

Synthesis of latices with hydrophobic cores and poly(vinyl acetate) shells.

2. Use of poly(vinyl acetate) seeds

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Abstract

A strategy is explored for synthesizing latex particles with polystyrene cores and poly(vinyl acetate) shells. The seed particles are poly(vinyl acetate), which theory indicates should be immune to secondary particle formation when a second-stage seeded emulsion polymerization with styrene is carried out. The objective is to form a single hydrophobic core by inversion of the second and first stages. While this morphology is favoured thermodynamically, conditions need to be optimized so that it is kinetically achievable: many attempts to implement this using straightforward synthetic procedures result in either no core (acorn morphology) or multiple polystyrene cores. A series of experiments enables this goal to be implemented by ensuring sufficiently fast diffusion of the first-stage hydrophilic polymer (using chain-transfer agent to reduce the molecular weight and, more importantly, the degree of branching of the parent poly(vinyl acetate) seed polymer), an initiator which minimized grafting between the first- and second-stage polymers, and modifying the seed poly(vinyl acetate) to increase its hydrophilicity.

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1. Introduction

There are synthetic and physical challenges which must be met in order to produce true core-shell polymers: transmission electron microscopy often reveals that many procedures purporting to produce an ideal concentric core-shell morphology in actuality lead to something else, e.g. non-concentric, multiple-core morphologies. This paper explores the synthesis of latex particles with polystyrene (PS) cores and poly(vinyl acetate) (PVAc) shells. This is of technical interest, because it may help overcome the well-known problems of PVAc latices, which are that they have poor water resistance, poor creep resistance and poor heat resistance [1]: core-shell PS–PVAc particles might retain the excellent film-forming and adhesive properties of PVAc latices, leaving the PS cores embedded as domains which might give improved water, heat and/or creep resistance. Neither copolymerization (not that such is possible with this

pair of monomers [2,3]) nor blending could be employed to this effect.

There are extensive discussions in the literature of the thermodynamic, kinetic and mechanistic factors involved in the formation of core-shell latex particles [4–24]. Rather than attempt a detailed discussion of the contributions of individual authors, we shall here investigate synthetic strategies aimed towards the stated goals, these strategies being a digestion of those in the literature, modified where necessary by the major advances in mechanistic understanding that have emerged over recent years (e.g. [25]).

Given that there is non-zero interfacial energy between the two polymer phases comprising the latex particle, there is a thermodynamic driving force for the more hydrophobic component to form a single domain (i.e., a core). There is no thermodynamic driving force for this core to be concentric in a core-shell latex (as long as the hydrophobic core is shielded from the particle/water interfacial region). In a conventional (non-inverse) core-shell synthesis, a concentric morphology is expected if the growth of the shell is uniform, i.e. there is a kinetic driving force for core concentricity. However, there are no thermodynamic or

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kinetic driving forces for the core and shell to be concentric in an inverse system.

In a previous paper [26] we carried out a modelling study of the phenomenon of secondary particle formation in emulsion polymerization: a prerequisite for the formation of structured latex particles is avoidance or minimization of new particle formation when a second monomer is polymerized in the presence of a seed latex of a first monomer. This can be implemented [25–28] by considering only the competition between propagation, termination and entry of oligomeric radicals in the aqueous phase. The starting point for a synthetic strategy is to operate with aqueous-phase surfactant concentrations below the critical micelle concentration, thereby avoiding secondary particle formation by micellar nucleation. While the simplest strategy for synthesizing a PS/PVAc core-shell particle with PS as the core would appear to be starting with a PS seed, our calculations [26] showed that when vinyl acetate (VAc) is the second-stage monomer, its rapid aqueous phase propagation kinetics give it a high tendency to undergo homogeneous nucleation [29] and form new particles, confirmed by subsequent experimental investigations [30]. Thus it is not possible to produce PS–PVAc core-shell particles by polymerizing VAc in the presence of moderately sized or large PS latex particles. Another prediction of our calculations [26] is that when styrene is polymerized in the presence of a PVAc seed there should be very little new particle formation: aqueous phase propagation of styrene is very slow in emulsion polymerization, and thus it takes a very long time before radicals are able to ‘precipitate’ out and nucleate new particles and so will instead enter a particle. This means that second-stage polymerization of styrene in the presence of a PVAc seed should produce structured latex particles, a prediction which is put to the test in this paper. However, meeting this requirement is only a necessary but not sufficient condition for formation of core-shell particles. In the present case one can anticipate that inverse core-shell polymerization might take place, in that the second-stage PS might displace from the particle centres the much more hydrophilic PVAc from the first stage of polymerization, thus giving the desired PS–PVAc core-shell morphology. While this is the most *thermodynamically* favoured state for a PS–PVAc structured latex, there are also *kinetic* issues.

