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Synthesis of latices with polystyrene cores and poly(vinyl acetate) shells. 1. Use of polystyrene seeds

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Abstract

Strategies for avoiding secondary particle formation in seeded emulsion polymerisation, based on a simple model for particle nucleation [Macromol. Symp. 92 (1995) 13], are discussed and exemplified in the context of growing latex particles with polystyrene cores and poly(vinyl acetate) shells. With a polystyrene seed of unswollen radius 44 nm, core–shell polymerisation was easily achieved. However, when the same recipes were used with a polystyrene seed of unswollen radius 200 nm, excessive new particle formation occurred and no poly(vinyl acetate) shells could be detected. A wide selection of the suggested strategies for overcoming this were implemented, but always either extensive secondary nucleation occurred or the system became colloidally unstable. These results are in full accord with the predictions of the simplified nucleation model. © 2002 Published by Elsevier Science Ltd.

Keywords: Emulsion polymerisation; Styrene; Core–shell

1. Introduction

Avoiding secondary particle formation (loss of control of particle size) is a common goal in seeded emulsion polymerisation, and has been the subject of extensive qualitative and quantitative theory in the literature [1–19]. In addition to complex and relatively complete modelling of the process, it is desirable to have simple semi-quantitative guides to conditions whereby secondary nucleation can be avoided. One particular application is finding conditions so that core–shell latex particles can be synthesised.

A key result to emerge in the understanding of emulsion polymerisation in recent years is the mechanism for radical entry into particles [20]: radical entry occurs only through an initiator-derived radical which has propagated in the water phase to (or beyond) a critical degree of polymerisation z, because at this point the resulting oligomeric radical is surface-active. What determines the entry flux is thus the extent to which initiator-derived radicals undergo termination before reaching the degree of polymerisation z. Given the success of this model [20], it was logical to extend it to describe secondary nucleation [17,21]. The idea is that a surface-active z- or higher-mer in the aqueous phase can either (a) form a new particle by entering a micelle, or (b) form a new particle by propagating to a degree of polymerisation j_{crit} at which it undergoes homogeneous nucleation ($j_{\text{crit}} > z$), or (c) enter a pre-existing particle, or (d) terminate with another radical in the aqueous phase. Thus, secondary nucleation can be thought of in terms of these competing fates of z- and higher-mers in the aqueous phase, and the criterion for absence of new particle formation is:

$$\begin{aligned}&\text{no secondary nucleation when :}\\ &\quad(\text{overall rate of entry}) + (\text{overall rate of termination})\\ &\quad\gg(\text{rate of entry into micelles})\\ &\quad+(\text{rate of forming } j_{\text{crit}}\text{-mers}) \qquad (1)\end{aligned}$$

In our present studies we deal only with polymerisation in the absence of micelles, and so fate (a) need not be considered. In the light of what has been learned about entry, the rate coefficient for entry of a z- or higher-mer into a pre-existing particle is most appropriately given by the diffusion-controlled limit. Thus, the quantification of our

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secondary nucleation model uses

$$\text{overall rate of entry} \propto (\text{rate of propagation to } z\text{-mers}) \times r_{\text{swollen}} N_{\text{c}} \quad (2)$$

where r_{swollen} is the swollen radius of the particle and N_{c} is the number of pre-existing particles per unit volume of continuous phase. All else being equal, the rate of entry is proportional to particle radius, as is consistent with sensitive data for this quantity [22]. However, the more normal situation is not to keep N_{c} constant, but rather to keep *solids content* constant. With constant solids content, as seed size is reduced there will be an increase in N_{c} (which is inversely proportional to the cube of unswollen radius) that far outweighs the decrease in r_{swollen}; the overall rate of entry will thus be increased, and secondary nucleation reduced, as size is reduced.

The above summarises the key aspects of our model for secondary nucleation which will be drawn upon in this paper. Most studies of secondary nucleation (e.g. by the Lehigh group which led to means of growing large particles [2–5]) were made prior to the establishment of this *z*-mer entry mechanism. The present paper revisits this question, exemplified by growing latex particles with polystyrene (PS) cores and poly(vinyl acetate) (PVAc) shells. This system is chosen for study because, while PVAc-based latexes have many uses [23], in many of these they are disadvantaged by the poor water resistance, poor creep resistance and poor heat resistance of PVAc [24]. A potential means for improving this situation is to include some PS. It is well known (because of unfavourable reactivity ratios) that VAc and styrene do not copolymerise [25,26]. Blending of PS and PVAc latexes is likely to generate at least as many problems as it might solve, because of the contrasting natures of these two polymers (e.g. the PS might impair the excellent adhesive bonding ability of PVAc). Therefore, the strategy of creating core–shell PS–PVAc particles is attractive, because one might be able to retain the film-forming properties of PVAc latexes, leaving the PS cores embedded as domains which might give improved water, heat and/or creep resistance.

In this paper we investigate the possibility of synthesising core–shell PS–PVAc particles by polymerisation of VAc in the presence of PS seed particles. Preferably, these seed particles should be large, because in many of its applications, PVAc particles must be large, ~0.5 μm radius or greater [24]. Structured particles of this size implies large PS cores (say ~0.4 μm radius), in order for the PS to have any beneficial impact on material properties. An advantage of synthesising the PS component first is that then one can be confident that any structured particles resulting from second-stage VAc polymerisation should be core–shell, not another morphology, on account of the hydrophobicity of PS compared with PVAc. The synthetic challenge is to eliminate formation of colloidally stable new particles when one carries out the second-stage polymerisation of VAc in the presence of a PS seed.

Our previous paper [13] gave results from a series of simulations based on the above simple model [14,17,21] for particle formation in surfactant-free systems. Numerical solutions for the equations for this model were obtained with parameter values appropriate for the polymerisation of VAc in the presence of PS seeds for a wide variety of polymerisation conditions. The resulting predictions for when secondary nucleation should and should not occur will be subjected to comprehensive experimental testing in this paper. In addition, the model provides a qualitative guide to the choice of conditions.

2. Experimental methods and preliminary results

2.1. Chemicals

Styrene (Sty) (Huntsman) was purified by distillation under reduced pressure with the first and last 10% of distillate being discarded. Inhibitor was removed from vinyl acetate (Celanese) by passing the monomer through a column packed with quaternary ammonium anion exchange resin (Aldrich 30,631-2). The first and last 10% of monomer through the column were discarded. Monomer was stored in darkness at 0 °C for not longer than a week before use. Potassium peroxydisulphate (KPS; BDH AnalR grade), benzoyl peroxide (BPO) (BDH, stabilised with 25% water), sodium chloride (Scharlau reagent grade), sodium hydrogencarbonate (BDH AnalaR grade), potassium dihydrogenorthophosphate (BDH AnalaR grade) and sodium dihexylsulphosuccinate (AMA 80) (Cytec) were used as received.

