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# Retardation by oxygen in emulsion polymerisation

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## Abstract

The extended retardation of the free-radical seeded emulsion polymerisation of vinyl acetate by oxygen has been modelled and fitted to experimental data. It is argued that the unusually long retardation observed in this system is due to the high entry efficiency of the aqueous-phase oligomeric radicals which allows latex particles to compete with dissolved oxygen for these initiating radicals. This, in the case of VAc, is due to the high value of the product of the propagation rate coefficient and the water solubility. As oxygen is consumed the competition increasingly favours entry of initiating radicals into particles and the polymerisation rate gradually increases. The model also qualitatively predicts the much shorter retardation behaviour of styrene and MMA which is due to the lower values of the product of the propagation rate coefficient and the water solubility for these monomers. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords*: Vinyl acetate; Free-radical emulsion polymerisation; Retardation

## 1. Introduction

In free-radical seeded emulsion polymerisation it is common to observe a lengthy inhibition (induction) period during which little or no polymerisation occurs. The inhibition is often ascribed to dissolved oxygen [1] which reacts with free radicals at close to diffusion-controlled rates to form stable radical species [2]. “Stable”, in this context, means radicals that are sufficiently unreactive that their most probable fate is to terminate with another radical to form unreactive products.

In seeded emulsions the inhibition period may be followed by a retardation period during which the polymerisation rate, $R_p$, usually increases to a steady-state value [3,4]. There are distinct differences in retardation behaviour: VAc is slow (this work), styrene is fast [5] and MMA is intermediate [6]. The observed retardation behaviour is not related to particle formation, as this behaviour is seen in seeded emulsions. Neither can it be attributed to some particular effect of the reactivity of certain radicals towards oxygen as the rate coefficients for the addition of oxygen to alkyl radicals is of the order of $10^9\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ and is only slightly affected by substituents [7].

The three monomers just named have qualitatively different behaviour: the propagation rate coefficient for VAc $\gg$ MMA $>$ styrene, and the same holds for the water solubility, so it seems that radical entry is a likely candidate.

The retardation ascribed here to oxygen must be distinguished from a slow (but retardant-free) approach to the steady-state rate that may be due to the kinetics of particular emulsion polymerisation systems. For example: a low propagation rate coefficient, and/or low aqueous-phase water solubility, may result in low radical entry efficiency and consequently a relatively slow approach to steady state, as is the case for styrene [5]. The slow, retardant-free approach to steady state is readily observed with the gamma radiolysis method described later. When this is taken into account the retardation due to oxygen may be a matter of seconds for styrene [8,9], minutes for MMA (methyl methacrylate) [6] and longer still for VAc (this work).

A general kinetic scheme for retardation is given in Scheme 1. Inhibition/retardation by oxygen is complicated by the possibility of reinitiation by hydrogen transfer (Scheme 1, path 2) or addition reactions (Scheme 1, path 3) as outlined by Moad and Solomon [2]. However, in view of its effectiveness in inhibiting free-radical polymerisation [3,4,6] oxygen is generally treated as an ideal inhibitor. Thus, when an aqueous-phase oligomeric radical encounters an oxygen molecule it is considered to be effectively capped and to terminate rapidly with another aqueous-phase radical

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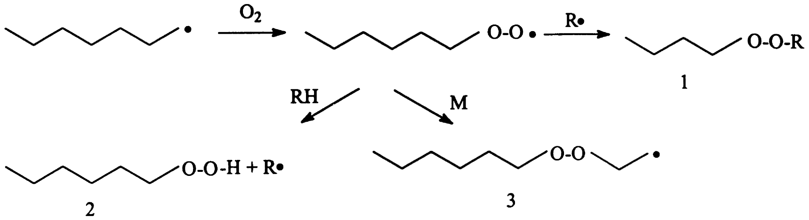

Scheme 1.

(Scheme 1, path 1). The peroxides so formed play no significant part in the polymerisation during the retardation period for reasons that are discussed later.

The proportion of initiator-derived radicals that enter particles is termed the entry efficiency, $f_{\mathrm{entry}}$. As is shown below, $f_{\mathrm{entry}}$ is crucial to the retardation behaviour. Termination of aqueous-phase oligomeric radicals (Scheme 1, path 1) causes inhibition and/or retardation by preventing entry of these initiating radicals into the latex particles which are the main locus of polymerisation. In persulfate-initiated systems radicals are generated in the aqueous phase by thermolysis of the peroxydisulfate anion, $S_2O_8^{2-}$, to produce two sulfato radicals, $SO_4^{\bullet -}$. These react with aqueous-phase monomer and propagate to a length, $z$, at which the increasingly hydrophobic oligomeric free radical becomes sufficiently surface active to enter a particle and initiate polymerisation [3,4]. The polymerisation rate depends in part on how efficiently these radicals can be transported into the particles.