2. Experimental methods

2.1. Chemicals

Styrene (Huntsman) and butyl acrylate (BA) (BDH laboratory reagent grade) were purified by distillation under reduced pressure, with the first and last 10% of distillate being discarded. Inhibitor was removed from vinyl acetate (VAc) (Celanese) by passing the monomer through a column packed with quaternary-ammonium anionic

exchange resin (Aldrich 30,631-2), the first and last 10% being discarded. All monomers were stored in darkness at 0 °C for not longer than a week before use. The sodium salt of vinylsulfonic acid (SVS) (Aldrich, 25 wt% solution in water, stabilized with 100 ppm 4-methoxyphenol) and the surfmer (surface-active monomer) sodium 1-allyloxy-2-hydroxypropane sulfonate (Sipomer COPS 1) (Rhone Poulenc) were used as received.

All other reagents were also used as received. Initiators: potassium peroxydisulfate (KPS), ammonium peroxydisulfate (APS) (BDH AnalaR grade), benzoyl peroxide (BPO) (BDH, stabilized with 25% water) and 2,2'-azobis(2-isobutyronitrile) (AIBN) (Akzo); chain transfer agent: 1-dodecanethiol (DDM) (Aldrich); electrolyte: sodium chloride (Scharlau reagent grade); buffer: sodium hydrogencarbonate (BDH AnalaR grade); surfactants: sodium dihexylsulfosuccinate (MA 80) (Cytec), sodium dioctylsulfosuccinate (OT 75) (Cytec) and sodium dodecyl benzene sulfonate (provided by Mr P. Coveny); reducing agent: sodium metabisulfite (Riedel-De Haën, reagent grade).

2.2. Vinyl acetate *ab initio* polymerizations

PVAc seeds were made using recipes based on those of De Bruyn [31,32]. Reactant amounts and conditions are given in Table 1. MA 80 and OT 75 (surfactants) and NaHCO₃ (buffer) were weighed into a beaker with approximately half the initial charge of water. This was stirred on a hotplate until the NaHCO₃ had all dissolved and the surfactant was dispersed. This mixture was then added to the reactor and washed in with the remaining initial charge of water. The reactor was heated to the reaction temperature, stirring was begun and a flow of high-purity nitrogen was started to flush oxygen from the reactor. When the reactor had attained the set temperature, the KPS, dissolved in a small quantity of water, was added, followed immediately by the initial charge of VAc together with any chain transfer agent and/or Sipomer COPS 1. The reactor was sealed and gradual feed of VAc was begun (ensuring avoidance of an uncontrollable exotherm); slow monomer feed also reduces the polydispersity of these latex particles [31]. However, this slow monomer feed is likely to result in more chain transfer to polymer, and hence branching, due to the lower monomer concentration in the particles, an important subsequent consideration. After monomer addition was complete, the reactor was left for one hour to allow polymerization of remaining monomer.

2.3. Preparation of a poly(vinyl acetate) seed incorporating hydrophilic comonomer

The recipe (Table 2) is based on one of Vandezande and Rudin [33]. The rationale behind aspects of it will be outlined in due course (Section 3.6.2). The reactor was charged with 250 g water and heated to 70 °C. Stirring was started and nitrogen flushing begun. Monomer, water and surfactant were

Table 1
Recipes and reaction conditions for synthesizing vinyl acetate seeds

Latex label	CF:VA1	CF:VA2	CF:VA3	CF:VA4
Temperature (°C)	70	70	70	70
Stirring				
Turbine type	6 pitched blades	6 pitched blades	6 pitched blades	6 pitched blades
Distance from reactor floor (mm)	34	34	34	34
Speed (rpm)	300	300	300	300
Water (g)	470	470	470	470
MA 80 (g)	5.0	5.0	5.0	5.0
OT 75 (g)	5.0	5.0	5.0	5.0
NaHCO ₃ (g)	1.0	1.0	1.0	1.0
K ₂ S ₂ O ₈ (g)	1.0	1.0	1.0	1.0
Water (g)	30	30	30	30
1-Dodecanethiol (g)	–	2.0	0.2	2.0
Sipomer COPS 1 (g)	–	–	–	2.0
Vinyl acetate				
Initial charge (g)	30	30	30	30
Remainder (g)	170	170	170	170
Feed rate (g min ^{−1})	0.945	0.945	0.945	0.945
Reaction time after monomer feed (h)	1	1	1	1
% Solids content	29.8	30.1	29.5	30.1
Average particle radius (nm)	66	65	65	60
Measurement technique	CHDF	CHDF	CHDF	TEM

Table 2
Recipe and reaction conditions for synthesis of butyl acrylate/vinyl acetate copolymer seed latex