2.2. Ab initio styrene polymerisations

Small surfactant-stabilised PS seeds were made using

Table 1
Recipes and reaction conditions for synthesising PS seeds

Latex label	CF:ST1	CF:ST2	CF:ST3	CF:ST4
Temperature (°C)	90	80	80	70
Water[a] (g)	560	642	875	875
Styrene (g)	247	298	91.25	91.25
MA 80 (g)	10.82	7.4	–	–
$NaHCO_3$ (g)	0.94	1.3	–	–
$K_2S_2O_8$ (g)	0.95	1.2	0.67	0.81
Water[b] (g)	30	50	25	25
NaCl (g)	–	–	–	0.81
Reaction time (h)	3	3	24	24
% Solids content	30.5	30.7	8.6	8.3
Average particle radius (nm)	44	130	200	405
Measurement technique	CHDF	TEM	TEM	TEM

[a] Initial charge.

[b] For dissolving $K_2S_2O_8$.

recipes based on those of Clay [27]: CF:ST1 and 2 of Table 1. AMA 80 (surfactant) and $NaHCO_3$ (buffer) were dissolved in water and added to the reactor with the remaining initial charge of water. The reactor was heated to the reaction temperature, stirring was begun, and a flow of nitrogen was started in order to flush oxygen from the reactor. When the reactor had attained the set temperature, styrene was added and the temperature allowed to return to the set value. Further, 10 min were then allowed to ensure the establishment of full chemical and thermal equilibrium. KPS, dissolved in a small quantity of water was then added. After initiator addition, the reactor was sealed and left for 3 h; high conversion was obtained.

The production of large PS latices requires surfactant-free conditions. Recipes CF:ST3 and 4 of Table 1 were used. These are based on those of Goodwin et al. [28], whose recipes can be tailored to give monodisperse particles of radius 125 to over 500 nm. The absence of surfactant meant the particles were less colloidally stable, and hence prone to shear-induced coagulation. The procedure was as above except that reaction was allowed to occur for 24 h to reach near-complete conversion.

2.3. Vinyl acetate polymerisation in the presence of a PS seed

A variety of strategies was needed because of the difficulty of inducing PVAc shell formation. The general procedure was as follows. The required volume of buffer solution was added to the seed latex, which was then filtered to remove coagulum if necessary. This solution was then added to the reactor, along with water to reduce the final solids content so as to ensure a stable latex at the end of the reaction. The reactor was heated to the reaction temperature while being stirred and purged with nitrogen. Once the reaction mixture had reached the desired temperature, KPS dissolved in a small quantity of water was added. A feed of VAc was started, and was continued until the desired amount had been added. The system was left for a further hour after the completion of the monomer feed to allow reaction of remaining monomer. Buffering of vinyl acetate polymerisations is necessary to prevent hydrolysis and subsequent coagulation of the latex. This was achieved with $NaHCO_3$ and small amounts of NaOH solution, care being taken to avoid high local ionic strength.

2.4. Transmission electron microscopy and associated

Particle sizing and particle morphology determination are vital in this work. Our transmission electron microscopy (TEM) procedures are given in sufficient detail that they can be reproduced, since documentation of TEM techniques for PVAc is hard to find.

Depositing latices on grids. Grids were prepared for TEM as follows. Grids were initially coated with a thin film of Formvar® (poly(vinyl formal)) or Pioloform™ (poly(vinyl butyral)), then a thin carbon coating was deposited to increase the strength and conductivity of the film. An amount of latex was diluted with either distilled water or with a staining solution. This dilution needed to be sufficient to allow coverage of the TEM grid to be less than a monolayer of particles. A small sample of the diluted sample was dropped onto the grid and allowed to dry overnight at room temperature. In some cases a vapour stain (such as ruthenium tetroxide) was also applied, so as to further enhance phase contrast (see below). Grids prepared in this manner were used to check for the presence of secondary nucleation, to measure particle size and to determine particle morphology.

PVAc is a relatively soft polymer, so it was often necessary to prevent the latex particles deforming as the latex dried, and also during exposure to the electron beam. A number of staining methods are outlined below. The general techniques are known [29] but a certain amount of trial and error was needed to tailor them to achieve the desired contrast for the specific task of imaging composite PS–PVAc particles.

Uranyl acetate negative staining. Uranyl acetate (UAc) acts as a negative stain in the same way as phosphotungstic acid (PTA). One drop of latex was placed in 1 ml of 0.1% by weight UAc in water solution. After 10 min a drop of this solution was placed on a grid and allowed to dry. The stain would deposit on the support film covering the grid as the diluted latex sample dried. The resulting grids appeared less prone to staining artefacts than those employing PTA as a negative stain.

Ruthenium tetroxide staining. RuO_4 reacts with PS but not PVAc [29,30]. Vapour staining was found to be the most effective method of using this material. A 2% solution in water was first prepared by dissolving ruthenium(III) chloride and sodium periodate and allowing reaction to occur. This solution could be stored in a freezer for a number of weeks before a reduction in staining power was noted. This was easily checked by exposing a small piece of natural rubber glove to the vapour, and noting the time taken for black staining to be visible. Around 10 ml of this solution was placed in a specially constructed stainless-steel chamber (Fig. 1). The chamber was supported on small legs to allow good heat transfer from the bath to the solution. The bath was kept at 40 °C to increase the vapour pressure in the chamber and thus accelerate staining rate. The TEM grids supporting the polymer to be stained were placed on the mesh for 1–5 min to effect staining.

Fig. 2 shows the effectiveness of the stain. The two micrographs show samples from the same latex, prepared in the same manner. UAc has been used as a negative stain to define the edge of the particles, i.e. the particles appear light against the darker UAc-stained grid. The grid shown on the right was additionally stained with vapour. The PS domains are clearly visible as the darker regions in the particles, whereas without the stain there is little contrast between the two polymer types.