The size of the entering oligomeric radical is an important parameter in the determination of $f_{\mathrm{entry}}$. This is because the time spent in the aqueous phase growing to a $z$-mer determines the likelihood of bimolecular termination occurring before entry can take place. From thermodynamic considerations Maxwell et al. [10] postulated that, for persulfate-initiated oligomers, $z$ may be estimated from the following equation:

$$z \approx 1 - \frac{23/\mathrm{kJ\ mol}^{-1}}{\mathrm{R}T\ \ln[\mathrm{M}_{\mathrm{aq}}^{\mathrm{sat}}]/\mathrm{mol\ dm}^{-3}} \tag{1}$$

where $T$ is the reaction temperature and $[\mathrm{M}_{\mathrm{aq}}^{\mathrm{sat}}]$ is the saturation concentration of aqueous-phase monomer. They also showed that, in the absence of inhibitors and retarders, $f_{\mathrm{entry}}$ can be estimated from a simple analytical approximation to the complete set of rate equations that describe all the aqueous-phase events [10]

$$f_{\mathrm{entry\ (no\ inhibitors/retarders)}} = \left\{ \frac{(k_{\mathrm{d}}[\mathrm{I}]k_{\mathrm{t,aq}})^{0.5}}{k_{\mathrm{p,aq}}[\mathrm{M}_{\mathrm{aq}}]} + 1 \right\}^{1-z} \tag{2}$$

where $k_{\mathrm{d}}$ is the rate coefficient for decomposition of initiator, [I] the initiator concentration, $k_{\mathrm{t,aq}}$ the average rate coefficient for bimolecular termination of aqueous-phase radicals, $[\mathrm{M}_{\mathrm{aq}}]$ the aqueous-phase concentration of monomer and $k_{\mathrm{p,aq}}$ the rate coefficient for propagation in the aqueous phase. It has been shown [11–13] that $k_{\mathrm{p,aq}}$ is generally about the same as $k_{\mathrm{p}}$ measured in bulk for ordinary monomers; however, there may be a difference between these quantities for polar monomers such as vinyl acetate.

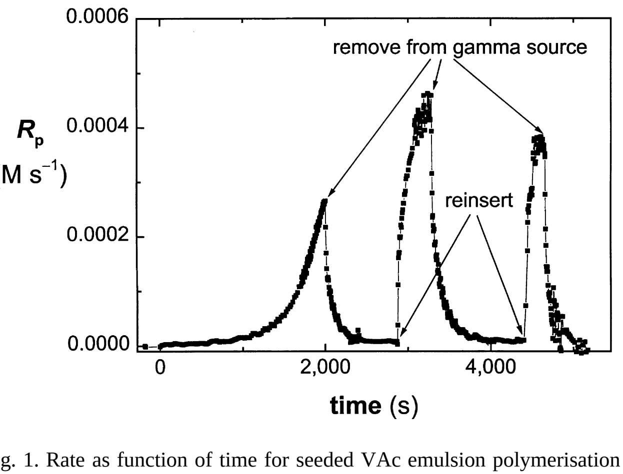

Fig. 1. Rate as function of time for seeded VAc emulsion polymerisation initiated by $\gamma$ radiolysis. 2°C, Dose rate $= 0.029\ \mathrm{Gy\ s}^{-1}$, experimental details: see Table 1.

For VAc and MMA, entry efficiency is high and aqueous-phase termination events other than termination with oxygen are relatively insignificant. For VAc at 50°C and $[S_2O_8^{2-}] = 1$ mM, $[\mathrm{M}_{\mathrm{aq}}^{\mathrm{sat}}] = 0.3$ M so $z \approx 8$ (Eq. (1)) and, in the absence of inhibitors, $f_{\mathrm{entry}} > 99\%$ (Eq. (2)). This estimate is not very sensitive to the calculated value of $z$ or to the assumed value for $k_{\mathrm{p,aq}}$. Poehlein and co-workers [14] found experimentally that $z$ was in the range 5–14 for VAc. Even if $z$ is taken as the upper limit found in Poehlein's work and $k_{\mathrm{p,aq}}$ halved, $f_{\mathrm{entry}}$ is still greater than 98%. Similarly for MMA, $z \sim 4 - 5$ and $f_{\mathrm{entry}} \sim 85 - 95\%$.

