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Modelling secondary particle formation in emulsion polymerisation: application to making core–shell morphologies

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Abstract

A simple model for particle formation in surfactant-free emulsion polymerisation [Macromol. Symp. 92 (1995) 13; Emulsion polymerization: a mechanistic approach, 1995], with extension to allow for induced decomposition of initiator, is explored. The object is to find conditions for secondary particle formation, especially to find conditions under which it would be possible to grow core–shell particles of vinyl acetate in styrene, and vice versa; core–shell particle formation requires that secondary particle formation be avoided. The system is described by homogeneous nucleation: a radical generated in the aqueous phase will either enter a latex particle, undergo termination, or grow in the aqueous phase until it becomes the nucleus of a new particle. The simplified kinetic description contains only easily specified parameter values and requires minimal computational resources. The model implies that secondary particle formation is suppressed by decreasing seed radius, by increasing solids content, and by starved-feed conditions; seed radius is by far the most influential, while monomer-catalysed initiator decomposition has negligible effect. The model predicts that new particle formation will be rampant when vinyl acetate is polymerised in the presence of large polystyrene particles (implying that large core–shell polystyrene/poly(vinyl acetate) (PS/PVAc) particles cannot be obtained in this way), but that there should be relatively little secondary particle formation when styrene is polymerised in the presence of large PVAc particles (implying that large core–shell PS/PVAc particles can be created by inverse core–shell polymerisation). The model was also used to estimate the particle numbers expected in ab initio, surfactant-free styrene and vinyl acetate systems. The model explains why such styrene systems give large, monodisperse particles, whereas such vinyl acetate systems give much smaller particles. Comparison of predictions of the model with those of more sophisticated treatments suggests that model contains the kinetic events which are most essential in determining the rate of particle formation, and thus is sufficient for stating whether or not massive secondary nucleation will occur. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Core–shell morphologies; Emulsion polymerisation; Starved-feed conditions

1. Introduction

The synthesis of core–shell particles in emulsion polymerisation is of interest because structured latex particles have different and in many cases more desirable properties than the corresponding blend or copolymer. This and the following papers concern the synthesis of latex particles with polystyrene (PS) cores and poly(vinyl acetate) (PVAc) shells and with a total radius of approximately 500 nm. At least two possibilities exist for creating such PS core–PVAc shell particles: to start from a PS seed and grow a PVAc shell onto and around it, or start with a PVAc seed and perform a second-stage emulsion polymerisation of styrene, whereupon the different hydrophobicity of the polymers would suggest that core–shell inversion should occur, leaving a PS core and a PVAc shell [1–3]. Whichever the chosen route, it is essential to avoid secondary particle formation during the second-stage growth. It is useful to have guidance from modelling in seeking to find conditions where this new nucleation can be avoided, as opposed to purely empirical searching for the right conditions. The present paper uses and extends a simple model for this purpose [4]. Although the model is conceptually simple, it is rigorously based on what is known about the kinetics and mechanisms of emulsion polymerisation.

Gaining an understanding of secondary particle formation is a topic of interest in its own right. Styrene–vinyl acetate systems are an excellent vehicle for study of this topic in general, because both monomers are so different in terms of their kinetics (one polymerises slowly, the other

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rapidly) and in terms of their physical properties (one hydrophobic, the other hydrophilic; one with high glass transition temperature, the other low). Commercial PVAc latexes often have large particle size, ~0.5 μm radius or greater. For PS to exert any influence on material properties of PS–PVAc core–shell particles, the cores need to occupy a significant volume of each core–shell particle. If the synthetic route to be followed starts with a PS seed, then this PS seed latex must have a radius close to 0.5 μm. PS particles with size this large can be created by polymerising the monomer in the absence of added surfactant [5]. The next stage would be to polymerise vinyl acetate using the large PS latex as a seed, with conditions being such that the formation of PVAc shells is favoured. Hergeth and Schmutzler [6] followed this route and reported successful PVAc shell formation, with their PS seed being about 150 nm radius. In this paper we examine this claim, and use our model to investigate the conditions under which successful core–shell particle formation is expected to be possible. It will be seen that seed particle size is a very important parameter in this regard, and that as seed particle size is increased, new particle formation becomes more and more likely compared with formation of structured particles.

The model described in this paper is for surfactant-free conditions, although this restriction could be removed without difficulty [7]. The presence of surfactant can only act to encourage the formation of new particles, so in effect our modelling results will indicate the circumstances under which generation of structured particles is most likely.

2. Particle formation model

Extensive models for particle formation (and hence for secondary particle formation) have been presented in the literature [8–18]. A major difficulty with a priori prediction is that such models usually contain many parameters whose values are unknown, and need to be fitted to experiment; this reduces predictive power. However, ongoing advances in the determination of rate parameters (such as the PLP method for determining the propagation rate coefficient [19–22]) and in mechanistic knowledge [7] have reduced the extent of this problem. An extensive particle formation model, when applied to systems wherein most rate parameters have been determined independently, is able to produce acceptable accord with a large range of observations, including rate, particle number and amount of secondary nucleation for a variety of monomers [18,23]. However, this model, which generates the entire particle size distribution, requires extensive computational resources. While this enables prediction of important experimental details with acceptable reliability, this treatment is difficult to use for simply exploring an extensive parameter space in order to find a range of experimental conditions for which secondary nucleation does not occur. In fact this is a task that does not require precise quantitative agreement between model and experiment; rather, all that is required is a reliable qualitative assessment of whether the number of new particles is negligible or significant. For this purpose one can take the essential details of the large-scale model, incorporate them into a simplified model, and then use this simplified model to search for conditions under which secondary nucleation does not occur. Although the numerical predictions of the simplified model may only be semi-quantitatively correct, they should still be qualitatively useful. This will be checked here by comparing results of the simplified model with corresponding results from the more complete treatment [18,23].

The model used in this paper is a slightly extended version of that put forward by Morrison and Gilbert [4,7,24] for particle formation by secondary nucleation (which is the dominant event in systems with surfactant concentration below the critical micelle concentration). If the number concentration of newly formed particles, N_{new}, is found to be low compared to that of the seed, N_{seed}, then it may be expected that polymerisation will occur in seed particles, i.e. core–shell polymerisation will dominate, without vitiation by extensive secondary nucleation. Thus the simulations should shed light on when core–shell morphologies are possible in two-stage emulsion polymerisations.

3. Model description

The (secondary) nucleation treatment of Morrison and Gilbert [4,7] is as follows. The aqueous kinetics of (seeded) emulsion polymerisation are based on the homogeneous nucleation theory first proposed by Fitch and Tsai [25], updated to include more recent developments in aqueous-phase emulsion polymerisation chemistry, while retaining the simplicity of the original theory [4,7,24]. The basic idea is that particles are formed as a result of growth of aqueous phase radicals until they ‘precipitate’ out and thereby become particles. Formation of particles exclusively by this mechanism is confined to systems wherein the surfactant concentration is kept significantly below the critical micelle concentration (cmc). Indeed, secondary particle formation is hard to avoid if micelles are present, since the rate of entry of surface-active oligomeric radicals into micelles is extremely rapid, and this results in particle formation by this means [7]. The particular formulation used here should not be used for investigating systems with sufficient added surfactant that micelles could form; however, it is noted that the simple treatment could be extended to account for this common situation [7].