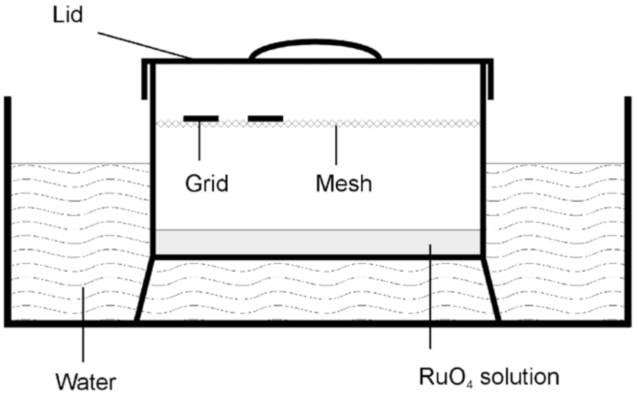

Fig. 1. Illustration of chamber used for vapour staining in TEM sample preparation.

Capillary hydrodynamic fractionation (CHDF). This was used in some instances for particle sizing and to indicate whether new particle formation had occurred. The instrument used was a Matec Applied Sciences CHDF 1100, calibrated with PS standards. It needs to be borne in mind, however, that current CHDF technology may not unambiguously detect the presence or absence of a population of polydisperse small particles in the presence of larger ones.

2.5. Putting PVAc shells onto small PS seeds

As is well known and implicit in the model used here, new particle formation is reduced by reducing seed size (Section 1) and by increasing the solids content (the rate of entering pre-existing particles being proportional to their concentration, see Eq. (2)). Modelling suggests [13] that for second-stage VAc polymerisation, the PS unswollen radius should be much less than 200 nm for new particle formation to be acceptably low; this prediction is experimentally tested in this section. Reaction conditions for experiments are given in Table 2. As thin shells are difficult to detect by TEM, for all experiments the relative amount of VAc to seed PS was high in order to make TEM examination easier.

Latex CF:ST-VA2 employed latex CF:ST1 as seed (unswollen radius 44 nm). TEM carried out on CF:ST-VA2 established that no new particles had formed, and that a core–shell morphology had resulted, as shown in Fig. 3. The dark domains in the centre of each particle can be attributed to PS selectively stained with RuO_4. A UAc negative stain was used to better define the particle edges, which otherwise would have had very little contrast against the support film. The agglomerations of particles visible in this micrograph are a phenomenon associated with the drying process, occurring because of the ability of PVAc to form films near room temperature. This result establishes that core–shell morphology can be produced using small, surfactant-stabilised PS seeds, as predicted [13].

In experiment CF:ST-VA3, recipe CF:ST-VA2 was repeated but using a dialysed seed latex to determine if surfactant played a role in determining the morphology formed. The presence of surfactant would encourage the formation of secondary particles, but the effect on morphology was unknown. The formation of complete shell layers depends amongst other things on the relative interfacial tensions between the polymer and aqueous phases [31–36]. One might expect that the presence of surfactant would help to stabilise an otherwise unfavourable morphology. The desired morphology had formed in the present case where surfactant was present, but this might not always be so. The additional recipe changes in CF:ST-VA3 are also a consequence of seed dialysis: to overcome the effect of dilution, more latex was required to achieve the same N_c; buffer had to be replenished, as it is necessary to avoid acid-catalysed hydrolysis when VAc is polymerised. Otherwise, the reaction was carried out in the same manner as CF:ST-VA2. TEM examination revealed no discernible difference in morphology, establishing that the absence of seed latex surfactant is no hindrance to the formation of core–shell morphology.

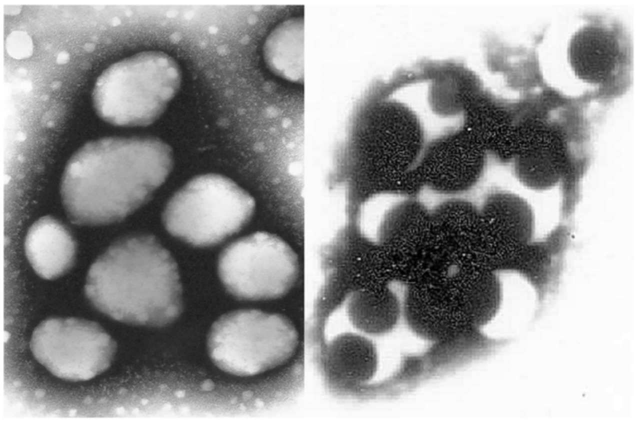

Fig. 2. TEM micrographs of the same composite PS/PVAc latex. Left: stained with UAc only. Right: additionally stained with ruthenium tetroxide to enhance the PS domain contrast (darker areas).

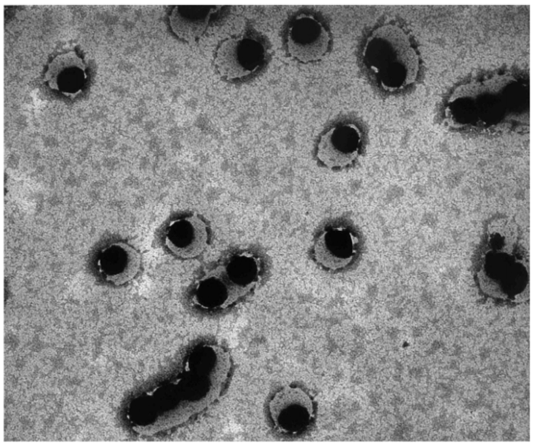

Fig. 3. TEM micrograph of latex CF:ST-VA2, a PS/PVAc core–shell latex made from small PS particles.

Table 2
Recipes and reaction conditions for core–shell polymerisation with PS seeds