In systems that are inhibited by oxygen as in Scheme 1, oxygen is consumed and as its concentration decreases, entry efficiency becomes a competition between the rate at which sulfato radicals grow to $z$-mers and the rate at which aqueous-phase oligomeric radicals are terminated by oxygen.

The aim of this paper is to investigate the effect of dissolved oxygen on free-radical emulsion polymerisation kinetics and to develop a model that semi-quantitatively predicts retardation behaviour in a variety of seeded emulsion polymerisation systems.

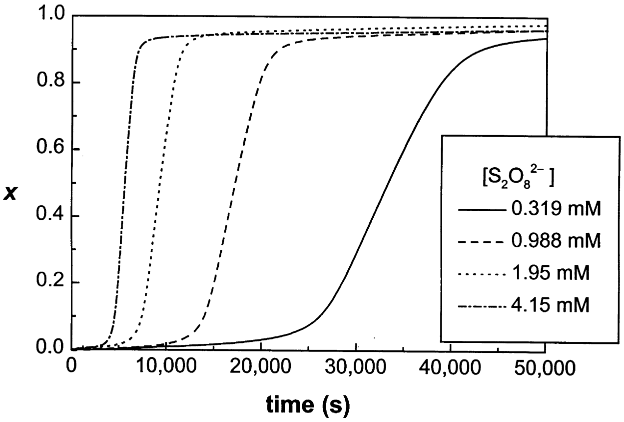

Fig. 2. Conversion, *x*, as function of time and persulfate concentration for series of interval III, seeded VAc homopolymerisations at 50°C, experimental details: see Table 1.

Table 1
Details of emulsion polymerisations of VAc with chemical and $\gamma$ initiation

| | VAc/chemical | VAc/$\gamma$ |
|---|---|---|
| $CH_3COONa$ (g) | 0.12 | – |
| AMA-80 (g) | 0.12 | 0.15 |
| Total $H_2O$ (g) | 45.8 | 45.6 |
| Monomer (g) | 7.5 | 4.24 |
| Seed latex (g) | 7.2 g solids | 11.25 g solids |
| Temperature (°C) | 50 | 2[a] |
| Dilatometer volume (ml) | 62.6 | 60.0 |
| $D_{N,(seed)}$ (nm) | 102 | 102 |
| $N_c$ ($dm^{-3}$) | $2.3 \times 10^{17}$ | $2.9 \times 10^{17}$ |
| $[K_2S_2O_8]$ (mM) | 0.319–4.95 | – |
| $\gamma$ dose rate ($Gy\ s^{-1}$) | – | 0.029 |

[a] The gamma radiolysis data were acquired at 2°C for practical reasons discussed in Ref. [15].

## 2. Materials and methods

In the model developed below it is assumed that the parameters that determine retardation behaviour are oxygen concentration, initiator concentration and the properties of the monomer such as $k_{p,aq}$ and $[M_{aq}]$.

As mentioned above, it has been reported for VAc that retardation is independent of initial $[O_2]_{(aq)}$, provided that there is enough oxygen to cause inhibition. Therefore, experiments were designed primarily to test dependence of the retardation behaviour on initiator concentration. The retardant-free approach to steady state for VAc was measured by the gamma radiolysis method developed by Gilbert and co-workers [3]. In this method, polymerisation is initiated with $\gamma$ radiation. When a steady state is reached the reactor (usually a dilatometer) is removed from the $\gamma$ source and the polymerisation is allowed to relax. After a suitable time the reactor is reinserted into the $\gamma$ source and the ensuing approach to steady state is usually free of inhibitor artefacts (Fig. 1).

The experiments in this work were seeded homopolymerisations of VAc (to obviate the complexities of particle formation) and commenced in interval III (absence of monomer droplets) to minimise the incidence of secondary nucleation, thereby maintaining a constant particle number.

VAc was obtained from Aldrich inhibited with 3–5 ppm hydroquinone. The inhibitor was removed on a column of basic alumina. The monomer was distilled under nitrogen at 72–73°C, with the first and last 20% being discarded. GC-MS conducted on the purified monomer showed no hydroquinone remaining. Bulk polymerisations performed with VAc purified in this way and degassed by multiple freeze–thaw cycles had inhibition periods of just a few minutes indicating the satisfactory nature of the purification procedure. The monomer was either used immediately or stored overnight at 4°C.