	CF:VB1
Temperature (°C)	70–80
Stirring	
Turbine type	6 pitched blades
Distance from reactor floor (mm)	34
Speed (rpm)	400
Pre-emulsion	
Water (g)	150
Vinyl acetate (g)	332.5
Butyl acrylate (g)	61.5
Sodium dodecyl benzene sulfonate (g)	0.22
Initial reactor charge	
Pre emulsion (g)	40.0
(NH ₄) ₂ S ₂ O ₈ (g)	0.25
Water (g)	270.0
Monomer feed	
Pre-emulsion (g)	504
Sodium vinyl sulfonate solution (g)	15.0
1-Dodecanethiol (g)	2.0
NaHCO ₃ (g)	0.85
Water (g)	16.0
Feed rate (g min ^{−1})	1.1–3.9
Initiator feed	
(NH ₄) ₂ S ₂ O ₈ (g)	0.27
Water (g)	18.0
Feed rate (g min ^{−1})	0.075
Sodium metabisulfite (g)	1.0
Water (g)	20.0

emulsified in a separate reservoir, and an initial portion of this was added to the reactor along with APS in 20 g water. The reaction temperature was increased to 80 °C over 20 minutes. SVS, DDM and NaHCO₃ dissolved in water were added to the remaining pre-emulsion. Feed of this monomer mixture was started when the temperature reached 80 °C; the monomer mixture was added to the reactor over 220 min, starting at 1.1 g min^{−1} and increasing to 3.9 g min^{−1} by 0.4 g min^{−1} increments every 30 min. A 2.25 g amount of initiator solution was added every 30 min while the monomer feed was progressing. The reaction was allowed to proceed for a further hour after completion of the monomer feed. A quantity of sodium metabisulfite solution was then added to reduce residual peroxydisulfate.

2.4. Large-size PVAc seed

A commercial PVAc latex from Mercator Technologies, Auckland, with a large particle size (number-average radius ~0.5 µm) was used for some experiments. One of the stabilizers used in synthesis of the latex was poly(vinyl alcohol); the latex had not been compounded with additives such as plasticizer and fungicide.

2.5. General procedure for styrene polymerizations in the presence of PVAc seeds

The general procedure used for carrying out the inverse core-shell polymerizations of Table 3 was as follows. The PVAc seed latex was added to the reactor along with water. No buffer was required as the seed latices contained residual buffer and the second-stage initiator was almost always

Table 3
Recipes and reaction conditions for inverse core-shell polymerizations

Latex label	CF:VA-ST1 ^a	CF:VA-ST2	CF:VA-ST3	CF:VA-ST4	CF:VA-ST5	CF:VA-ST6	CF:VA-ST7	CF:VA-ST8	CF:VA-ST9	CF:VA-ST10
Stirring speed (rpm)	400	400	400	400	400	400	400	400	400	400
Seed latex recipe	CF:VA1	CF:VA1	CF:VA1	CF:VA2	CF:VA2	CF:VA2	CF:VA2	CF:VA2	CF:VA2	CF:VA3
Seed latex (g)	200	300	300	300	300	300	300	200	150	300
Water (g)	100 ^b	100	100	100	100	100	100	100	150	100
Sodium metabisulfite (g)	–	–	–	–	–	–	–	–	–	–
Styrene to swell seed (g)	120	15	50	–	15	60	105	90	105	–
1-Dodecanethiol (g)	–	–	–	–	–	–	–	–	–	–
Initiator	K ₂ S ₂ O ₈	BPO	BPO	BPO	BPO	BPO	BPO	BPO	BPO	BPO
Mass initiator (g)	0.7	1.8 ^c	1.8 ^c	0.7 ^c	1.4 ^c	1.4 ^c	1.4 ^c	1.4 ^c	1.4 ^c	1.4 ^c
Styrene to dissolve initiator (g)	–	30	30	11.25	30	30	30	30	30	11.25
Sty/seed polymer mass ratio	2.0	0.5	0.89	0.125	0.5	1.0	1.5	2.0	3.0	0.125
Latex label	CF:VA-ST11	CF:VA-ST12	CF:VA-ST13	CF:VA-ST14	CF:VB-ST1	CF:VB-ST2	CF:VB-ST3	CF:VA-ST15	CF:VA-ST16	
Stirring speed (rpm)	400	400	400	400	300	300	300	400	400	
Seed latex recipe	CF:VA1	CF:VA2	CF:VA2	CF:VA4	CF:VB1	CF:VB1	CF:VB1	commercial PVAc	commercial PVAc	
Seed latex (g)	300	300	300	300	240	120	120	150	150	
Water (g)	100	100	100	100	100	200	200	150	150	
Sodium metabisulfite (g)	–	–	1.0	–	–	–	–	–	–	
Styrene to swell seed (g)	–	–	–	–	–	–	–	45	45 ^d	
1-Dodecanethiol (g)	0.56	–	–	–	–	–	–	–	–	
Initiator	BPO	AIBN	BPO	BPO	AIBN	AIBN	BPO	BPO	BPO	
Mass initiator (g)	0.7 ^c	0.53	0.70 ^c	0.70 ^c	0.67	0.53	0.67 ^c	1.4 ^c	1.4 ^c	
Styrene to dissolve initiator (g)	11.25	11.25	11.25	11.25	80.0	10.0	10.0	30	30 ^d	
Sty/seed polymer mass ratio	0.125	0.125	0.125	0.125	0.91	0.23	0.23	1.0	1.0 ^d	

Temperature: 80 °C; stirring: 6 pitched blades, 34 mm from reactor floor; BPO, benzoyl peroxide; AIBN, 2,2'-azobis(2-isobutyronitrile).