Latex label	CF:ST-VA1	CF:ST-VA2	CF:ST-VA3	CF:ST-VA4	CF:ST-VA5	CF:ST-VA6	CF:ST-VA7	CF:ST-VA8	CF:ST-VA9	CF:ST-VA10	CF:ST-VA11	CF:ST-VA12	CF:ST-VA13	CF:ST-VA14
Stirring														
Turbine type	Six pitched blades					2 × rushton type impellers		Six pitched blades + baffles	Six pitched blades					
Distance from reactor floor (mm)	34	34	34	34	34	74 and 140	74 and 140	34	84	84	84	84	84	34
Speed (rpm)	300	300	300	300	300	300	300	300	300	300	300	225	300	200
Seed latex recipe	CF:ST2	CF:ST1	CF:ST1[a]	CF:ST1	CF:T1	CF:ST3	CF:ST3	CF:ST3	CF:ST3	CF:ST3	CF:ST3	CF:ST3	CF:ST3	CF:ST4
Seed latex (g)	480	200	240	200	200	500	500	450	400	400	450	450	450	450
Water (g)	305	175	135	115	115	–	–	30	120	100	50	50	50	50
Buffer	0.7 g $NaHCO_3$	–	0.23 g $NaHCO_3$	–	–	–	–	1.5 g KH_2PO_4, 0.3 g NaOH	1.5 g KH_2PO_4, 0.3 g NaOH	1.5 g KH_2PO_4, 0.3 g NaOH	1.5 g KH_2PO_4, 0.3 g NaOH	1.5 g KH_2PO_4, 0.3 g NaOH	1.5 g KH_2PO_4, 0.3 g NaOH	1.5 g KH_2PO_4, 0.3 g NaOH
1-Dodecanethiol	–	–	–	–	0.6 g	–	–	–	–	–	–	–	–	–
Initiator	5.7 g KPS	0.654 g KPS	0.654 g KPS	0.529 g KPS	0.529 g KPS	1.04 g KPS	1.04 g KPS	1.04 g KPS	2.42 g BPO, 17.3 g toluene	2.42 g BPO, 20.0 g EA	2.42 g BPO, 20 g EA, 1.04 g KPS	0.10 g BPO, 3.0 g LA, 10.4 g KPS	0.10 g BPO, 3.0 g BA, 10.4 g KPS	0.10 g BPO, 3.0 g BA, 10.4 g KPS
Water[b] (g)	25	25	25	25	25	50	50	50	–	–	50	50	50	50
Vinyl acetate														
Amount added (g)	200	120	120	60	60	56.4	75.0	170	64.8	74.0	64.8	9.25	49.0	60.0
Feed rate (g min^{-1})	1.5	0.745	0.745	0.745	0.745	0.94	0.94	1.5	0.74	0.74	0.74	0.31	0.45	0.752
PSty/VAc mass ratio	0.61	0.5	0.5	1.0	1.0	0.8	0.6	0.25	0.55	0.50	0.55	0.33	0.94	0.68
Post-addition reaction period (min)	60	60	85	60	60	60	95	90	260	75	260	10	45	60

Temperature: 80 °C; BPO, benzoyl peroxide/water; EA, ethyl acetate; LA, lauryl acrylate; BA, butyl acrylate.

[a] Dialysed.

[b] For dissolving KPS.

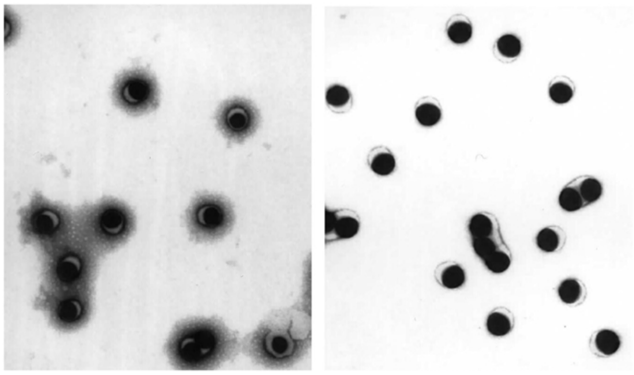

Fig. 4. TEM micrographs of PS/PVAc core–shell particles made from small PS cores. Left: latex CF:ST-VA4; right: latex CF:ST-VA5.

In CF:ST-VA4 and CF:ST-VA5, the VAc charge was reduced so as to create an equal mass of PVAc and PS. Additionally, 1-dodecanethiol was added in CF:ST-VA5 before the start of the VAc feed in order to effect a reduction in PVAc chain length. This was done to ascertain the effect of enhanced PVAc chain mobility, and to allow comparison with work (in a later paper in this series) on the analogous inverse emulsion system. TEM micrographs of the resulting latices are presented in Fig. 4, which shows that the desired core–shell morphology had formed, exactly as it had for the previous examples. Fig. 4 reveals that the cores and shells appear to be less concentric (i.e. more acorn-like) in the particles whose shells were synthesised in the presence of chain transfer agent.

2.6. Synthesis of large PS seeds

Conditions. We briefly discuss factors which can be used to control the size of large PS seeds. More *initial monomer* (higher solids content) means larger particle size, but surfactant-free recipes give increasingly unstable latices as monomer amount is increased (presumably due to a combination of decreased surface charge density and increased ease of coalescence). The syntheses used here were found to give adequate colloidal stability with solids content up to ~10%. For well understood reasons [13,21,28], large particles are favoured by *lower temperatures* and *low initiator concentrations*. For surfactant-free latexes, Goodwin et al. [28] showed that increasing the *ionic strength* through adding NaCl resulted in an increase in particle size. The mechanism usually advanced is the decrease in the stability of small particles due to the reduction in the thickness of the electrical double layer—this could result in a faster rate of coagulation of forming and/or recently formed particles [16]. Another possibility is that adding salt reduces the aqueous phase concentration of monomer, and thus reduces the rate of particle formation in surfactant-free systems [13].

Goodwin et al. [28] provide reaction conditions that produce PS seeds of radius ~400 nm, but to a solids content somewhat less than 10%. Recipe CF:ST4 was developed to increase solids content. This recipe includes added electrolyte, high monomer amount, low initiator concentration and relatively low temperature. However, such reaction conditions tend to produce unstable latices, which easily result in coagulation, especially when used as seeds in second-stage polymerisations (the added NaCl is considered likely to be the major cause of this). The smaller (but still large) seed latex CF:ST3 was used for most experiments in which it was attempted to put PVAc shells onto large PS seeds. Elementary rate considerations [17] (see Eq. (2) and criterion 1) show that, for a given solids content, larger seed particles must result in even greater new particle formation.

3. Results and discussion

3.1. Putting PVAc shells onto large PS seeds—standard methods

Our modelling [13] suggested that it should not be possible to grow PVAc shells onto large PS seeds without excessive secondary nucleation. This section gives results of experiments designed to refute this inference. The first attempts were to polymerise VAc in the presence of large PS particles in the same way as was successfully used to create structured particles from small PS seeds. Specific conditions and recipes are given in Table 2. We follow the example of Hergeth and Schmutzler [37], who claimed to be successful in placing PVAc shells on relatively large PS particles (these authors suggested that the mechanism involved was coagulation onto the seed particles of small particles resulting from secondary nucleation). A starved-feed of VAc was employed, following the modelling [13] predictions, which are that lowering the monomer concentration should reduce the incidence of secondary particle formation (that said, we note recent reports of unexpected secondary nucleation in styrene systems under starve feed [12,15,38], perhaps due to the particles being glassy). We also follow Hergeth and Schmutzler [37] in using a relatively high initiator concentration. Normally, a high initiator concentration would promote new particle formation [13], but in combination with a starved-feed of monomer it may suppress new particle formation by keeping the aqueous phase exhausted of monomer [13].