Emulsifiers AMA-80 and AOT-75 were used as obtained from Cyanamid. The buffer used was sodium acetate and the initiator used to prepare the seeds was potassium persulfate. Both were obtained from Merck and used without further purification. Milli-Q water, 18.2 MΩ $cm^{-1}$ was used throughout.

The VAc seed latex was prepared at 60°C under nitrogen as a starved-feed process. An initial charge of VAc (40 g) was solubilised in water (600 g) in which the emulsifiers (AMA-80: 5.2 g and OT-75: 5.05 g) and buffer ($CH_3COONa$: 1.00 g) had been previously dissolved. The potassium persulfate (1.00 g) was dissolved in water (30 ml) and an initial charge of about 25% of the persulfate solution added to commence the reaction. The remaining monomer (221.6 g) and initiator solution were added at rates of 1.4 and ~0.15 ml $min^{-1}$, respectively.

Rate data were obtained by the following experimental procedure (see Table 1). A thermostated dilatometer was charged with VAc, sodium acetate, AMA-80 and degassed water and the mixture emulsified under partial vacuum by stirring with a magnetic bar. The seed (which had been allowed to equilibrate with atmospheric oxygen) was added and allowed to swell with monomer at 50°C for 30 min (also under partial vacuum to remove some of the dissolved gases as it is essential that no bubbles form in the dilatometer). In the chemically initiated experiments persulfate was dissolved in water (~20 ml) and 1.00 ml of the solution injected into the dilatometer. The capillary was then fitted and water added to the appropriate meniscus height.

Polymerisations were monitored to about 95% conversion. Some polymerisations were allowed to run for a further 20 h during which time the polymerisation rate was about 0.1% $h^{-1}$, ultimately reaching conversions of over 98% (Fig. 2).

The number average particle diameters of the latexes were determined by capillary hydrodynamic fractionation (CHDF) using a Matec Applied Sciences CHDF1100 fitted with a C570 high sensitivity column claimed to be suitable for particle diameters of 15–700 nm. The eluent used was GR500™ at a flow rate of 1.40 ml $min^{-1}$.

## 3. Results and discussion

In γ-initiated experiments the first insertion showed retardative behaviour similar to that reported for persulfate initiated polymerisations [4]. However, the subsequent insertions (Fig. 1) show no retardation, which suggests that the initial retardation is not due to any kinetic effects and must therefore be an inhibitor artefact. Ballard observed a similar effect, though less pronounced, in the emulsion polymerisation of MMA [6].

The main features of persulfate-initiated VAc emulsion polymerisations are clearly seen in Fig. 2. These are: an induction period that is approximately inversely proportional to the initiator concentration, a retardation period which decreases with increasing initiator concentration and a steady-state rate which is nearly constant until the rate decreases abruptly at high conversions.

The major reactions involving aqueous-phase radicals and oxygen (and their rate coefficients at 50°C) are

$$SO_4^{\cdot-} + M_{(aq)} \xrightarrow{k_{p,I}} {}^{-}SO_4M^{\cdot}_{(aq)}$$

$$k_{p,I} \approx 10^9\ M^{-1}\ s^{-1}\ [16] \tag{3}$$

$$\begin{gathered} {}^{-}SO_4M^{\cdot}_{i(aq)} + M_{(aq)} \xrightarrow{k_{p,aq}} {}^{-}SO_4M^{\cdot}_{i+1(aq)} \\ k_{p,aq(VAc)} = 6.7 \times 10^3\ M^{-1}\ s^{-1}\ [17] \end{gathered} \tag{4}$$

$$\begin{gathered} {}^{-}SO_4M^{\cdot}_{i(aq)} + O_{2(aq)} \xrightarrow{k_{t,O_2}} {}^{-}SO_4M_iOO^{\cdot}_{(aq)} \\ k_{t,O_2} \approx 10^9\ M^{-1}\ s^{-1}\ [7] \end{gathered} \tag{5}$$

$$2\,{}^{-}SO_4M^{\cdot}_{i(aq)} \xrightarrow{k_{t,aq}} ({}^{-}SO_4M_i)_{2(aq)}$$

$$k_{t,aq} \approx 10^9\ M^{-1}\ s^{-1}\ [18] \tag{6}$$

$$\begin{gathered} {}^{-}SO_4M^{\cdot}_{i(aq)} + {}^{-}SO_4M_jOO^{\cdot}_{(aq)} \xrightarrow{k_7} {}^{-}SO_4M_iOOM_jSO^{-}_{4(aq)} \\ k_7 \approx 10^9 M^{-1} s^{-1} [7] \end{gathered} \tag{7}$$