^a Polymerisation period of 4 h (as opposed to standard 3 h).

^b 30 g used to dissolve initiator prior to addition.

^c Includes 25% water by mass (as supplied).

^d Vinyl acetate used (not styrene).

BPO or AIBN, in only one case being persulfate. In some cases it was desired to pre-swell the seed with monomer before heating was commenced, in which event the desired amount was added at this point. The reactor was then heated to reaction temperature, stirring commenced and nitrogen purging begun. In the cases where the seed had been pre-swollen with monomer, the purging was less rigorous so as not to flush excessive monomer from the reactor. Persulfate was dissolved in a small quantity of water while BPO and AIBN were dissolved in the remaining monomer. When the reactor had attained the desired temperature and been allowed to equilibrate for ten minutes, the initiator and monomer were added. After addition of monomer the reactor would be sealed and three hours of polymerization allowed. The final solids content was determined gravimetrically after most experiments and was almost always found to correspond to a monomer conversion of above 95% (although we note that for obvious reasons the actual final conversion is rarely a morphology determining factor).

Specific variations of this general procedure will be covered as appropriate in the text.

2.6. Characterization

The transmission electron microscopy (TEM) staining procedures are particularly important: uranyl acetate was used to define particle edges, and ruthenium tetroxide to darken the PS domains as detailed previously [30]. For one pair of latices with added poly(vinyl alcohol) an osmium tetroxide stain was used instead, as follows. Cross-linking with osmium tetroxide stops the particle deforming on drying and under the electron beam, together with the localization of the stain to the particle surface better defining the particle edge. A 0.5% solution by weight of 88% hydrolyzed poly(vinyl alcohol) (molecular weight $\sim 25000 \text{ g mol}^{-1}$) was prepared and mixed with an equal volume of latex. This was then left for an hour to allow the system to come to equilibrium. One drop of this solution was then placed in 1 ml of 2% osmium tetroxide solution for ten minutes for cross-linking to occur. A drop of this solution was placed on a Formvar®-coated grid and allowed to dry. This method allowed PVAc particles to be identified, seemingly with very little coagulation or deformation.

Capillary hydrodynamic fractionation (CHDF) was done using a Matec Applied Sciences CHDF 1100, calibrated with polystyrene standards. Size exclusion chromatography (SEC) was carried out using a Waters GPC with RI detection, THF as eluent and polystyrene standards.

3. Results and discussion

3.1. Inverse core-shell polymerization with aqueous-phase initiation

Modelling predicts that polymerization should occur

predominantly inside the PVAc particles rather than in new PS particles when persulfate-initiated polymerization of styrene is carried out in the presence of PVAc seed [26]. Experiment CF:VA-ST1 of Table 3 was a test of this prediction. It is evident from Fig. 1, a TEM micrograph of a typical latex from such experiments, that this prediction was fulfilled: there was negligible secondary particle formation. Of course Fig. 1 does not preclude the occurrence of a small amount of secondary nucleation, but even if this did occur (it is unclear), it would not compromise our conclusion here.

Experiment CF:VA-ST1 used PVAc latex CF:VA1, which has a small size. It can be seen from Fig. 1 that recipe CF:VA-ST1 did not achieve a core-shell structure: the polystyrene domains were on the surface, and on average there were more than one per particle. An analogous recipe but with a larger PVAc seed would be even less likely to produce the desired perfect core-shell morphology, because the PS would have to diffuse further away from the particle surface to accumulate at the particle centre. It was therefore decided to continue working with relatively small PVAc seeds and to address morphology issues. We next examine how changes in reaction conditions affect the morphology of the particles from inverse core-shell styrene–PVAc polymerization. In particular, in order to create core-shell morphology, conditions need to be found such that *all* forming PS migrates towards the centre of PVAc seed particles.

The formation of core-shell morphology involves both thermodynamic and kinetic factors. Thus although styrene is more hydrophobic than VAc, styrene polymerization in the presence of PVAc seed can yield a PS shell around a PVAc core [34,35]. This could only be because the forming PS was too immobile to migrate away from the particle surface. Hergeth and Schmutzler [34,35] reported having achieved this kinetic control by operating under a rigorous starved feed regime, giving a high polymer fraction throughout the second-stage polymerization. In recipe CF:VA-ST1 we