In our first experiments, CF:ST-VA6 and CF:ST-VA7 (Table 2), gross coagulation occurred. We believe this to be a result of acid-catalysed hydrolysis of VAc. This problem was successfully addressed in experiment CF:ST-VA8 by adding buffer solution to maintain pH at a level such that the hydrolysis rate was minimised. It was found that this recipe could successfully tolerate different ratios of VAc to PS (details not specifically included in Table 2). Examination of the resulting latices by TEM and CHDF both indicated that extensive new particle formation had occurred. Typical

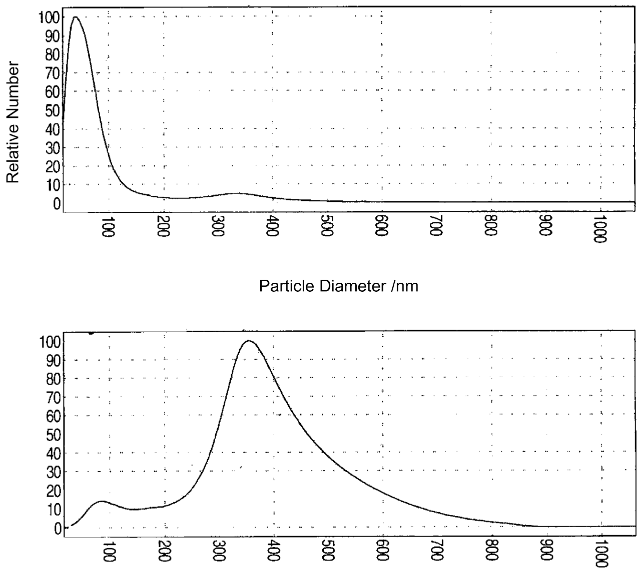

Fig. 5. CHDF results for a latex produced as latex CF:STVA8, but with a smaller ratio of VAc to PS. Upper plot: number particle size distribution; lower plot: weight particle size distribution.

CHDF results are presented in Fig. 5, in which formation of new particles is most obviously indicated by the number distribution (upper plot). The weight distribution (lower plot) also clearly shows a mass of new, small particles. The original seed (diameter ~400 nm) is also seen. The weight distribution shows that the majority of mass in the system was in the large seed particles. In this particular experiment, equal masses of VAc and PS were used (cf. the 4:1 ratio of CF:ST-VA8). If the weight distribution were quantitatively accurate, it would mean either that VAc conversion was very low or that a lot of VAc did indeed polymerise in the seed particles. However, the weight distribution from present CHDF technology was found to give extremely variable results when PVAc was involved (and indeed in any system containing particles less than ~60 nm in diameter), and it could not therefore be used to reliably establish the amount of polymer located in the new and seed particles, and hence determine if shell formation had occurred. PVAc shells for this type of latex could not be detected using TEM, even when the VAc to PS mass ratio was as high as 4:1 (recipe CF:ST-VA8).

Both CHDF and TEM results confirm the modelling prediction [13] of extensive new particle formation. The reason for this is the fast rate of aqueous phase propagation of VAc (rapid rate of production of both z and j_{crit}-mers) coupled with the low rate of entry when the seed particle number is low due to these particles being large (Eq. (2)). Extensive new particle formation does not preclude the occurrence of significant polymerisation in the seed particles, but in this particular case the best indications, from TEM, are that little VAc polymerisation occurred in the PS seed particles.

3.2. Putting PVAc shells onto large PS seeds—alternative strategies

In the polymerisations of Section 3.1 there was extensive formation of new PVAc particles (even if concurrent PVAc shell formation could not be ruled out). The important postulate of the model is that in the absence of micelles a new particle forms if a growing radical in the aqueous phase reaches a degree of polymerisation j_{crit}. Using Eq. (2) and criterion 1, it is possible to envisage changes in reaction conditions that should favour entry (or, less productively, termination) over homogeneous nucleation, thereby limiting or even preventing new particle formation. The following sections discuss some such strategies.

3.2.1. Organic phase (or non-charged) initiator and/or controlled addition of surfactant

It has been shown that an excellent strategy for avoiding secondary nucleation in systems with large particles is to use an organic-phase initiator [4], thereby eliminating homogeneous nucleation. Another strategy is to add surfactant during the course of polymerisation so that surface charge density is maintained while the system remains below the CMC [3]. These strategies have been both discussed and successfully implemented by the Lehigh group [2–5] and so will not be further considered here.

3.2.2. High seed latex solids content

Increasing the solids content increases the rate of entry simply by increasing the particle concentration (Eq. (2)). Unfortunately the large PS latices of this work were made surfactant-free, which means they are not particularly stable and it is difficult to increase their solids content even above 10%. Further, even if the maximum theoretical volume fraction of 70% could be achieved, our modelling [13] predicts that this seven-fold increase in solids content, although having an appreciable effect, would still result in heavy secondary nucleation when a 400 nm diameter PS seed is used. Thus while increasing solids content is in principle an approach for promoting core–shell polymerisation, in practice we could not implement it.

3.2.3. High ionic strength

In ab initio, surfactant-free polymerisations, particle formation is reduced by increasing the ionic strength [28], and this effect should also be operative in a seeded system, as the same principles will apply. Our model [13,14,17] is oversimplified in that it does not explicitly include a mechanism for ionic strength to affect secondary nucleation (although more complex models take this into account [16, 39,40]). A practical consideration in the present system is that ionic strength can only be increased to a limited extent otherwise catastrophic coagulation occurs; even before this, stability to shear induced coagulation is reduced. The addition of surfactants to reduce this instability is possible [3], e.g. steric stabilisers such as alkyl phenyl ethoxylates [41].