The simplified model is as follows. The formulation used here involves minor extensions and variants to that presented elsewhere [4,7,24] but is given fully for completeness. Primary radicals, $I^{\bullet}$, are created in the aqueous phase by decomposition of initiator species. These add to monomer relatively quickly, so that effectively one has

$$\text{initiator} \xrightarrow{k_d} 2\mathrm{IM}_1^{\cdot} \tag{1}$$

These $\mathrm{IM}_1^{\cdot}$ species can then react further with monomer in the aqueous phase:

$$\mathrm{IM}_i^{\cdot} + \mathrm{M} \xrightarrow{k_{\mathrm{p,aq}}^i} \mathrm{IM}_{i+1}^{\cdot}, \qquad i \geq 1 \tag{2}$$

At the same time, these species can at any stage terminate with any other aqueous phase radical, denoted $\mathrm{T}^{\cdot}$:

$$\mathrm{IM}_i^{\cdot} + \mathrm{T}^{\cdot} \xrightarrow{k_{\mathrm{t,aq}}} \text{dead oligomer(s)} \tag{3}$$

For convenience, termination is taken as being chain length independent; although it may be included without undue difficulty, the effect is not important in these systems, because only oligomers, which all terminate rapidly, are involved. If a radical does not undergo termination, then after a number of propagation steps it will become a surface-active oligomer and will enter any particle that it encounters. The degree of polymerisation at which entry becomes possible is denoted z whose value depends on the monomer and the initiator end group:

$$\mathrm{IM}_i^{\cdot} + \text{latex particle} \xrightarrow{k_e^i} \text{entry}, \qquad i = z, \ldots, j_{\mathrm{crit}}^{-1} \tag{4}$$

The rate coefficient for entry, k_e^i, is assumed to be diffusion-controlled. It is not known precisely how the diffusion coefficients of oligomeric radicals depend on chain length; here they are taken as being given by D_W/i, where D_W is the diffusion coefficient for $IM_1^{\cdot}$ in water. This represents quite a strong chain length dependence, but calculations with a weaker chain length dependence (e.g. $DW/\sqrt{i}$) do not give significantly different results. Aqueous phase radicals may enter either seed or new particles, so both these contributions need to be summed. The overall rate of entry for an $\mathrm{IM}_i^{\cdot}$ species is taken to be given by the diffusion-controlled expression for capture by new and seed particles, of monomer-swollen radii R_{new} and R_{seed}:

$$f_e^i = 4\pi\left(\frac{D_W}{i}\right)(R_{\mathrm{new}}N_{\mathrm{new}} + R_{\mathrm{seed}}N_{\mathrm{seed}}), \qquad i = z, \ldots, j_{\mathrm{crit}}^{-1} \tag{5}$$

R_{new} is found as described below. In the model, such new particles are formed by aqueous phase growth of radicals to a critical chain length j_{crit} at which they become totally insoluble in the aqueous phase, and thus undergo a coil-to-globule-like transition and form a particle:

$$\mathrm{IM}_{j_{\mathrm{crit}}}^{\cdot} \rightarrow \text{new particle} \tag{6}$$

This step is assumed to be instantaneous on the timescale of other kinetic events, i.e. a new particle is assumed to form as soon as the degree of polymerisation j_{crit} is reached. Once formed, a new particle swells with monomer and begins to grow by further propagation of the chain. The rate coefficient, K, for the volumetric growth of an unswollen particle is given by [7]:

$$K = \frac{\bar{n}k_p M_0 C_P}{d_{P,\mathrm{new}} N_A} \tag{7}$$

Here $\bar{n}$ is the average number of radicals per particle, k_p is the (long-chain) propagation rate coefficient, M_0 is the molecular mass of (second-stage) monomer, C_P its concentration in the particle, and $d_{P,\mathrm{new}}$ the density of polymer. This equation is used to calculate a value of R_{new} for use in Eq. (5) by assuming that (a) $\bar{n} = 1$ and (b) all new particles have a volume equal to that they would have if they formed at time $t = 0$. One can include specific expressions for $\bar{n}$ [7,24] but calculations using this additional sophistication showed insignificant effects compared to the effect of the presence or absence of extensive particle formation [24]. The second assumption is justified on the grounds that the rate of new particle formation is highest at $t = 0$ and the nucleation period is only brief (e.g. see the results of Fig. 1). Both assumptions were tested by carrying out simulations using a more sophisticated model. The success of these assumptions indicates that entry into newly formed particles is a very minor event in the type of system studied here, which means that the value of $\mathrm{d}N_{\mathrm{new}}/\mathrm{d}t$ is essentially a result of competition between the processes of aqueous phase growth and entry into seed particles. (However, in situations where there is extensive secondary particle formation, entry into new particles becomes significant, so that eventually new particle formation stops.) It requires considerable effort to dispense with the assumption that all particles have the same volume, since it is then necessary to compute the entire particle size distribution, with considerable increase in computational demands [18,23].

There is assumed to be no coagulation of particles. In reality there is probably some coagulation involving 'precursor' particles, especially since the conditions considered here are seeded systems without added surfactant (i.e. there is no surfactant to stabilise newly formed

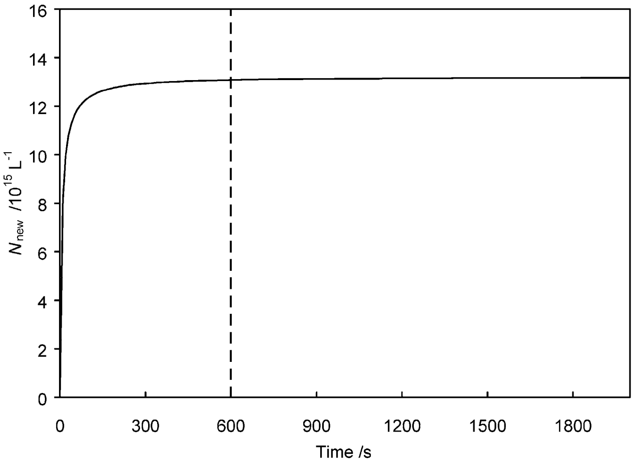

Fig. 1. Predicted time evolution of new PVAc particle concentration in the presence of a 10% solids content PS seed of 200 nm unswollen radius. The broken line shows the time chosen as the end of new particle formation.

particles). Any coagulation will reduce N_{new}, i.e. the present model calculates an upper bound for N_{new}. Comparison with more complete simulations showed that ignoring coagulation could lead to significant overestimation of the particle number, especially when large number of new particles are forming. However, because ignoring coagulation will overestimate the number of new particles, the present treatment should always indicate regions in which new particle formation can be avoided (while at the same time realising that this region may be more extensive than the model indicates). Other limitations of the present model include that its implementation here ignores the size dependence of several quantities in the system (e.g. of C_{p}, which is known from theory to be smaller for very small particles [26]) and it ignores particle-phase kinetics (e.g. see discussion below on exit). More complete treatments [18, 23] evaluate the time evolution of the complete particle size distribution and take all the above factors into account.

In implementing the above model, steady state aqueous-phase radical conditions were assumed, giving:

$$[\mathrm{IM}_1^{\cdot}] = \frac{2k_{\mathrm{d}}[\mathrm{I}]}{k_{\mathrm{p,aq}}^{1}C_{\mathrm{W}} + k_{\mathrm{t,aq}}[\mathrm{T}^{\cdot}]} \tag{8}$$

$$[\mathrm{IM}_i^{\cdot}] = \frac{k_{\mathrm{p,aq}}^{i-1}[\mathrm{IM}_{i-1}^{\cdot}]C_{\mathrm{W}}}{k_{\mathrm{p,aq}}^{i}C_{\mathrm{W}} + k_{\mathrm{t,aq}}[\mathrm{T}^{\cdot}]}, \qquad i = 2,\ldots,z-1 \tag{9}$$

$$[\mathrm{IM}_i^{\cdot}] = \frac{k_{\mathrm{p,aq}}^{i-1}[\mathrm{IM}_{i-1}^{\cdot}]C_{\mathrm{W}}}{k_{\mathrm{p,aq}}^{i}C_{\mathrm{W}} + k_{\mathrm{t,aq}}[\mathrm{T}^{\cdot}] + f_{\mathrm{e}}^{i}}, \qquad i = z,\ldots,j_{\mathrm{crit}}-1 \tag{10}$$

$$[\mathrm{T}^{\cdot}] = \int_{i=1}^{j_{\mathrm{crit}}-1}[\mathrm{IM}_i^{\cdot}] \tag{11}$$

In the above equations, C_{W} is the aqueous phase concentration of monomer. Implicit in Eq. (11) is the assumption that over the period of nucleation there is negligible contribution of exit to the overall aqueous phase radical concentration. If radicals exiting from particles do contribute significantly to [T], then the rate of aqueous phase termination will be increased, and so the rate of new particle formation will be reduced; again, this can be readily incorporated into the model [24] but the effect is not large. This minor effect again means that the model overestimates the number of new particles, and so leads to a conservative estimate of the true region of negligible secondary nucleation (see above).