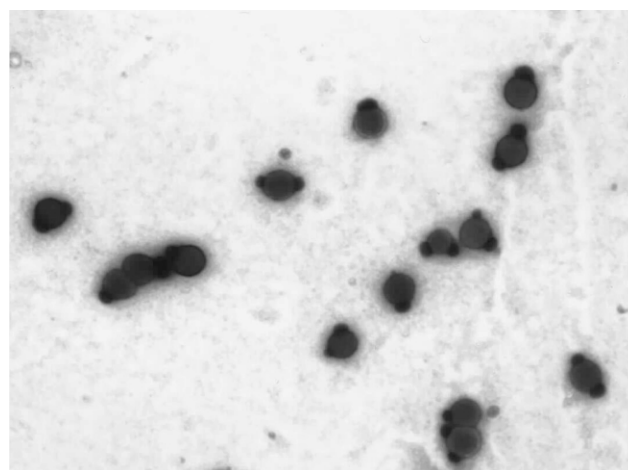


Fig. 1. TEM micrograph of latex CF:VA-ST1 after staining with uranyl acetate and ruthenium tetroxide. This shows the result of using KPS as initiator.

avoided PS shell formation (Fig. 1), presumably because monomer-saturated conditions prevailed for a significant portion of the reaction. However it seems that PS and PVAc mobilities were insufficient to obtain the desired result of a single PS domain per particle.

The starting point for improved strategy was using batch addition of styrene rather than starved-feed addition. Polymer diffusion is thus promoted in two ways: (1) through plasticization, and (2) through minimizing grafting, thus giving minimal branch formation.

3.2. Inverse core-shell polymerization with organic-phase initiation

In recipe CF:VA-ST1, KPS was used as second-stage initiator. Thus a sizeable fraction of the PS chains that were formed must have had sulfate endgroups (as opposed to those chains initiated by chain transfer processes, e.g. to monomer). PS chains with a charged endgroup would tend to be anchored to the particle surface, presumably a significant factor in explaining the results of Fig. 1, in which PS remains in surface-bound domains rather than displacing the more hydrophilic PVAc from the particle interiors. This suggests dispensing with KPS as initiator and instead using an initiator which generates uncharged radicals, suggested by Vanderhoff and co-workers in a different context [36] as a good strategy for avoiding secondary nucleation.

Benzoyl peroxide (BPO) was used first. Now, if polymer initiated by BPO (with no charged endgroups) were to form a shell layer, then considerable surfactant would be needed to keep the system colloidal stable. However in the present case one would not expect the PS chains initiated by BPO to form a shell layer, and the sulfate endgroups on the chains of the PVAc seed should continue to provide colloidal stability for the system. In experiments CF:VA-ST2 and CF:VA-ST3 of Table 3, the BPO concentration was chosen so as to give approximately the same radical flux as KPS in CF:VA-ST1 (note that in emulsion systems, radical flux is not the same as rate of initiation of polymerization [28]). The same PVAc seed, CF:VA1, was used. In each case it was pre-swollen with a portion of the styrene so as to ensure maximum possible mobility of the first PS chains formed. If the first PS chains were to form before the particles had been fully swollen with monomer, then it is conceivable that such highly viscous conditions could trap these initial PS chains at or near the particle surfaces, and that PS domains would then form around these chains; this is avoided by pre-swelling the particles with monomer.

Fig. 2 shows a typical portion of the TEM grid of latex CF:VA-ST2. It can be seen that, as expected, the PS domains are far more embedded than in Fig. 1. However, there is still on average more than one PS domain per particle. In order to ensure that this morphology was not simply a consequence of the styrene amount, the experiment was repeated in CF:VA-ST3 but with more styrene. TEM

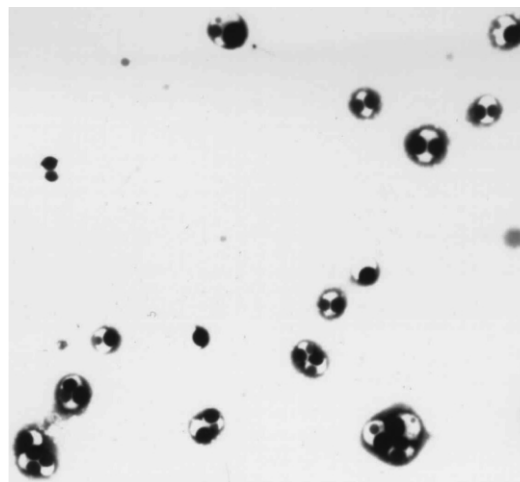


Fig. 2. TEM micrograph of latex CF:VA-ST2 after staining with uranyl acetate and ruthenium tetroxide. This shows the effect of using BPO as initiator.

examination (results not presented) showed that multiple PS domain formation still occurred.

3.3. Effect of PVAc molecular weight

In the experiments to date, inverse core-shell polymerization has always led to particles with multiple PS domains. Now, a single PS domain is thermodynamically favoured. However, once a PS domain is established, it is likely to swell preferentially with styrene and become a centre for further PS formation and these large domains are unlikely to diffuse together and amalgamate. On the other hand, in the experiments of the preceding section there was no obvious reason for multiple PS domains to form in the first place. For a start, PS chains with uncharged, hydrophobic endgroups were generated in monomer-swollen particles, and thus there were no obvious impediments to PS motion. Further, the seed particles were relatively small, meaning that no great distance had to be diffused for a PS chain to reach a PS/styrene-rich domain (by contrast, if large particles had been used, one could well understand multiple-domain formation on this account). Attention is thus focussed on PVAc diffusion, which is also necessary for PS cores to form: PVAc chains must be able to diffuse away from the particle centres to make way for arriving PS.