3.2.4. Lower temperature

Reducing the temperature has the effect of reducing the aqueous phase propagation frequency, via two means: the saturated aqueous monomer concentration, C_W^{sat}, decreases with decreasing temperature [42], as does the aqueous phase propagation rate coefficient. If the rate of aqueous propagation is slowed down, then a growing radical will take a longer time to reach the critical length j_{crit}, which means it will have a greater chance of terminating or of undergoing entry (Eq. (2)). Thus, the rate of new particle formation will be reduced. Calculations performed with our model [13] were used to determine if either of these effects could be responsible for a significant reduction in the number of new particles forming. All parameters and rate coefficients were held constant at their 80 °C values except the propagation coefficient and saturated aqueous monomer concentration. The propagation rate coefficient for VAc was varied using data from pulsed-laser polymerisation [43]. An accurate temperature dependence for the water solubility of VAc is not available, but independently determined values of 0.23 M at 20 °C [44] and 0.32 M at 50 °C [45] were appropriately fitted in order to obtain estimates of C_W^{sat} at various temperatures. Simulations were carried out for 80 °C as a reference, for 50 °C as an effective lower limit for thermally decomposing initiators, and for 5 °C as a practical lower limit for emulsion polymerisation initiated by a redox couple. An unswollen seed size of 200 nm and 10% solids content were used. Table 3 gives the result of these calculations. It can be seen that a reduction in the new particle concentration does occur. However, this reduction only reaches a significant extent when the temperature is dropped to a level so low that only a redox initiator under slow feed conditions could be used. For core–shell polymerisation in the presence of seed particles approaching 0.5 μm radius, the ultimate aim of this work, our model unfortunately predicts insufficient reduction of secondary particle formation.

3.2.5. Starved feed of vinyl acetate

Another method of reducing the overall rate of aqueous phase propagation is to reduce the monomer concentration in this phase. This could be achieved by 'salting out' the monomer by adding electrolyte, but the simplest way is to operate under starved feed conditions. Simulations [13] revealed that severely starved feed can indeed reduce the rate of aqueous phase oligomer growth to a level where almost all radicals either enter or terminate and so there is essentially no new particle formation. At more practical levels of feed starvation the suppression of new particle formation is only modest. The main way in which starved-feed conditions are realised in practice is obviously through slow feed of monomer, but it should also be remembered that assistance is provided by any process which increases the rate of in-particle polymerisation, thereby driving monomer from the aqueous phase into the particles. Increasing initiator concentration is one such process, although it may also have the adverse effect of increasing the rate of secondary nucleation by increasing the aqueous phase radical concentrations. Thus, the effect of increased initiator concentration is complex, but it is possible that it can act synergistically with slow monomer feed in reducing secondary nucleation.

Table 3
Results of simulations to show the effect on new particle concentration, N_{new}, of lowering the aqueous phase propagation coefficient, $k_{p,aq}^i$, and saturated aqueous phase monomer concentration, C_W^{sat}, for second-stage VAc polymerisation

Temperature (°C)	$k_{p,aq}^i$ (l mol^{-1} s^{-1})	C_W^{sat} (mol l^{-1})	N_{new} (l^{-1})
80	2.58×10^4	0.420	2.05×10^{16}
50	6.70×10^3	0.320	5.93×10^{15}
5	1.93×10^3	0.189	8.18×10^{10}

A potential problem with a system that starts with starve feed of monomer is monomer build-up during the induction or retardation period, for example, due to dissolved oxygen or monomer incompatibility. Such a build-up of monomer would counteract the starved-feed conditions. Oxygen inhibition can be overcome by using a more rigorous oxygen removal procedure, but monomer incompatibility is a more serious problem, especially in the present case of VAc polymerisation in the presence of PS seeds. Styrene is well known to inhibit VAc polymerisation [25,26], so it is important that minimal residual styrene monomer is present at the start of the VAc reaction. Possible methods to remove residual styrene from the seed latex include dialysis, steam stripping, use of a chaser, and polymerising a monomer that is mutually compatible with both styrene and VAc and would thus scavenge the remaining styrene. If the chaser initiator strategy is used, as it was in this work, then the initiator should be hydrophobic, as most of the remaining monomer will be present in the particles. If the 'scavenger monomer' strategy is used, as also in this work, it is important to make sure that its polymerisation does not create any new particles. Both these strategies have the advantage over dialysis and steam stripping of consuming rather than wasting any residual styrene.

In the experiments of the following section, a gradual feed of VAc was always used. However, bearing in mind the possible complications outlined above, especially that of diminished polymerisation rate, it was not possible to starve the feed to the extreme extent [13] which of itself would eliminate new particle formation.

3.2.6. Redox couples

Use of organic phase initiation to eliminate homogeneous nucleation [4] may result in coagulation (the initiator endgroups do not impart any colloidal stability) and may also give uncertain morphology (the second-stage polymerisation may occur anywhere in the particles). Thus one is led to the idea of generating radicals at or near the particle surfaces: the radicals will not be in the aqueous phase, so there should be minimal homogeneous nucleation, and the locus of polymerisation should be at or near the particle surface, thus giving rise to a colloidally stable system and to the desired core–shell morphology [46,47]. 'Inisurfs' can be used here [48–50], or a redox couple comprising of a hydrophobic part and a hydrophilic part. Radicals should be generated where the two parts meet, namely at the interface of the particle and water phases [46, 47,51,52]. Rapid exit of radicals into the aqueous phase, which occurs with VAc because of its high transfer constant and high water solubility [53], is the major problem with this strategy. A radical trap could possibly be employed to eliminate new particle formation from such unwanted aqueous phase radicals [4].

3.2.7. Opposite charge for new and seed particles

Another method that has been used to make core–shell type particles is to create a seed using a positively or negatively charged initiator species and then use an oppositely charged initiator species for the second-stage polymerisation [54]. This approach relies on oppositely charged particles attracting one another (however, the entry mechanism [20] suggests that there will be no increase in entry rate if particle and entering species have opposite charges, all other things being equal). Thus even if secondary nucleation occurred, the new particles would undergo electrostatically driven coagulation with the seed particles. In cases where the second polymer is above its glass transition temperature, coagulated secondary particles would transform into a smooth shell layer. In the case where the second polymer is hard, the consequence of coagulation would be a raspberry morphology [54]. A possible problem with this method is that it will only work effectively as long as there is sufficient original seed particle charge present to attract the newly created particles. When the new polymer completely covers the seed, the initiator endgroups on the seed particle surface will be covered, and the electrostatic driving force will no longer operate. Thus only very thin shells could be created in this way, which therefore makes it an unsuitable strategy for this work. With this approach there is also the issue of overall latex stability, especially in a surfactant-free system. At some point the seed particles will have no net surface charge, and at this point the latex will be very unstable.