Eqs. (8)–(11) are easily evaluated using an iterative technique, with the initial guess for $[\mathrm{T}^{\cdot}]$ being the value from ignoring loss of aqueous radicals by entry and nucleation:

$$[\mathrm{T}^{\cdot}] \approx \left(\frac{2k_{\mathrm{d}}[\mathrm{I}]}{k_{\mathrm{t,aq}}}\right)^{1/2} \tag{12}$$

With the aqueous phase radical population distribution established, the rate of new particle formation is calculated as that of propagation of chains containing one monomer unit fewer than the number required to form a new particle (Eq. (6)):

$$\frac{\mathrm{d}N_{\mathrm{new}}}{\mathrm{d}t} = k_{\mathrm{p,aq}}^{j_{\mathrm{crit}}-1}C_{\mathrm{W}}[\mathrm{IM}_{j_{crit}-1}^{\cdot}] \tag{13}$$

This equation was solved by fourth-order Runge–Kutta. The model may equally be used for particle formation in ab initio systems (with low surfactant concentration) by putting $N_{\mathrm{seed}} = 0$.

3.1. Starved-feed conditions

The model was used to simulate both polymerisations under saturated monomer conditions (i.e. both aqueous and particle phases saturated with monomer) and also under starved-feed conditions. The latter was implemented as follows. In order to specify the degree of starved feed in the system, the total saturated monomer amount is first calculated:

$$\text{saturated monomer amount} = C_{\mathrm{W}}^{\mathrm{sat}}V_{\mathrm{aq}} + C_{\mathrm{P}}^{\mathrm{sat}}V_{\mathrm{particles}} \tag{14}$$

Here $C_{\mathrm{W}}^{\mathrm{sat}}$ and $C_{\mathrm{P}}^{\mathrm{sat}}$ are the saturated monomer concentrations in the aqueous and particle phases, respectively, while V_{aq} is the volume of the aqueous phase and $V_{\mathrm{particles}}$ is that of the particle phase (when saturated with monomer). The amount of monomer in the system is then be set to any desired fraction of the saturated monomer amount, e.g. a fraction of 1 would mean that the particle and aqueous phases were saturated with monomer. This fraction is the index used to quantify the degree of starved-feed.

Having specified the total amount of monomer in the aqueous and seed particle phases, the concentration of monomer in each of these phases must be calculated. The partitioning of monomers such as vinyl acetate between aqueous and particle phases is not ideal [7,27]. The following empirical relation gives good agreement with experimental data for equilibrium partitioning of monomers such as vinyl acetate and methyl methacrylate [7,28,29] at all except high weight-fraction polymer [30]:

$$\frac{C_{\mathrm{W}}}{C_{\mathrm{W}}^{\mathrm{sat}}} = \left[\frac{C_{\mathrm{p}}}{C_{\mathrm{p}}^{\mathrm{sat}}}\right]^{0.6} \tag{15}$$

The values of C_{W} and C_{P} are evaluated iteratively using the above relation and the specified total monomer amount [7, 28]. This procedure also yields swollen particle volume, from which R_{seed} is calculated (for use in Eq. (5)). The seed particle value for C_{P} is also assumed to hold for new particles. From the unswollen volume of a new particle, calculated as Kt (see Eq. (7) and discussion thereof), and from the value of C_{P}, the swollen volume of a new particle is calculated, and hence R_{new} is obtained (for use in Eq. (5)). Notice that this procedure made the reasonable assumption that new particles take up negligible volume in the system and thus that they exert negligible influence in determining the partitioning of monomer between the particle and water phases. (This assumption should not lead to significant error, because the volume of the new particle phase will be relatively small during the brief period of new particle formation.)

Values of C_W and C_P are held constant throughout simulations, even for those of Interval III (starved-feed) conditions. This is justified because the periods of nucleation are so brief that there will be negligible consumption of monomer during them.

3.2. Seed particle concentration

The number concentration of seed particles in the unswollen latex is found using standard mass balance relations [7]:

$$\frac{1}{n_{\text{seed}}} = \left(1 + \frac{\left(\frac{100}{x} - 1\right) d_{\text{P,seed}}}{d_{\text{W}}}\right) \frac{4}{3}\pi r_{\text{seed}}^3 \qquad (16)$$

Here $d_{\text{P,seed}}$ is the density of seed polymer and d_{W} the density of water (a monodisperse seed particle distribution is implicit in the above equation, as it also is throughout this work, e.g. also Eq. (5)). By assuming saturated monomer conditions, $V_{\text{particles}}$ and thence V_{aq} are next calculated for use in Eq. (14). The fraction of saturated monomer amount is then specified, and the actual monomer concentrations in the particle and aqueous phases calculated, as described above. The expansion in system volume due to monomer swelling of particle and aqueous phases is then factored in to calculate N_{seed}, the number concentration of particles in the polymerising system (the value used in Eq. (5)).

3.3. Catalysed initiator decomposition

An additional minor extension of the model is to take account of any monomer-catalysed initiator decomposition. For example, it is known that the presence of vinyl acetate accelerates the consumption of persulfate initiator [31]. The likely mechanism for this is transfer to initiator [32]:

$$^{-}\text{O}_4\text{S}{-}\text{M}_i^{\cdot} + \text{S}_2\text{O}_8^{2-} \xrightarrow{k_{\text{tr,init}}} {}^{-}\text{O}_4\text{S}{-}\text{M}_i{-}\text{SO}_4^{-} + \text{SO}_4^{\cdot -} \qquad (17)$$

The newly formed tetraoxidosulfate (·1 −) radical is able to react with monomer in the usual manner to begin the formation of a new chain. The total number of aqueous radicals remains unchanged by this reaction, but the chain length distribution of aqueous phase radicals will be altered if $k_{\text{tr,init}}$ is sufficiently large. The reaction will have the effect of lowering the rate of particle formation because it reduces the number of chains that are able to grow to length j_{crit}. In fact this effect is enhanced because of termination being diffusion controlled: reaction (17) converts long and therefore relatively slowly terminating oligomers into short and therefore more rapidly terminating oligomers. Thus there is an increase in the overall rate of aqueous phase termination and so it is more difficult for an oligomer to grow to length j_{crit}. However this subtle effect is not taken into account by the model, which assumes chain-length-independent aqueous phase termination (Eq. (3)). So the model will tend to underestimate the reduction in particle formation rate that the transfer to initiator reaction will cause. However, this oversight is not expected to be misleading: the model should still give a qualitative guide as to the effect of transfer to initiator on (secondary) particle formation: indeed, underestimation of the true region of no secondary nucleation.

The other effect that reaction (17) will have is to reduce the initiator concentration at a rate in excess of that in the absence of catalysing monomer. This is unlikely to affect particle formation significantly (which is predicted to be over in a matter of minutes in this system), and consequently has not been incorporated into the model, which assumes negligible consumption of initiator over the period of nucleation. However, if kinetic simulations to longer times are to be attempted, initiator consumption should be taken into account.

To account for reaction (17) in simulations, appropriate loss terms are added to Eqs. (8)–(10), and an appropriate gain term for reinitiation is added to Eq. (8). These updated expressions are given by Eqs. (18)–(20)

$$[\text{IM}_1^{\cdot}] = \frac{2k_{\text{d}}[\text{I}] + k_{\text{tr,init}}[\text{I}][\text{T}^{\cdot}]}{k_{\text{p,aq}}^{1} C_{\text{W}} + k_{\text{tr,init}}[\text{I}] + k_{\text{t,aq}}[\text{T}^{\cdot}]} \qquad (18)$$

$$[\text{IM}_i^{\cdot}] = \frac{k_{\text{p,aq}}^{i-1}[\text{IM}_{i-1}^{\cdot}] C_{\text{W}}}{k_{\text{p,aq}}^{i} C_{\text{W}} + k_{\text{tr,init}}[\text{I}] + k_{\text{t,aq}}[\text{T}^{\cdot}]}, \qquad i = 2, \ldots, z-1 \qquad (19)$$

$$[\text{IM}_i^{\cdot}] = \frac{k_{\text{p,aq}}^{i-1}[\text{IM}_{i-1}^{\cdot}] C_{\text{W}}}{k_{\text{p,aq}}^{i} C_{\text{W}} + k_{\text{tr,init}}[\text{I}] + k_{\text{t,aq}}[\text{T}^{\cdot}] + f_{\text{e}}^{i}}, \qquad (20)$$

$i = z, \ldots, j_{\text{crit}} - 1$

For the purposes of this modelling, all $\text{SO}_4^{\cdot -}$ from catalysed decomposition was assumed to add to monomer, an assumption consistent with Eq. (1).

4. Parameter values

The model is first applied to polymerisation of vinyl acetate in the presence of PS seed particles without added surfactant. Many of the required rate parameters are known for this system, and are as listed in Table 1 for 80 °C, the temperature in both the experiments of Hergeth and Schmutzler [6] and those carried out in association with the present work discussed in a subsequent paper. Regarding the parameter values in Table 1, the following should be noted.