There is good reason to suspect PVAc immobility as being a major factor in determining morphology in the present systems: PVAc readily undergoes transfer to polymer, which gives rise to branched structures, which can decrease the mobility of PS chains and PS domains. Branching is more prevalent when the concentration of monomer is low, which is relevant because the PVAc seeds were created under starved-feed conditions. Thus it is reasonable to suspect that latex CF:VA1 contained branched and therefore highly immobile PVAc chains. The obvious way of investigating this issue is to use a chain transfer agent (CTA) in PVAc seed preparation (adding a CTA does

not reduce the rate of the branching reaction, but by reducing the polymer molecular weight it reduces the number of branch points per molecule).

PVAc latexes CF:VA2 and CF:VA3 were prepared exactly as CF:VA1 but for the addition of 1-dodecanethiol (DDM, 1.0 and 0.1%, respectively, by weight of monomer Table 1).

The CF:VA1 polymer would not dissolve sufficiently in THF that SEC analysis of it could be carried out, consistent with extensive branching (which can lead to cross-linking). By contrast, polymer from latices CF:VA2 and CF:VA3 could be put through the SEC, suggesting that the extent of branching had been significantly reduced. For CF:VA3 (0.1% DDM) it was found that $\bar{X}_n = 280$ and $\bar{X}_w = 3500$, these being number- and weight-average degrees of polymerization respectively. For CF:VA2 (1.0% DDM) it was found that $\bar{X}_n = 151$ and $\bar{X}_w = 760$, if the data are interpreted assuming linear PVAc chains (in fact some branching must occur).

Inverse core-shell polymerizations were first of all performed with latex CF:VA2 (1.0% DDM). Six polymerizations were carried out with variation in the amount of styrene added in the second stage polymerization: recipes CF:VA-ST4 to CF:VA-ST9 of Table 3. The procedure was the same as that used in the previous section.

Latex CF:VA-ST5 is shown in Fig. 3. Except for a trivial alteration in BPO amount, the only difference between this latex and latex CF:VA-ST2, shown in Fig. 2, is the seed latex. Comparison of these figures shows that making the seed latex with DDM has the desired result of most (or perhaps all) particles containing just one PS domain, consistent with the hypothesis that branched and therefore highly immobile PVAc was previously preventing the formation of core-shell morphology.

Having established the effect of PVAc chain length and architecture on morphology, Fig. 4 illustrates effect of PS amount, by showing results from increasing the styrene to PVAc weight ratio from 0.125 to 1.5. Where the amount of added styrene was small (image A), the PVAc domain

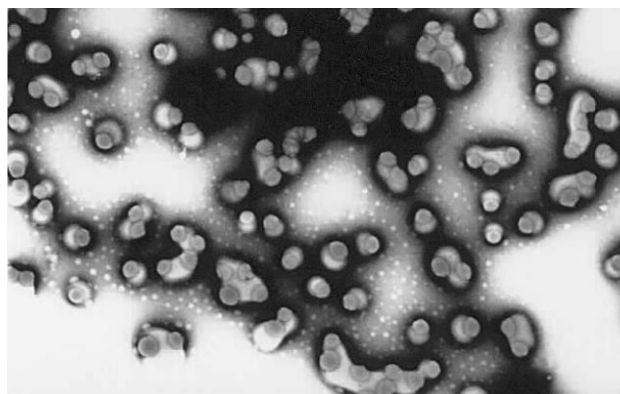


Fig. 3. TEM micrograph of latex CF:VA-ST5 after staining with uranyl acetate and ruthenium tetroxide. This shows the effect of using DDM in making PVAc seed.

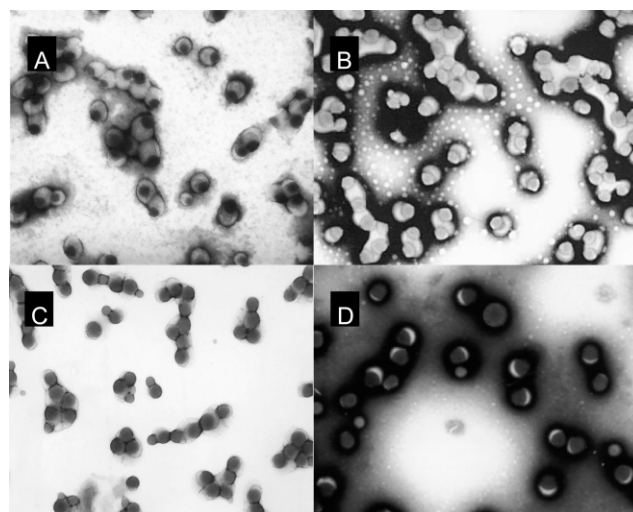


Fig. 4. TEM micrographs of latices CF:VA-ST4 (A, weight of styrene to PVAc in recipe = 0.125) CF:VA-ST5 (B, 0.5), CF:VA-ST6 (C, 1.0) and CF:VA-ST7 (D, 1.5). All latices have been stained with uranyl acetate and ruthenium tetroxide.