$$\begin{gathered} 2\,{}^{-}SO_4M_iOO^{\cdot}_{(aq)} \xrightarrow{k_8} ({}^{-}SO_4M_iOO)_{2(aq)} \\ k_8 \approx 10^7\ M^{-1}\ s^{-1}\ [7] \end{gathered} \tag{8}$$

$$\begin{gathered} {}^{-}SO_4M_iOO^{\cdot}_{(aq)} + M_{(aq)} \xrightarrow{k_9} {}^{-}SO_4M_iOOM^{\cdot}_{(aq)} \\ k_{9(VAc)} \approx 2.5\ M^{-1}\ s^{-1}\ [19] \end{gathered} \tag{9}$$

$k_8$ estimated from value for model compound (acetoxypentylperoxyl radical).

Reaction 3 is very fast and can only be rate-determining for monomers with extremely low water solubility, much lower than, say, styrene.

The probability of an aqueous-phase monomeric radical growing to a $z$-mer, $f_{entry}$, is then given by the competition between the rate at which it propagates $z - 1$ times (Reaction 4) and the sum of the rates of the termination reactions (5–7)

$$f_{entry} \cong \left\{ \frac{k_{p,aq}[M_{aq}]}{k_{p,aq}[M_{aq}] + k_{t,O_2}[O_2] + k_{t,aq}[M^{\cdot}_i] + k_7[M_iOO^{\cdot}]} \right\}^{z-1} \tag{10}$$

Further reactions of the peroxides produced in reactions 7 and 9 have been disregarded for the following reasons:

(i) thermal decomposition is likely to be quite slow, as similar peroxides have half lives of many hours at 50°C. In the case of VAc for example, the half-life of the peroxide could be expected to lie between those of di-alkyl and di-acyl peroxides. At 50°C di-ethyl peroxide has a half life of about 30 years while di-propanoyl peroxide has a half life of 80 h (calculated from the Arrhenius parameters presented by Howard [19]) and any influence is therefore negligible on the timescale of emulsion polymerisations.
(ii) radical-induced decomposition of these peroxides can be extremely rapid, the rate being very sensitive to substituents [19]. However, in the aqueous-phase chemistry of free-radical emulsion polymerisations the net result of radical-induced decomposition is merely radical transfer from a short chain alkyl radical to a short chain alkoxy radical [19]. Such alkoxy radicals would be expected to reinitiate in the aqueous phase thereby incorporating ethereal oxygen in the aqueous-phase oligomeric radicals. This may have a small effect on the solubility of the aqueous-phase oligomeric radical but otherwise should have little effect on entry of radicals into particles. Furthermore, the stoichiometry of the termination of aqueous-phase oligomeric radicals with oxygen is unaffected; i.e. two initiator-derived radicals are oxidised by one oxygen molecule.

Eq. (10) may be simplified by considering the following:

(i) In high entry-efficiency systems such as VAc and MMA [3,10] reaction 6 is insignificant and has negligible effect on the retardation period. In low entry efficiency systems (e.g. styrene) the retardation period itself is insignificant [8,9]. The term $k_{t,aq}[M^{\cdot}_i]$ may be significant after the retardation period, as it limits the maximum value of $f_{entry}$ in low entry efficiency systems, but otherwise has little effect on the retardation behaviour.
(ii) The peroxy radicals formed in reaction 3 will be consumed in reactions 7–9. As the rate of consumption of peroxy radicals must be approximately equal to their rate of production one can say that

$$\begin{aligned} k_{t,O_2}[O_2][M^{\cdot}_i] \cong{}& k_7[M_iOO^{\cdot}][M^{\cdot}_i] + k_8[M_iOO^{\cdot}]^2 \\ &+ k_9[M_iOO^{\cdot}][M_{aq}] \end{aligned} \tag{11}$$