- $k_{\text{p,aq}}^{1}$ is probably larger than k_{p}, the long chain value, and here has simply been set equal to $2k_{\text{p}}$, due to the absence of any more detailed information [33]. The sensitivity of results to the value of $k_{\text{p,aq}}^{1}$ was investigated and for the

Table 1
Parameter values used for simulating vinyl acetate polymerisation in the presence of polystyrene seed at 80 °C

Parameter	Symbol	Value	Source
Initiator concentration	[I]	1×10^{-3} mol l^{-1}	
Initiator dissociation rate coefficient	k_d	8.60×10^{-5} s^{-1}	[44]
Particle-phase propagation rate coefficient	k_p	2.58×10^{4} l mol^{-1} s^{-1}	[43]
Aqueous phase propagation rate coefficient for monomeric radicals	$k^1_\mathrm{p,aq}$	2.58×10^{4} l mol^{-1} s^{-1}	Assumed $= 2k_\mathrm{p}$
Aqueous phase propagation rate coefficient for longer chains	$k^i_\mathrm{p,aq}$	1.29×10^{4}l mol^{-1} s^{-1}	Assumed $= 2k_\mathrm{p}$
Aqueous phase termination rate coefficient	$k_\mathrm{t,aq}$	1.13×10^{10} l mol^{-1} s^{-1}	[7]
Saturated aqueous phase monomer concentration	$C^\mathrm{sat}_\mathrm{W}$	0.3 mol l^{-1}	[7,46]
Saturated particle phase monomer concentration	$C^\mathrm{sat}_\mathrm{p}$	7.7 mol l^{-1}	[7]
Diffusion coefficient for $\mathrm{IM}^{\cdot}_1$ in water	D_W	1.88×10^{-9} m^2 s^{-1}	[7]
Density of new polymer	$d_\mathrm{P,new}$	1.15 kg l^{-1}	[45]
Density of seed polymer	$d_\mathrm{P,seed}$	1.044 kg l^{-1}	[47]
Density of water	d_W	0.972 kg l^{-1}	[48]
Minimum chain length for radical entry into a particle	Z	7	[34]
Chain length for particle formation by homogeneous nucleation	j_crit	20	[34]
Rate coefficient for transfer to initiator	$k_\mathrm{tr,init}$	3×10^{3} l mol^{-1} s^{-1}	[32]

systems of the present work was found to have very little effect on results.

- The value of $C^\mathrm{sat}_\mathrm{p}$ for swelling of PS by vinyl acetate is unknown, so for this value $C^\mathrm{sat}_\mathrm{p}$ for swelling of PVAc by vinyl acetate is used. While the value of $C^\mathrm{sat}_\mathrm{p}$ has a considerable quantitative effect on results, it does not make a qualitative change.
- The value of $k_\mathrm{t,aq}$ is that for small aqueous phase radicals. While this value is appropriate for systems such as styrene, which have low z and j_crit values (approximately 2 and 5, respectively), it may be less so for the longer oligomer radicals formed in vinyl acetate systems. This effect was not investigated in the present work.
- The values for z and j_crit were obtained from semi-empirical relationships that take into account the balance between hydrophilic character imparted by the persulfate end-group and the hydrophobic character imparted by the growing polymer chain [34]. Especially in the case of vinyl acetate where the values for z and j_crit are large, it is unlikely that such sharp cut-offs exist between non-entry/entry and no nucleation/nucleation. The formulation of a more realistic model would require much more experimental data than are currently available.

Fitting the data of Morris and Parts [31] gave [32] $k_\mathrm{tr,init} = 3 \times 10^3$ l mol^{-1} s^{-1} at 80 °C, the value initially used for simulations with transfer to initiator.

5. Modelling results

The model predicts new particle number as a function of time, so the first step was to establish the length of time over which new particles are typically formed. Fig. 1 shows the results of a simulation for vinyl acetate emulsion polymerisation in the presence of PS seed with unswollen radius $r_\mathrm{seed} = 200$ nm and 10% solids content. The results showed a very short period of particle formation. As will be seen, the simple model predicted similar lengths of time for particle formation as a more sophisticated model [18,23] that included effects such as coagulation. Thus for the seeded systems being considered here, it was considered likely that secondary particle formation was indeed over very quickly.

The results in Fig. 1 are for a system with considerable new particle formation. In simulations with the present model that yielded lower N_new, new particle formation occurred over a slightly longer timescale. Based on such simulations, a value of 600 s (shown as a broken line in Fig. 1) was chosen as a time at which particle formation is effectively over in all simulations. It is noted that new particle formation is not always completely over at this time: e.g. for simulations with very low N_new, the model gives a constant and extremely low rate of particle formation that persisted for a long time. This was because such simulations are characterised by negligible entry into new particles (N_new being extremely low). Consequently all entry was into seed particles, and because in the model this occurred at a constant rate, there is also a constant rate of new particle formation for a relatively long time. This rate is extremely low, because almost all aqueous phase radicals are captured by seed particles rather than growing to become new particles. Effectively nucleation is complete after ~600 s, because N_new is so much lower than N_seed that essentially no secondary nucleation has occurred.

5.1. Effect of particle size and solids content

A series of simulations were carried out to evaluate the effect of particle size and solids content on secondary nucleation. The results are shown in Fig. 2 in terms of concentration of new particles. Two trends are evident from this figure.

(i) For each solids content, N_new increases as r_seed increases. This is because the rate of particle formation is

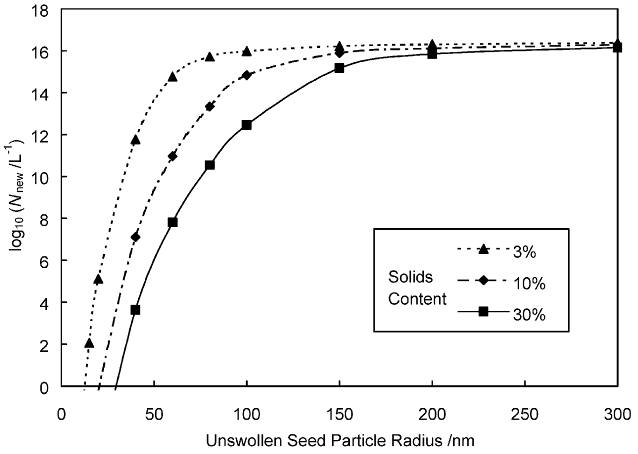

Fig. 2. Predicted new particle number as a function of seed particle radius for emulsion polymerisation of vinyl acetate in the presence of PS seed. Results are shown for three seed particle concentrations.

intimately connected with that of entry into pre-existing particles, since these two processes compete [4]. The rate of entry of aqueous radicals into pre-existing particles is determined amongst other things by the product of seed particle number and size (Eq. (5)). For constant particle number, entry would actually be enhanced (and hence new particle number decreased) with increasing R_{seed}. However, this effect is swamped by the much stronger effect of decreasing N_{seed}, because, at constant solids content, n_{seed} has an inverse cubic dependence on unswollen particle radius. Hence there is a strong decrease in the frequency of entry, so there is a large increase in the number of oligomers growing to j_{crit}, and thus there is more particle formation. It is stressed that this effect is due to N_{seed} necessarily decreasing as r_{seed} increases, i.e. it is a concentration effect. For each system there comes a point where the number of new particles formed reaches a ceiling value: the number that would have formed in the absence of seed. In other words as r_{seed} is increased, eventually N_{seed} becomes so low that entry into seed particles is a negligible process.

(ii) The second trend is that as solids content increases, N_{new} decreases. This is because entry is promoted as N_{seed} increased with increasing solids content (Eq. (16)). (Note that solids content means the quantity x in Eq. (16), i.e. the solids content of the unswollen seed latex.)