3.3. Putting PVAc shells onto large PS seeds—implementation of strategies for avoiding secondary particle formation

3.3.1. Second-stage polymerisation with benzoyl peroxide as initiator

Firstly, we use the organic-phase initiator benzoyl peroxide to trial the strategy of Section 3.2.1. The rate coefficient for BPO decomposition is reported as being in the range $2.5–4.4 \times 10^{-5}\ \mathrm{s}^{-1}$ at 80 °C in a variety of solvents [55] (cf. $8.6 \times 10^{-5}\ \mathrm{s}^{-1}$ at 80 °C for KPS [56]). These values were used to calculate a BPO concentration to give a primary radical flux approximately the same as that in our earlier experiments with KPS. The initial reaction carried out was CF:ST-VA9, as detailed in Table 2. The BPO, dissolved in toluene, was added to the reactor once the seed latex had attained the reaction temperature. VAc feed was begun 1 h after initiator addition, so as to enable the BPO first of all to polymerise any residual styrene. At the end of the reaction we observed considerable coagulum, the consistency of which suggested formation via bulk polymerisation. To test whether the coagulation was connected with the use of toluene, which is known to act as a degradative chain-transfer agent [57] in styrene systems, the experiment was repeated using ethyl acetate instead as the solvent for the BPO (experiment CF:ST-VA10 of Table 2). This resulted in the same type of coagulum.

The most likely cause of the observed coagulation is that the particles were becoming coated in a layer of PVAc chains with uncharged endgroups, thus rendering the latex unstable. If this is so, then it would be expected that PVAc shells were indeed forming in these systems. However, investigations using TEM to determine the actual morphology could not be undertaken, as these latices had sufficient coagulation that 'representative' samples could not be confidently taken. As discussed above, surfactant could be added to avoid colloidal instability, a strategy successfully exploited in the past [4], but this avenue was not pursued due to the desire to avoid secondary particle formation by micellar entry.

3.3.2. Employing benzoyl peroxide in the role of monomer scavenger

In order to assure that the new particle formation observed for experiment CF:ST-VA8 was not simply a result of monomer incompatibility, a combination of particle and aqueous phase initiation was tried. This might also overcome the coagulation problem of Section 3.3.1. The recipe used was CF:ST-VA11 in Table 2. BPO, dissolved in ethyl acetate, was added in the same manner as described above, to polymerise any residual styrene present from seed formation. After an hour of reaction, KPS solution was added. VAc addition was begun at this stage, and the reaction allowed to proceed. Once again coagulation was observed. This was unexpected, as the seed particles and any newly created particles should have had charged surface groups from the KPS. We postulate that a large proportion of the second-stage initiation occurred as a result of BPO species still present after an hour, and that not a high enough proportion of PVAc molecules with charged endgroups were formed in order to render the system stable. This postulate could be tested by reducing the level of BPO, but even if one succeeded in creating a stable system, the previous experiments of this paper have shown that core–shell polymerisation would be minimal and secondary particle formation dominant. The important result of this section is that residual styrene in large seed latex particles cannot have been responsible for preventing core–shell polymerisation in earlier attempts using KPS.

3.3.3. Use of a scavenger monomer

An advantage of dissolving the BPO in ethyl acetate or toluene is that these solvents reduce the particle viscosity, and thus help residual styrene to react, but a disadvantage is that these solvents remain at the end of the polymerisation. A way around this problem is to use a 'scavenger monomer' as a solvent to dissolve the organic phase initiator. The chosen monomer should be mutually compatible with styrene and VAc. This strategy was implemented here using first lauryl acrylate and then butyl acrylate as the scavenger monomer. The reaction conditions for these experiments are given in Table 2. The buffered seed latex was added to the reactor followed by the scavenger monomer and dissolved benzoyl peroxide. This was stirred for 20 h to allow monomer to swell the seed particles, then the reactor was heated to the reaction temperature and KPS, dissolved in a small quantity of water, was added. VAc was fed in the normal manner.

Lauryl acrylate was used as scavenger monomer because it is very insoluble in water, which means that it should partition almost exclusively into the seed particles, and therefore there should be no chance of new particle generation [58,59]. At the completion of this reaction, CF:ST-VA12, there was a layer of what appeared to be partially polymerised lauryl acrylate at the top of the reactor, but otherwise no coagulum. It was suspected that the lauryl acrylate was too insoluble in the aqueous layer to be able to migrate through it into the seed particles, despite swelling for 20 h with stirring. (This problem could be overcome by adding a surfactant or a transport agent such as β-cyclodextrin [60].)

In view of this result, it was decided to try butyl acrylate as styrene scavenger. It is mutually compatible with styrene and VAc, and while it is more water-soluble than lauryl acrylate, it is still sufficiently water-insoluble as to reduce the likelihood of new particle formation. At the conclusion of experiment CF:ST-VA13 there was no discernable coagulum on top of the latex, indicating that the butyl acrylate had been able to migrate to the particles as anticipated. Given this encouraging result, a number of polymerisations were undertaken which were variations on CF:ST-VA13. Specifically, the amount of VAc was varied with the intention of forming a series of core–shell latices with varying structure. However, TEM revealed that extensive secondary particle formation had occurred. It would seem likely that most of these new particles were PVAc rather than poly(butyl acrylate), although this could not be established with certainty. This finding continues to confirm the result of theory [13], which is that even as one removes kinetic and thermodynamic obstacles to in-particle polymerisation of VAc, one cannot escape the realities of aqueous phase kinetics, which inexorably result in new particle formation with KPS.

3.3.4. Increased ionic strength

Experiment CF:ST-VA14 (Table 2) was carried out to investigate the strategy in Section 3.2.3. This experiment was in essence the same as CF:ST-VA13, except that seed latex CF:ST4 was used. Recall from Section 2.5 that high ionic strength was a factor in achieving the larger size of this latex (Table 1). Thus, the ionic strength in experiment CF:ST-VA14 would have been appreciably higher than in CF:ST-VA13. The result was a lot of coagulation in CF:ST-VA14 where there had been none in CF:ST-VA13. It is implausible that this coagulation was caused by the larger seed particle size or the larger feed of VAc in CF:ST-VA14. Therefore, it was probably caused by the increased ionic strength. This suggests that in experiments like CF:ST-VA13 the ionic strength was already close to the limit at which the system became colloidally unstable.

3.4. Quantitative comparison of modelling results with experiment

Our model [13] yields the ratio $N_{\text{new}}/N_{\text{seed}}$, the number of new particles to that of seed particles. In cases where this number is either very small or very large, the model is essentially providing a yes/no prediction as to whether new nucleation occurs, and quantitative comparison of model and experiment is impossible, because one cannot accurately measure very small or very large values of $N_{\text{new}}/N_{\text{seed}}$. For example, in the case of polymerisation in the presence of small seeds, examination by TEM revealed no visible new particle formation, which is as rigorous a test as is possible of the model's prediction that $N_{\text{new}}/N_{\text{seed}} \ll 1$ in this case. In such cases the precise value of $N_{\text{new}}/N_{\text{seed}}$ is of no practical use. Nevertheless, there will be cases when $N_{\text{new}}/N_{\text{seed}}$ is closer to 1 in value, and thus it is both feasible and sensible to subject the model to quantitative testing, as has been done previously with both the present simplified model and more complex ones [16,17].