Reaction 8 is probably not significant due to the low

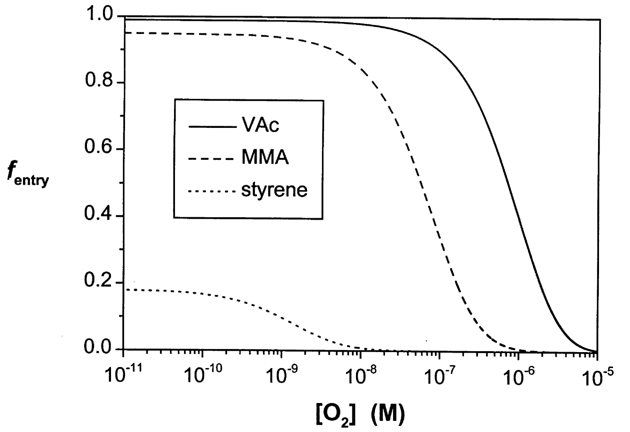

Fig. 3. $f_{entry}$ calculated as function of $[O_2]$ at 50°C (Eqs. (2) and (13)) $k_{t,O_2} = 2\times10^8\ M^{-1}\ s^{-1}$ (VAc : $k_p = 6.7\times10^3\ M^{-1}\ s^{-1}$, $[M_{aq}] = 0.3$ M; MMA : $k_p = 650\ M^{-1}\ s^{-1}$, $[M_{aq}] = 0.15$ M; styrene : $k_p = 258\ M^{-1}\ s^{-1}$, $[M_{aq}] = 0.0043$ M). Note : $[O_2]^{sat} \sim 1.4\times10^{-3}$ M.

concentration of reactants and the relatively low rate constant. However, if such a tetroxide forms, at 50°C it will most likely decompose rapidly to yield a single molecule of oxygen, an alcohol and an aldehyde by the non-radical Russell mechanism [19]. The net result, as far as the kinetics of entering radicals is concerned, is the same as reaction 7, i.e. one oxygen molecule consumes two initiator-derived free radicals.

Copolymerisation (reaction 9) incorporates oxygen and may therefore accelerate the consumption of oxygen and decrease the retardation period. Typically, $[^{-}SO_4M^{\cdot}_{i(aq)}] \approx 10^{-9}$ M in emulsion polymerisations [3] and for VAc $[M_{aq}] \approx 0.3$ M. Thus $k_7[^{-}SO_4M^{\cdot}_{i(aq)}] \approx k_9[M_{aq}]$ and reactions 7 and 9 may compete for peroxy radicals, with higher [I] favouring reaction 7. However, the good agreement between the model (which ignores reaction 9) and the experimental data, as discussed later, suggests that the consumption of oxygen by copolymerisation is negligible, except perhaps at low [I].

Hence

$$k_{t,O_2}[O_2][M_i^{\cdot}] \cong k_7[M_iOO^{\cdot}][M_i^{\cdot}] \tag{12}$$

and Eq. (10) reduces to

$$f_{entry} \cong \left\{ \frac{k_{p,aq}[M_{aq}]}{k_{p,aq}[M_{aq}] + 2k_{t,O_2}[O_2]} \right\}^{z-1} \tag{13}$$

Using literature values for these coefficients [3,4] $f_{entry}$ may be plotted as a function of $[O_2]$ for some representative monomers (see Fig. 3).

Thus, in the case of VAc at dissolved oxygen concentrations below about $10^{-5}$ M, inhibition ceases and the polymerisation is retarded until $[O_2]$ drops below about $10^{-8}$ M. As $O_2$ is consumed, $f_{entry}$ increases and the rate of consumption of oxygen by initiator-derived radicals decreases according to

$$\frac{d[O_2]}{dt} = -k_d[I](1 - f_{entry}) \tag{14}$$

In order to relate the modelled $f_{entry}$ to the experimental observable, $R_p$, it is necessary to consider the fate of the entering radicals. The entered particle may contain oxygen, a propagating radical, a peroxy radical or no terminating species.

Oxygen is quite soluble in monomers; e.g. $[O_2]^{sat} = 1.5\times10^{-3}$ M in VAc [20] which is similar to that in water ($1.4\times10^{-3}$ M) under the same conditions (760 mmHg, 20°C) [21]. Hence, oxygen is likely to be found in the swollen particles which act as a reservoir replacing aqueous-phase oxygen as it is consumed during the inhibition period.

At the end of the inhibition period for VAc, $[O_2]_{(aq)} \approx 10^{-5}$ M (Fig. 3) and $[O_2]_{(particle)}$ should be about the same. A 120 nm diameter swollen particle should, on average, contain less than one oxygen molecule at the beginning of the retardation period. If there were more than one this would soon be reduced to one by the various termination reactions described above. Such oxygen molecules may "cap" a growing chain and eventually terminate with an entering oligomeric radical (as in Scheme 1, path 1), but are more likely to reinitiate (as in Scheme 1, path 3). This is because the entry rate is much lower than the reinitiation rate. This argument is quantified as follows.