The aim of this modelling is to determine conditions under which secondary particle formation would be avoided. As can be seen, the model predicts that particle formation always occurred to some extent. A cut-off is needed between new particle formation and no new particle formation. An arbitrary but acceptable criterion for deciding if significant secondary particle formation had occurred is when the number of new particles did not exceed 1% of the number of seed particles (as a reminder, $N_{\mathrm{new}}/N_{\mathrm{seed}}$, which is for the swollen system, will equal $n_{\mathrm{new}}/n_{\mathrm{seed}}$, the value for the unswollen system). The results of Fig. 2 were represented as $N_{\mathrm{new}}/N_{\mathrm{seed}}$ in Fig. 3, in which the region of negligible secondary nucleation has been shaded. It is evident that core–shell polymerisation (which required that there be only minor secondary particle formation) should be possible as long as a small enough r_{seed} is employed. However, as seed particle radius increased, higher solids contents needed us to avoid secondary nucleation. Of course the extent to which solids content could be increased is limited, so an r_{seed} is reached beyond which significant secondary nucleation is unavoidable. For the present results this point is for $r_{\mathrm{seed}} \sim 150$ nm. Hence the simulations indicate that for PS seeds greater in radius than 150 nm, vinyl acetate would tend to form new particles rather than polymerise inside the PS seed particles, no matter what the solids content. This suggests that it would not be possible to make PVAc shell–PS core particles directly from large PS seed particles (radius ~ 0.5 μm).

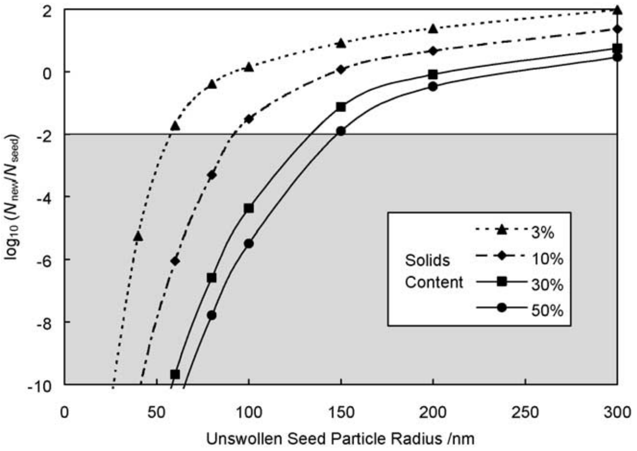

Fig. 3. Predicted value of $N_{\mathrm{new}}/N_{\mathrm{seed}}$ versus seed particle radius for four selected seed particle concentrations. The shaded region represents that of negligible new particle formation.

5.2. Starved-feed conditions

A series of simulations were carried out to assess the effect of lowering the overall monomer concentration

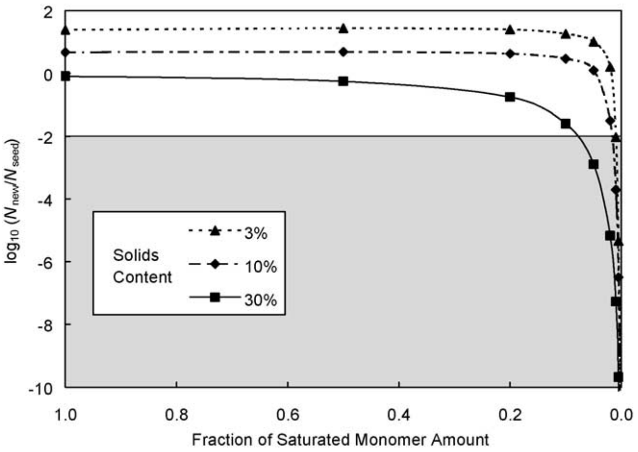

Fig. 4. Predicted value of $N_{\mathrm{new}}/N_{\mathrm{seed}}$ versus fraction of saturated monomer amount in the system for 200 nm radius particles of three solids contents, for starved-feed conditions.

(starved-feed conditions). Results are shown in Fig. 4 for a range of seed particle concentrations, all for an unswollen seed particle radius of 200 nm. As already shown in Figs. 2 and 3, increased seed concentration results in lower N_{new}. More importantly, the results show the expected trend, which is that as monomer amount is reduced, new particle formation is suppressed because of lower aqueous phase growth of oligomeric radicals. It also must be remembered that the only partial swelling of seed particles results in them having smaller radii, an effect which reduces entry rates and so promotes new particle formation; on the other hand, there is one report in the literature [35] that secondary nucleation is *enhanced* under some starved feed conditions, a result which would not be encompassed within the mechanisms assumed here. However, a large reduction in the monomer concentration is needed in order to lower the incidence of new particle formation to a significant extent, especially at lower solids contents.

As an example of the use of these simulation data, they suggest that the starved-feed conditions of the experiments of Hergeth and Schmutzler [6] were unlikely to have resulted in significant promotion of core–shell polymerisation over new PVAc particle formation, because the seed polymer concentration used in these experiments was under 3% (see below).

5.3. Catalysed initiator decomposition

Further calculations were carried out to assess the effect of catalysed initiator dissociation, and of changing the rate coefficient of this reaction under various conditions. Table 2 gives the concentration of newly formed particles for various values of $k_{\text{tr,init}}$ with $r_{\text{seed}} = 200$ nm and $x = 10\%$. As expected (see earlier discussion), in all cases the number of newly created particles is reduced when compared with the case when no transfer to initiator is allowed. However, it can be seen that changing $k_{\text{tr,init}}$ has very little quantitative effect on the number of new particles that form. Therefore for the systems under investigation it could be assumed that transfer to initiator had a negligible effect in reducing the extent of secondary nucleation.

5.4. Comparison with experimental data from the literature

Hergeth and Schmutzler [6] carried out experiments designed to create a core–shell morphology. PS latexes were synthesised with initiation by potassium persulfate in a surfactant-free system at 80 °C. These latexes were used as seeds in subsequent starved-feed, potassium persulfate-initiated polymerisations of vinyl acetate. These conditions might be expected to favour the formation of shells, as opposed to other morphologies or secondary particle formation, because of the following well-known general principles:

- The seed particles were created without added surfactant, and none was added in the second stage polymerisation. The absence of surfactant makes it more difficult for any new particles to form (whatever the mechanism of particle formation).
- The vinyl acetate was added under starved feed conditions, rather than all being added at the start of the second stage polymerisation. This reduced the concentration of monomer in the aqueous phase, thereby slowing the propagation rate of aqueous radicals to a length where they could form particles by homogeneous nucleation, i.e. there was greater opportunity for radicals to enter particles.
- The high concentration of initiator (7×10^{-1} mol l^{-1} persulfate) would normally tend to favour new particle formation because it leads to higher aqueous-phase radical concentrations, which result in higher rates of growth to length j_{crit}. However, in this case there was starved feed addition of vinyl acetate, so an increased initiator concentration assisted in maintaining a low monomer concentration in the aqueous phase by causing fast monomer consumption.

Quantitative modelling of these conditions was undertaken, in which a PS seed of 2.3% solids and 153 nm unswollen radius was used. From the results above it is evident that the present simulations predict that such conditions should not achieve significant core–shell polymerisation. This is not to say that no core–shell particles were made, but that a much larger portion of the vinyl acetate would go into making secondary PVAc particles, rather than forming shells. A later paper will give experimental data to elucidate this issue.

Table 2
Effect of varying $k_{\text{tr,init}}$ on the number of newly created particles

$k_{\text{tr,init}}$ (l mol^{-1} s^{-1})	N_{new} (l^{-1})	Percent change
0	1.308×10^{16}	–
1×10^3	1.307×10^{16}	−0.04
3×10^3	1.306×10^{16}	−0.13
3×10^4	1.291×10^{16}	−1.31

6. Simulation of inverse core–shell polymerisation

The simulations of secondary particle nucleation for vinyl acetate with a PS seed indicated that it would not be possible to prevent particle formation using seeds with particle radii ≥150 nm. A number of simulations were carried out to assess the viability of making larger core–shell particles using an inverse core–shell route. This well-known procedure for creating core–shell morphology involves creating a seed latex that will become the particles' shells, and polymerising a second monomer that will migrate to the centre of the particles to become the core. This requires the core polymer to be more hydrophobic than the shell, and that there is sufficient polymer mobility to allow the core to migrate to the centre of the seed. The nucleation model has no power to predict the morphology that will form (for which extensive models have been developed by Durant, Sundberg and co-workers [36–38] and by Gonzalez-Ortiz and Asua [39–41]) however, inverse core–shell morphology would not form unless the growing aqueous radicals were captured by existing particles, rather than being able to form new particles. In other words, favourable latex kinetics are a necessary (but not sufficient) condition to obtain core–shell morphology.

