k_{tr} mentioned above, but it does accord with the experimentally determined k.

5. Conclusions

The radical-loss measurements in this work show conclusively that in the VAc emulsion polymerization system, this loss is by transfer to monomer to form a species which exits and undergoes termination (either in the aqueous phase or by re-entry into another particle which already contains a growing radical) rather than propagating. The straightforward mathematical analysis presented shows how exit and subsequent termination lead to the often observed independence of conversion rate on monomer concentration, without requiring any fortuitous cancellation of rate parameters.

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