appeared to envelop more (although not all) of the PS, but when more styrene was polymerized, an acorn-type morphology was observed (e.g. image D). The situation was even more extreme for higher amounts of PS (latices CF:VA-ST8 and CF:VA-ST9, images not given). Importantly, there was always only one PS domain formed per particle, regardless of the relative amount of PS. Because Fig. 4 suggests that a relatively low amount of PS is most conducive to the PS domains being centrally located, ensuing experiments will tend to follow recipe CF:VA-ST4 in using a low amount of styrene. This will also give PVAc layers of greater relative thickness, making them easier to observe.

While the results of Figs. 3 and 4 show single cores, these experiments use a seed latex in which the PVAc chains are so short that many of their material properties would be extremely poor, thus limiting practical application. Therefore latex CF:VA3 was investigated, it having been made with a lower level of DDM. This was experiment CF:VA-ST10, otherwise essentially the same as CF:VA-ST4. The result is given in Fig. 5. It is evident that there are multiple PS domains per particle, similar to when no DDM was used in seed preparation (Fig. 2). It may therefore be concluded that 0.1% DDM does not give a sufficient increase in PVAc mobility for core-shell morphology to be possible.

3.4. Effect of polystyrene molecular weight

Residual DDM from seed preparation could still be present during the second-stage styrene polymerizations of the previous section, which would reduce the PS chain length, thus making these chains more mobile. One way to test this suggestion is to use a seed made in the absence of DDM, and instead add the CTA only at the beginning of the styrene polymerization. Experiment CF:VA-ST11 was the

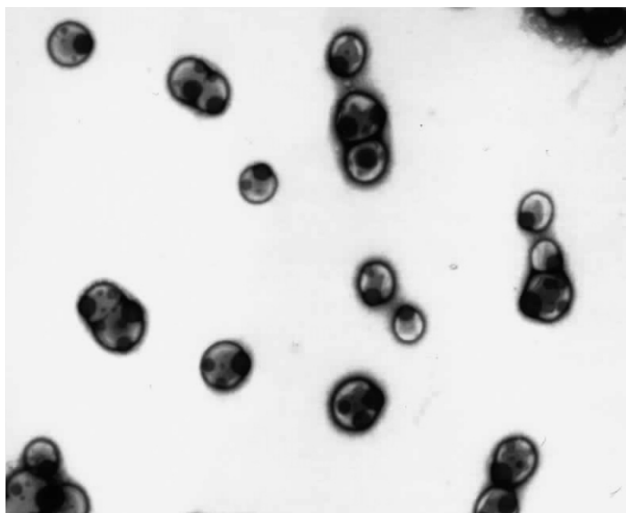


Fig. 5. TEM micrograph of latex CF:VA-ST10 after staining with uranyl acetate and ruthenium tetroxide. This shows the effect of using a lower level of DDM in making the PVAc seed.

same as CF:VA-ST4, except in that latex CF:VA1 (made without DDM) was once again used and DDM was added with the styrene (Table 3). A large amount of DDM was added ($\sim 0.5\%$ by weight relative to the total weight of styrene and PVAc).

Fig. 6 illustrates the morphology of latex CF:VA-ST11. There are several PS domains per particle, much the same as in Fig. 2 (the analogous experiment without DDM in the styrene feed). This illustrates that reduction in PS chain length has not affected morphology. By contrast, when a similarly high level of DDM was used in PVAc seed preparation, only one PS domain per particle was ultimately observed (Figs. 3 and 4). Taken together, these results suggest that formation of multiple PS domains is not a result of lack of PS mobility but only of PVAc immobility. Further, it seems highly likely from the present results that it is not so much PVAc chain length as PVAc architecture that



Fig. 6. TEM micrograph of latex CF:VA-ST11 after staining with uranyl acetate and ruthenium tetroxide. This shows the effect of using DDM only in the second-stage styrene polymerization.

is critical. This can be said because the PS chains formed in the second-stage polymerization should be relatively free of branches. So by adding DDM in experiment CF:VA-ST11, the predominant change brought about would have been that short, linear PS chains rather than long, linear ones would have been produced. Evidently this had no essential effect on morphology, suggesting that the long linear chains were already sufficiently mobile. Thus if seed latex CF:VA1 contained predominantly linear PVAc chains, then these chains should have been sufficiently mobile to enable formation of a single PS domain. Because they were not, this implies that the key change brought about by using DDM in PVAc seed synthesis is one of chain architecture. Although short linear chains diffuse more quickly than long linear chains, in terms of morphology control the more important difference seems to be between linear and highly branched chains, the latter being effectively immobile and more effective at reducing diffusion of other chains.