The model assumes that secondary particle formation occurs when aqueous radicals propagate to length j_{crit} without entry or termination occurring. The probability of reaching j_{crit} depends, amongst other factors, on the rate of propagation in the aqueous phase. In the case of vinyl acetate polymerisation in the presence of a PS seed, the rate of propagation to a length where homogeneous nucleation occurs is very rapid, as a consequence of the high water solubility and high propagation rate coefficient of vinyl acetate. Hence a monomer with a slower aqueous-phase propagation frequency would allow more time for entry or termination events to occur before the radical propagated sufficiently to become a new particle. This extra time available for entry into existing particles would result in fewer seed particles being needed to prevent secondary particle formation. This in turn allows the use of larger seed particles without the occurrence of secondary particle formation.

One aim of this paper is to obtain conditions to enable synthesis of core–shell polymers where PS forms the core and PVAc the shell. In the present case that would mean using a PVAc latex as a seed in a styrene polymerisation in order to achieve the desired morphology following phase inversion. Styrene has much lower propagation rate coefficient and water solubility than vinyl acetate, which would result in a slower rate of aqueous propagation. This should translate into a reduced propensity for particle formation, despite styrene's low water solubility also reducing value of j_{crit}. The model was thus used to assess the predicted incidence of new particle formation in the situation where styrene is the second polymerised monomer.

Parameter values that were changed for the inverse system are given in Table 3. The value of $k^1_{\text{p,aq}}$ has once again been set equal to $2k_\text{p}$, in the absence of any specific information on its exact value. The influence of $k^1_{\text{p,aq}}$ choice should be greater in the case of styrene polymerisation where there are fewer propagation steps before entry or homogeneous nucleation, but simulations revealed very little effect from altering the rate of this first propagation step. The value of $C^{\text{sat}}_{\text{p}}$ is for styrene swelling PS particles, which may not be justified in this case where styrene swells the PVAc seed particles; while in principle it should be possible to estimate this quantity using Flory–Huggins χ parameters inferred from solubility parameters, together with the Morton equation [26], such procedures and models have sufficient uncertainty that this is not considered worth-while. The diffusion coefficients for styrene and vinyl acetate oligomers were taken to be the same. The termination rate coefficient is also assumed to be the same as for vinyl acetate. The rate coefficient for transfer to initiator ($k_{\text{tr,init}}$) was set equal to zero as this reaction is not thought to be significant for styrene polymerisation.

Table 3
Parameter values used for simulating styrene polymerisation in the presence of poly(vinyl acetate) seed at 80 °C

Parameter	Value	Source
[I]	1×10^{-3} mol l^{-1}	
k_d	8.60×10^{-5} s^{-1}	[44]
$k^1_{\text{p,aq}}$	1326 l mol^{-1} s^{-1}	[42]
$k^i_{\text{p,aq}}$	663 l mol^{-1} s^{-1}	[42]
$k_{\text{t,aq}}$	1.13×10^{10} l mol^{-1} s^{-1}	[7]
$C^{\text{sat}}_{\text{W}}$	6.23×10^{-3} mol l^{-1}	[49]
$C^{\text{sat}}_{\text{p}}$	5.8 mol l^{-1}	[47]
D_W	1.88×10^{-9} m^2 s^{-1}	[7]
$d_{\text{P,new}}$	1.044 kg l^{-1}	[47]
$d_{\text{P,seed}}$	1.15 kg l^{-1}	[45]
d_W	0.972 kg l^{-1}	[48]
Z	2	[7]
j_{crit}	5	[7]

Results are shown in Fig. 5. It can be seen that the number of new particles generated were now many orders of magnitude lower than the conventional core–shell system considered previously. It can be seen that even for a 300 nm radius seed, inverse core–shell polymerisation should still be possible without secondary nucleation, even for low solid content seed. This result for the inverse core–shell system can be contrasted with that for the core–shell system presented earlier, where the maximum seed particle size that could be used without secondary nucleation is 150 nm radius, and that only with high solids content. Thus the model predicts that it will be possible to prevent secondary particle formation in the presence of large seeds by

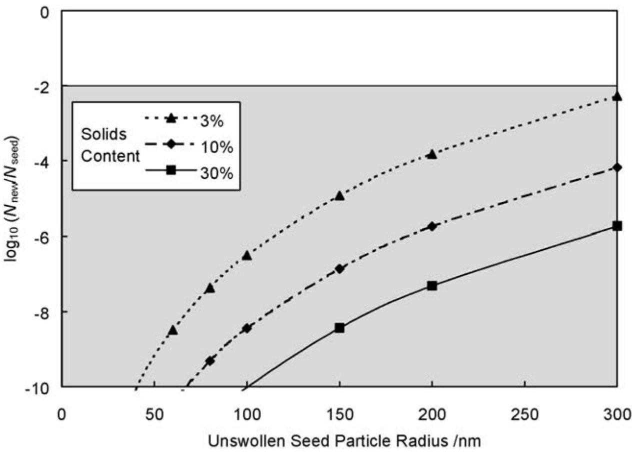

Fig. 5. Predicted value of $N_{\text{new}}/N_{\text{seed}}$ versus seed particle radius for three selected PVAc seed particle concentrations.

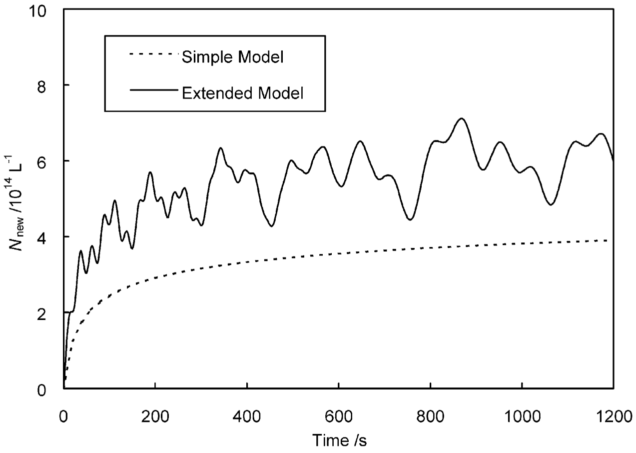

Fig. 6. Results of an ab initio styrene system: predicted number of new particles as a function of time for the simple model (Eqs. (1)–(17)) and more complete treatment [23] in which better account is taken of particle growth; coagulation is ignored for these particular calculations.

polymerising styrene in situations where vinyl acetate polymerisation would generate new particles.

7. Comparison with results from more complete model

The simple model proposed and discussed in this paper included a number of assumptions that may possibly have a significant effect on the accuracy of any predictions made. To assess the validity of these assumptions, calculations were made using a more sophisticated (and much more computationally demanding) treatment, details of which are published elsewhere [23]. This model includes compartmentalisation, coagulation and the complete particle-size dependence of all quantities, and calculates the time evolution of the complete particle size distribution. Comparing output generated using the same input parameters for both models allows us to assess the effects of the assumptions made in formulating the simple model.

Fig. 6 shows PS particle number versus time in an ab initio system calculated with both the simple and extended models. The same kinetic parameters were used in both the simple model and the more sophisticated treatment of Coen et al. [23] (these were given in Table 3, and were the same as those used in the modelling of inverse core–shell polymerisation, with parameter values appropriate for 80 °C). For purposes of comparison, effects of coagulation were not been included in the more complex model. The instability in the output for the extended model (oscillations in N_{new} as a function of time) arose from minor numerical instabilities: the extended model calculates the complete size distribution on a discrete basis, and so there are particle bins where there is only a minuscule particle concentration, and small numerical errors in this size range lead to the oscillations. It should be noted that the particle formation is predicted to occur over a longer time in styrene polymerisation compared to that for the seeded vinyl acetate system discussed earlier (Fig. 1); this is due to slower propagation of styrene. Another reason for the long particle nucleation period is that, unlike the seeded systems discussed earlier, the only particles into which radicals may enter are those formed during this nucleation period. Sufficient time is needed to allow these newly formed particles to grow to a point where they capture all aqueous radicals. As can be seen in Fig. 6, the main difference in particle formation rates between these two models is at early times. This difference can be attributed mainly to the extended model taking better account of the growth of the newly formed particles. The two models give qualitatively similar $N_{new}(t)$ curves, and they also predict very similar final N_{new} values. For seeded particle systems, where perforce there is less new particle formation, one might anticipate that the simplified model functions even more accurately.