The maximum entry rate in the absence of oxygen can be estimated from the Maxwell–Morrison equation [10]

$$\rho = \frac{2k_d[I]N_A}{N_c} \left\{ \frac{(k_d[I]k_{t,aq})^{0.5}}{k_{p,aq}[M_{aq}]} + 1 \right\}^{1-z} \tag{15}$$

where $\rho$ is the first-order rate coefficient for entry of radicals into particles. At the highest initiator concentration in this work (4.29 mM) Eq. (15) gives $\rho \approx 0.04\ s^{-1}$. At early times in the retardation period, $\rho$ will be even less (because of aqueous-phase termination of most of the oligomeric radicals by oxygen). Hence, for intra-particle termination to occur, an oxygen-capped radical must not reinitiate, on average, for at least 25 s despite being dissolved in monomer. Reinitiation via the particle phase equivalent of reaction 9 would be expected to take about 0.05 s for VAc (less for MMA and styrene where $k_9 = 4.5$ and $41\ M^{-1}\ s^{-1}$ respectively) [19]. Therefore, during the retardation period, particle-phase oxygen is expected to have little or no effect on $R_p$.

If the entered particle contains no terminating species, the entering radical will propagate and eventually transfer radical activity to a species that may exit. However, during the retardation period $N_c/N_A \approx [O_2]_{(aq)}$ and as the particles are so much larger than oxygen molecules, most exiting radicals will simply enter another particle and propagate. Hence, for the purposes of this discussion, provided the average number of radicals per particle, $\bar{n}$, is small, exit can also be ignored.

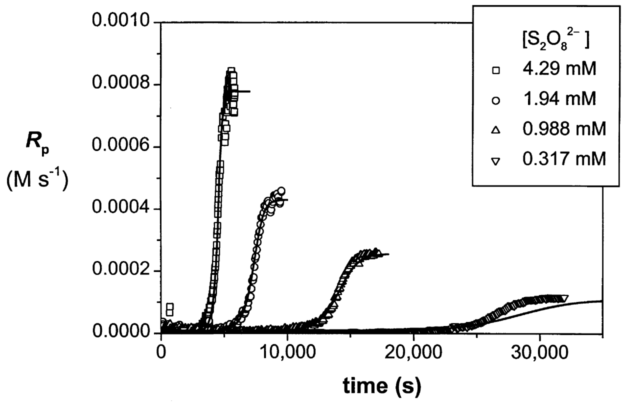

Fig. 4. $R_p$ (–) calculated (Eq. (16)); points: experimental data. VAc emulsion polymerisation at 50°C, $k_p = 6.7 \times 10^3$ M$^{-1}$ s$^{-1}$, $[M_{aq}] = 0.25$ M, $k_{t,O_2} = 2 \times 10^8$ M$^{-1}$ s$^{-1}$, $z = 5$.

If the entered particle contains a propagating radical, bimolecular termination is most likely after a short time (at least for small particles in most hydrophobic monomer systems [3]). The probability that the entered particle contains a propagating radical is $\bar{n}$. Hence, for low $\bar{n}$ systems (such as VAc, and obviously for most systems at early times in the retardation period) the probability that the entering radical initiates polymerisation is high. During the retardation period very little monomer is polymerised so that reaction conditions are approximately constant. Hence, $R_p$ will be approximately proportional to $f_{entry}$. A better approximation is that $R_p \propto f_{entry}(1 - 2\bar{n})$ as intra-particle bimolecular termination results in the loss of two radicals. This is a gross simplification of the many complexities of emulsion polymerisation kinetics but is a reasonable approximation for small particles and low $\bar{n}$.

Combining Eqs. (13) and (14) gives the rate of depletion of $[O_2]$ as

$$\frac{d[O_2]}{dt} = -k_d[I]\left\{1 - \left[\frac{k_{p,aq}[M_{aq}]}{k_{p,aq}[M_{aq}] + 2k_{t,O_2}[O_2]}\right]^{z-1}\right\} \quad (16)$$

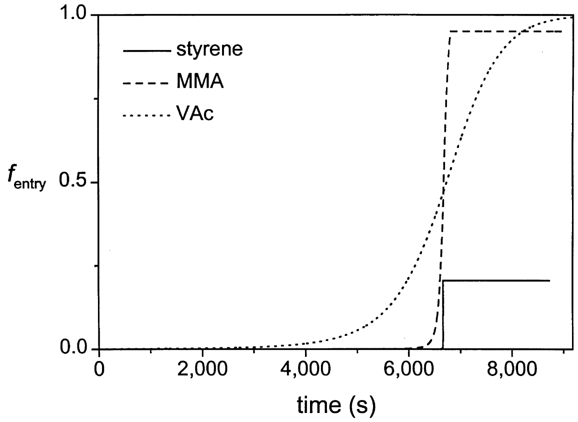

Fig. 5. $f_{entry}$ calculated as function of time (Eq. (16)) for VAc, MMA and styrene emulsion polymerisations at 50°C, $k_{t,O_2} = 2 \times 10^8$ M$^{-1}$ s$^{-1}$, $[O_2]_{(init)} = 10^{-5}$ M.