A problem with measuring $N_{\text{new}}/N_{\text{seed}}$ via determination of particle size distribution (PSD) is that all current particle-sizing methods have great difficulty in accurately measuring a PSD when a sample is bimodal and there is a large difference between the sizes of the two populations of particles. Another problem with the PSD approach is that N_{new} only follows from the average new particle size if one knows how much of the second-stage monomer has ended up in the new particles. Hence it was decided to determine $N_{\text{new}}/N_{\text{seed}}$ simply by counting particles from TEM images. Even this approach requires care, because if the (small) new particles consist of a different polymer to the (large) seed particles, then the new particles can be difficult to see, thus compromising determination of $N_{\text{new}}/N_{\text{seed}}$. While a

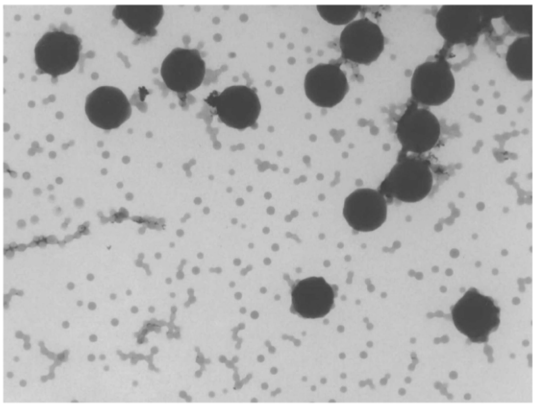

Fig. 6. Typical TEM micrograph of seed latex CF:ST-VA13, as used to determine the ratio of number of new particles to number of seed particles.

selective stain might help overcome this problem, this was not necessary in the current case, as is evident from Fig. 6, which shows a TEM micrograph of a diluted sample of latex CF:ST-VA13.

The micrograph of Fig. 6 and three others were used to determined $N_{\mathrm{new}}/N_{\mathrm{seed}}$ of 67 for latex CF:ST-VA13. More than 5000 particles were counted, and care was taken to use images felt to be representative of the latex. Simulation predicts $N_{\mathrm{new}}/N_{\mathrm{seed}} = 10.4$. This agreement with experiment is felt to be adequate when one considers the simplicity of the model and the complexity of quantitative measurement of $N_{\mathrm{new}}/N_{\mathrm{seed}}$ from experiment.

3.5. Comparison with previous attempts at synthesis

All efforts in this paper to put PVAc shells onto large PS seeds have been unsuccessful because of the occurrence of new particle formation, in accord with the predictions of our model [13]. Hergeth et al. [18,19,37] reported creation of quite large PS/PVAc core/shell particles from first-stage polymerisation of styrene and second-stage polymerisation of VAc. They stated that the core–shell formation resulted from extensive coagulation onto the PS core of small PVAc particles arising from secondary nucleation, that the final number of distinct new particles (not aggregated onto the PS) was relatively small, and that this is in accord with the predictions of a model proposed by one of them [61]. Recipe CF:ST-VA15 of Table 4 is as faithful a reproduction of their recipe as is possible on the basis of the information provided [37]. The reactor was charged with a large amount of water and heated. A solution of KPS was then added and a very slow feed of styrene started. Once all the styrene had been added, further polymerisation time was allowed. Another solution of KPS was then added and a feed of VAc commenced. The resulting latex was subjected to examination by TEM to determine if VAc particles had formed. The micrograph in Fig. 7 shows a typical portion of the TEM grid, which has been stained with UAc. It can be seen that there has been extensive secondary particle formation. This is in accord with our predictions [13] and thus is consistent with our simple model for secondary particle formation [13]. However, this conflicts with the results reported by Hergeth et al. We have no convincing explanation for these apparent differences, but they could arise from different TEM techniques having been used.

Table 4
Recipe and reaction conditions for attempted core–shell polymerisation following Hergeth and Schmutzler [37]

Latex label	CF:ST-VA15
Temperature (°C)	80
Stirring	
Turbine type	Six pitched blades
Distance from reactor floor (mm)	34
Speed (rpm)	350
Water (g)	450
$K_2S_2O_8$ (g)	0.946
Water[a] (g)	50
Styrene	
Amount added (g)	11.5
Feed rate (g min^{-1})	0.048
Post-styrene addition reaction period (min)	30
$K_2S_2O_8$ (g)	0.946
Water[a] (g)	20
Vinyl acetate	
Amount added (g)	26.9
Feed rate (g min^{-1})	0.75
Sty/VAc mass ratio	0.43
Post-vinyl acetate addition reaction period (min)	60

[a] For dissolving $K_2S_2O_8$.

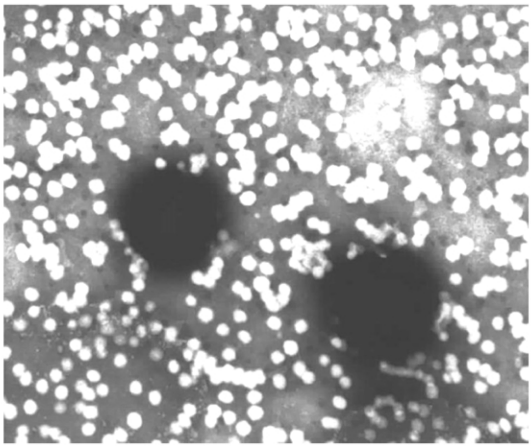

Fig. 7. TEM micrograph of seed latex CF:ST-VA15.

4. Conclusion

An extensive series of experiments based on formation of polystyrene/poly(vinyl acetate) core–shell particles, starting with a polystyrene seed, and examining secondary nucleation, were used to test the usefulness of a simple model for particle formation in emulsion polymerisation. A wide variety of strategies were used. The results were always in accord with model predictions: that the target morphology, without secondary nucleation, can only be achieved with small seed particles. Our inability to falsify our model evidences its robustness, and suggests that it is highly useful for two-stage polymerisations in general, not just the styrene/vinyl acetate system of this paper. The subsequent paper in this series will explore the use of inverse core–shell synthesis. Because the kinetics in this case favour the formation of structured particles, the challenge, as will be seen, switches to attaining the desired morphology.

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