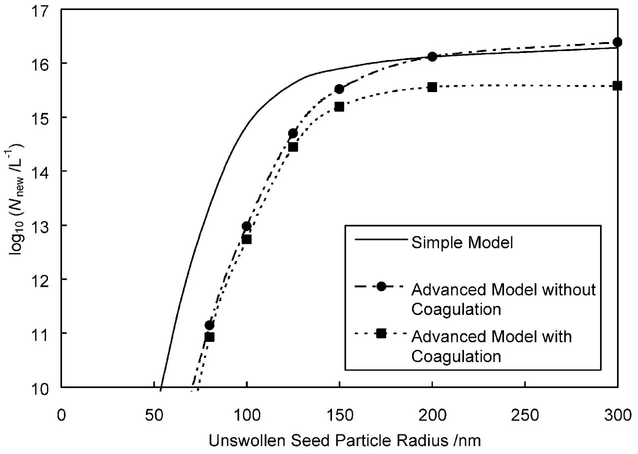

Fig. 7. Plot of N_{new} as a function of PS seed particle radius, with solid content of unswollen seed always 10%.

Having established that the basic assumptions of the simplified model are sound for the systems under consideration, it is of interest to investigate whether coagulation might be occurring in these systems. This was done using the more sophisticated treatment, which allowed coagulation of precursor particles to be taken into account. For this purpose, the simple 'cut-off' model of Ref. [23] was used (i.e. the one coagulation rate coefficient was used for coagulation involving any particle smaller than a given size, and zero coagulation is assumed for any other pair), although more sophisticated treatments have been developed [8,11,18]. Fig. 7 illustrates the effect of including coagulation of precursor particles for vinyl acetate polymerisation using a range of PS seed particle sizes (the seed particle solids being constant at 10%). All reported new particle concentrations are for a 600 second cut-off. The more complete simulations used a cut-off radius of 10 nm, and coagulation rate coefficient of $10^{10}\ \mathrm{l\,mol^{-1}\,s^{-1}}$ for particles smaller than this [23]. It can be seen that at higher seed particle sizes, where the most new particles are being formed (this situation most closely approximates that of an ab initio polymerisation discussed previously), there is little difference in final particle number between the simple model and extended model without coagulation (as already seen in Fig. 6). It can be seen that including coagulation has greatest effect at larger seed particle sizes. This can be explained by the fact that there is a considerably higher number of new particles forming, resulting in a higher concentration of particles under the 10 nm coagulation cut-off radius in the case of the large seed, which resulted in a higher rate of coagulation. This suggests that the simple model is of limited quantitative use in ab initio systems in which large numbers of new particles form.

At small seed particle sizes the simple and extended models differ significantly, but the addition of coagulation to the advanced model has very little effect on final particle number. For small particle sizes the simple model over-estimated the number of new particles that form. There are a number of reasons for this, the most important of which is once again the better account of particle growth taken by the advanced model. In the simple model it is assumed that seed particles do not grow as a result of polymerisation. This assumption is reasonable for large seed particle sizes, but for smaller particles there would be a large change in particle size due to growth, which would affect the entry rate. In the simple model where this seed growth is not taken into account there is thus an underestimation of entry rate, especially for small particles, with resulting overestimation of particle formation. The fact that the two models diverge for smaller seed sizes is not as important as it might first seem, because fewer new particles form when the seed particle size is low, and also there are more seed particles for a given solid content. For both these reasons the ratio of new to seed particles is very low, i.e. it does not matter that the N_{new} from the simple model is quantitatively in error: the simple model is still qualitatively correct in predicting negligible secondary nucleation.

It can be seen from Figs. 6 and 7 that the simple model is usually in acceptable qualitative and semi-quantitative agreement with the more complex model (apart from the one limitation mentioned above). This gives confidence that simulations carried out using the simple model should yield meaningful results. It is the intention of this modelling to determine merely whether secondary nucleation would be negligible or not, rather than to necessarily quantify the amount expected. However, the comparisons with the more complex model illustrate that the assumptions made in the simple one have not had a large effect on the accuracy of the predictions. Thus the simple model can be used to accurately predict the occurrence of secondary particle formation, using much less time than it would take with the complex model.

8. Ab initio systems

The model is applicable to ab initio (unseeded) systems [7]. For completeness, the model was applied to the cases of ab initio styrene and vinyl acetate polymerisations in which the surfactant concentration is below the critical micelle concentration. This is the first time that such results have been presented for vinyl acetate, and a much wider range of conditions (in comparison with the previous work [7]) has also been considered for styrene. Surfactant-free, ab initio systems are commonly used to make large and mono-disperse seed latexes; this is especially the case for styrene.

For the simulation results presented below, parameter values are as in Tables 1 and 3 (or references referred to therein), except for the temperature variations of the following equations (in which T is the temperature in Kelvin). The Arrhenius expression for the long chain aqueous propagation rate coefficient of styrene [42] is given by Eq. (21), and the corresponding expression for the vinyl acetate propagation rate coefficient [43] is given by Eq. (22). The propagation rate coefficient for one-mers, $k^1_{\text{p,aq}}$, was always taken as twice the long chain value for both of these monomers.

$$\text{Styrene}: \qquad k^i_{\text{p,aq}}(\text{l mol}^{-1}\ \text{s}^{-1}) = 10^{7.63}\ \text{e}^{-32.51\ \text{kJ mol}^{-1}/(RT)} \tag{21}$$

$$\text{Vinyl acetate}: \quad k^i_{\text{p,aq}}(\text{l mol}^{-1}\ \text{s}^{-1}) = 10^{7.166}\ \text{e}^{-20.66\ \text{kJ mol}^{-1}/(RT)} \tag{22}$$

The temperature dependencies of the dissociation rate coefficient for potassium persulfate initiator [44] (Eq. (23)), the termination rate coefficient [7] (Eq. (24)) and the diffusion coefficient for an $\text{IM}_1^{\cdot}$ species in water [7] (Eq. (25)) for both monomers were calculated as follows:

$$k_{\text{d}}(\text{s}^{-1}) = 8.0 \times 10^{15}\ \text{e}^{-135\ \text{kJ mol}^{-1}/(RT)} \tag{23}$$

$$k_{\text{t,aq}}(\text{l mol}^{-1}\ \text{s}^{-1}) = 6 \times 10^{9}\ \text{e}^{-20\ \text{kJ mol}^{-1}/(R(1/T-1/3215))} \tag{24}$$

$$D_{\text{W}}(\text{m}^2\ \text{s}^{-1}) = 10^{9}\ \text{e}^{-20\ \text{kJ mol}^{-1}/(R(1/T-1/3215))} \tag{25}$$

Vinyl acetate and PVAc densities were calculated using the empirical relationships below [45]:

$$d_{\text{vinyl acetate}}(\text{kg l}^{-1}) = 0.9584 - 1.3276 \times 10^{-3}(T - 2715) \tag{26}$$

$$d_{\text{PVAc}}(\text{kg l}^{-1}) = 1.2098 - 8.0608 \times 10^{-4}(T - 2715) \tag{27}$$

There are other parameters that may also have a temperature dependence, but in the absence of any specific information, these parameters have been assumed to be temperature independent. Two parameters that do have an empirical temperature dependence are z and j_{crit} [7]. However, for two reasons it was decided to fix these two parameters at their 80 °C values. First, they are expected to vary with saturated aqueous monomer concentration, which will also vary with temperature but which is here assumed to be temperature independent. Second, their values are both integers, so a small change in temperature could result in a jump in the value, a situation that was considered undesirable for model

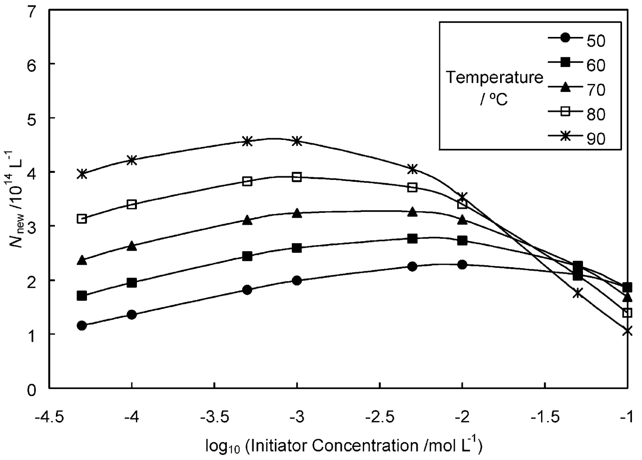

Fig. 8. Predicted N_{new} versus initiator concentration for different temperatures in ab initio styrene systems.

comparisons at varying temperatures. Both the ab initio styrene and vinyl acetate polymerisations were modelled using a transfer to initiator rate coefficient ($k_{tr,init}$) of zero, for reasons already discussed. All simulations were carried out to 1200 s, because the nucleation period for an ab initio polymerisation is longer than for a seeded one.