Eq. (16) was integrated numerically and fitted to the experimental data. A good fit to most of the data was obtained with the reasonable values $z = 5$ and $k_{t,O_2} = 2 \times 10^8$ M$^{-1}$ s$^{-1}$. These two parameters are strongly correlated and reasonable fits are also found for $z = 6$, $k_{t,O_2} = 1 \times 10^8$ M$^{-1}$ s$^{-1}$ and $z = 4$, $k_{t,O_2} = 3 \times 10^8$ M$^{-1}$ s$^{-1}$. As mentioned previously, it is entirely possible that some oxygen copolymerises and is thus consumed more rapidly than is accounted for by this model. This would most strongly influence the slowest polymerisations and may account for the relatively poor fit to the 0.317 mM run (Fig. 4).

Fig. 5 shows that the proposed model also qualitatively fits the retardation behaviour reported for the emulsion polymerisations of styrene and MMA, which is qualitatively different from that of VAc. In the case of styrene $f_{entry}$ increases from 2% to its maximum of 20% (Eq. (2)) in just 4 s ($k_{t,O_2} = 2 \times 10^8$ M$^{-1}$ s$^{-1}$, $[S_2O_8^{2-}] = 1$ mM, $[O_2]_{(init)} = 10^{-5}$ M). This is consistent with the absence of an observable retardation artifact reported in γ-relaxation studies of styrene emulsion polymerisation [6]. In the case of MMA, $f_{entry}$ increases from 5% to its maximum of 95% in 5 min ($k_{t,O_2} = 2 \times 10^8$ M$^{-1}$ s$^{-1}$, $[S_2O_8^{2-}] = 1$ mM, $[O_2]_{(init)} = 10^{-5}$ M). This is consistent with the retardation artefact reported in γ-relaxation studies of MMA emulsion polymerisation [6].

The reason for the qualitative difference between the retardation behaviour of these systems can be seen in Eq. (13). Initially, $2k_{t,O_2}[O_2] \gg k_{p,aq}[M_{aq}]$, $f_{entry}$ will be very small, and polymerisation inhibited, until sufficient oxygen is consumed (mainly via Scheme 1, path 1) such that $k_{p,aq}[M_{aq}]$ is of the order of $2k_{t,O_2}[O_2]$. In the case of VAc at 50°C, $k_{p,aq}[M_{aq}] \approx 2 \times 10^3$ s$^{-1}$ and inhibition ceases when the oxygen concentration is reduced to about $10^{-5}$ M, after which the polymerisation is retarded until $[O_2]$ drops below about $10^{-8}$ M (Fig. 3). For MMA and styrene $k_{p,aq}[M_{aq}] \approx 1 \times 10^2$ and 1.1 s$^{-1}$, respectively so that $[O_2]$ at the beginning of their retardation periods is about $10^{-6}$ and $10^{-8}$ M, respectively. Thus, as a first approximation, the duration of the retardation period corresponds to the time taken to consume about $10^{-5}$ M of oxygen (for VAc) and $10^{-6}$ and $10^{-8}$ M oxygen for MMA and styrene respectively. Consequently, the retardation for VAc is about ten times that for MMA and 1000 times that for styrene.

## 4. Conclusions

Inhibition/retardation in seeded emulsion polymerisations can be modelled with one straightforward expression, adjusting parameters only within a narrow range of independently measured values.

The inhibition period in vinyl acetate seeded emulsion polymerisation is due to dissolved oxygen terminating aqueous-phase oligomeric radicals before they can enter particles and initiate polymerisation. The unusually prolonged retardation period often reported for the seeded emulsion polymerisation of vinyl acetate can be attributed to the competition between entry into particles and termination with aqueous-phase oxygen at concentrations below about $10^{-5}$ M. This, in the case of VAc, is due to the high value of the product: $k_{\mathrm{p,aq}}[\mathrm{M}_{\mathrm{aq}}]$.

The lack of such an artefact in the seeded emulsion polymerisation of styrene is due to its low propagation rate coefficient and low water solubility. MMA, with intermediate values of both of these parameters, behaves accordingly and is possessed of a significant, though relatively short retardation period.

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