8.1. Results: styrene

Fig. 8 shows the variation of N_{new} with initiator concentration at constant temperature for styrene, while in Fig. 9 the results are presented to show the variation of N_{new} with temperature for constant [I]. As noted elsewhere [34], N_{new} can go through a maximum: at low [I] the dominant effect of increasing [I] is to increase all aqueous phase radical concentrations and more aqueous phase oligomers reach the critical chain length for new particle formation, but as radical concentration is increased still further, the effect of increasing rates of generation of free radicals by initiation is more than offset by faster rates of termination, and so particle numbers decline.

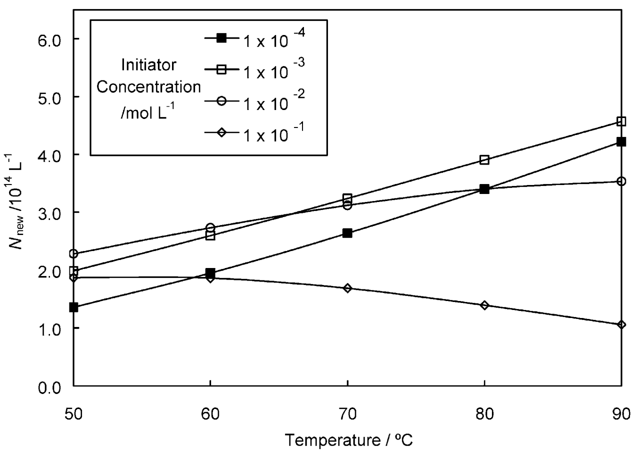

Fig. 9. Predicted N_{new} versus temperature for different initiator concentrations in ab initio styrene systems.

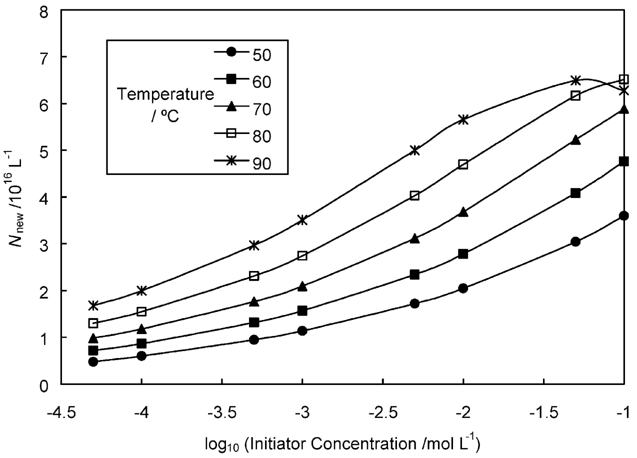

Fig. 10. Predicted N_{new} versus initiator concentration for different temperatures in ab initio vinyl acetate systems.

In Fig. 9 it can be seen that N_{new} increases with temperature for lower initiator concentrations. However, at higher initiator concentrations there is a reversal of this trend, with higher temperatures resulting in a reduced rate of particle formation. This is most simply interpreted as another manifestation of the effect just discussed in connection with Fig. 8. That said, care must be taken not to seek to understand these temperature variations in overly simplistic terms: because many parameter values vary with temperature, many factors contribute to the variation of N_{new} with temperature.

8.2. Results: vinyl acetate

Figs. 10 and 11 illustrate the dependence of N_{new} on initiator concentration and temperature, respectively, for ab initio vinyl acetate systems. In the plot of N_{new} versus initiator concentration in Fig. 10, it can be seen that the number of new particles increased with initiator concentration. This can once again be explained by the increase in the number of radicals being generated leading to more

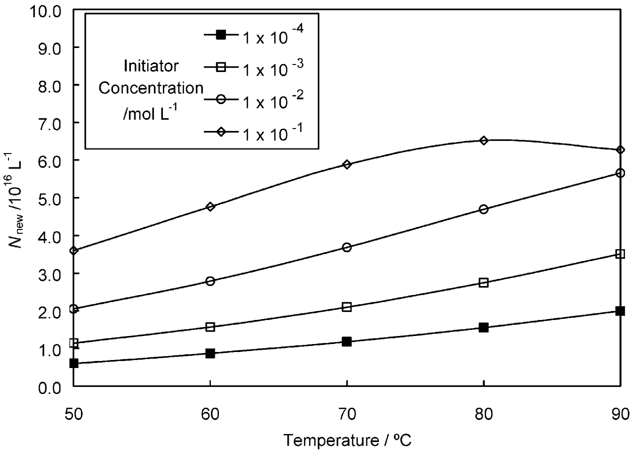

Fig. 11. Predicted N_{new} versus temperature for different initiator concentrations in ab initio vinyl acetate systems.

radicals growing to the length where nucleation occurred. The only trace of deviation from this behaviour is that at 90 °C, where at high initiator concentration, a slight reduction in the value for N_{new} is noted. This is the only point on the plot where there were sufficient radicals for termination to begin to dominate, resulting in reduced nucleation. This is in contrast to styrene, a difference which will be explained shortly. In Fig. 11 a similar trend is observed, where increasing the temperature results in a larger radical flux, and hence more new particle generation. Once again there is only one instance of this trend not being followed, that of the highest initiator concentration and temperature, where a slight drop-off in the number of new particles occurred.

8.3. Comparison of styrene and vinyl acetate results

The dominant difference between styrene and vinyl acetate is that N_{new} is about two orders of magnitude higher for vinyl acetate than for styrene. What this reflects is the much higher rate of propagation of vinyl acetate in the aqueous phase, which more than offsets the requirement that a vinyl acetate oligomer must grow to a longer length before it precipitates out to form a new particle. In other words, because the rate of propagation of styrene is so low, its radicals are much longer-lived in the aqueous phase, and so they have an overwhelming likelihood of terminating or entering rather than forming a new particle. The rapidity of vinyl acetate propagation in the aqueous phase explains why a decrease in N_{new} at high initiator concentration is not observed for vinyl acetate. Propagation to length j_{crit} occurs sufficiently quickly that termination is not effective in removing radicals from the aqueous phase. The consequence of all this is that surfactant-free, ab initio styrene systems produce much larger particles than do equivalent vinyl acetate systems, as is well known experimentally, and as has been exploited for making large monodisperse PS particles.

The results also explain the well-known monodispersity of latexes produced in surfactant-free ab initio systems: because Interval I is so fast on the timescale of the polymerisation, i.e. on the timescale of the whole polymerisation, particle formation is over almost instantaneously, with the result that all particles form essentially at the same time, and so have equal time in which to grow [7]. This is in contrast to a surfactant-stabilised polymerisation, where micellar nucleation dominates. The micelles persist for a long time (largely because adsorption onto small particles does not remove enough surfactant from the continuous phase to go below the cmc, until the particle number and size are relatively large), resulting in particle formation by this route long after any particle generation by homogeneous nucleation has ceased. While the modelling indicates that such monodispersity should also be possible in systems such as vinyl acetate, it additionally indicates that in vinyl acetate systems it would not be possible to obtain the large particle sizes which are possible in styrene systems.

Comparison of this simplified model with ab initio experimental data for surfactant-free styrene systems has been given elsewhere [7]. These earlier calculations, verified by calculations with the present treatment, showed that although the model can give acceptable accord with the observed order of magnitude of particle number, it is unable to reproduce trends accurately (except when there happens to be fortuitous cancellation between different effects not included in the simplified treatment), because of shortcomings that have been outlined above.

9. Conclusion

A simple nucleation model is able to give acceptable semi-quantitative accord with the predictions of final particle number from more complete models, at least with an accuracy that is sufficient for stating whether or not massive secondary nucleation will occur. The modelling here predicts that conventional second-stage polymerisation conditions were unlikely to produce core–shell morphology with vinyl acetate monomer and a large styrene seed. Basically this is due to the rapid aqueous phase propagation of vinyl acetate in combination with the low particle concentration when seed size is large. However, the model predicts that it should be possible to produce the desired morphology with large seeds using inverse core–shell polymerisation. Subsequent papers will report the results of a series of experiments that shed light on the modelling approach of this paper, and the effect that PS cores have on the physical properties of PVAc.

Acknowledgments

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