In summary, for the formation of single PS domains from inverse core-shell styrene-PVAc polymerization, (1) both PS and PVAc must be able to diffuse, and (2) chain architecture can be important in determining morphology.

3.5. Effect of type of organic-phase initiator

Results in the previous section suggested that chain branching arising from grafting is a major impediment to single-domain core-shell formation. This may arise both from chain transfer to polymer in VAc polymerization and grafting of second-stage polymer onto the seed polymer. Further, the issue in the latter event would not just be one of reduced mobility: if PS grafting onto PVAc seed chains occurred, this might prevent formation of single PS domains, because the presence of PVAc-graft-PS would increase the compatibility of PS and PVAc, thereby encouraging the formation of multiple PS domains or giving rise to blending.

In the present case the relatively high temperature (80°C) combined with the use of BPO as initiator gives rise to the possibility of PS graft formation, because the radicals from BPO have a greater tendency to abstract hydrogen atoms from polymer than do the radicals from other initiators such as AIBN [37–39]. This is thought to be due mainly to the increased reactivity of the oxygen-centred primary radical derived from BPO compared with the carbon-centred primary radical derived from AIBN. The benzoyloxy primary radical should preferentially abstract a hydrogen atom from a PVAc chain rather than from a PS chain, not just on the basis of reactivities [40], but also because the concentration of VAc residues is higher. Thus there is the potential for graft copolymer formation (rather than branched PS homopolymer), which may be inhibiting the formation of core-shell morphology. Note that although the experiment of the previous section used a high level of DDM in polymerizing the styrene, this would not have eliminated graft formation, because BPO was still being

used; rather, the DDM would just have given rise to shorter PS grafts.

To eliminate the possibility of PS graft formation and thereby investigate whether the use of BPO was having the above undesirable morphological effect, experiment CF:VA-ST12 (Table 3) was carried out. This experiment was the same as CF:VA-ST4 except in that AIBN rather than BPO was used as initiator. The same weight of AIBN was used (remembering that the reported weights of BPO in Table 3 include a water component). While this will result in a different rate of radical generation, due to the molar amount and the decomposition rate coefficient being different, this rate will not be significantly different, thus enabling the effect of AIBN versus BPO to be evaluated. Note that experiment CF:VA-ST12 used the latex with ‘mobile’ PVAc (CF:VA2), not that with ‘immobile’ PVAc (CF:VA1).

Fig. 7 shows the morphology of latex CF:VA-ST12 (note that the outer “domain” on some particles is not a third polymer domain but is just an artefact of TEM staining). There is no discernible difference from the analogous latex with BPO (Fig. 4A). While this does not preclude that some grafting is occurring with BPO (see below), the current findings show that in the present case the formation of core-shell morphology is not being inhibited by the use of BPO.

3.6. Modification of the surface free energy

3.6.1. Removal of residual peroxydisulfate

The hydrophobicity of polystyrene in relation to poly(vinyl acetate) drives the formation of inverse core-shell morphology. If the difference between the hydrophobicity of PS and PVAc could be increased, then the likelihood of inverse core-shell morphology forming would be increased. Although an organic phase initiator

has been used, there would have been residual peroxydisulfate in the aqueous phase from the VAc seed polymerization which could cause some initiation in the aqueous phase during second-stage polymerization. The chains initiated by these radicals would carry a charged endgroup, and so would tend to be surface-anchored. Once a PS domain formed near the particle surface, other PS chains would congregate in this domain, even ones initiated in the particles by BPO (or AIBN). Hence even a small amount of residual KPS might result in core-shell morphology not being achieved.

One way to eliminate any possibility of initiation by residual KPS during second-stage polymerization would be to pre-heat the seed latex to a high temperature in order to decompose any remaining persulfate. This would also remove some of the peroxides that are thought to contribute to spontaneous ‘thermal’ initiation [41]. However such heat treatment may also have unknown, undesired effects on the system. Therefore a more elegant way to accomplish the deactivation of any residual peroxydisulfate is through the use of sodium metabisulfite, which has the effect of reducing peroxydisulfate in the aqueous phase [42].

Experiment CF:VA-ST13 was the same as CF:VA-ST4 except in that sodium metabisulfite dissolved in water was added to the reactor with seed latex. Twenty minutes were allowed after the reactor vessel had reached the target reaction temperature for the metabisulfite to react with any residual KPS before the styrene and BPO were added to commence second-stage polymerization.

Comparing Fig. 8 (latex CF:VA-ST13) with Fig. 4A (latex CF:VA-ST4), it is evident that the addition of sodium metabisulfite resulted in no change in morphology. Specifically, it did not enable the PS domains to shift away from the particle edges. This indicates that initiation in the aqueous phase during the second stage was not occurring to a significant extent in our systems.

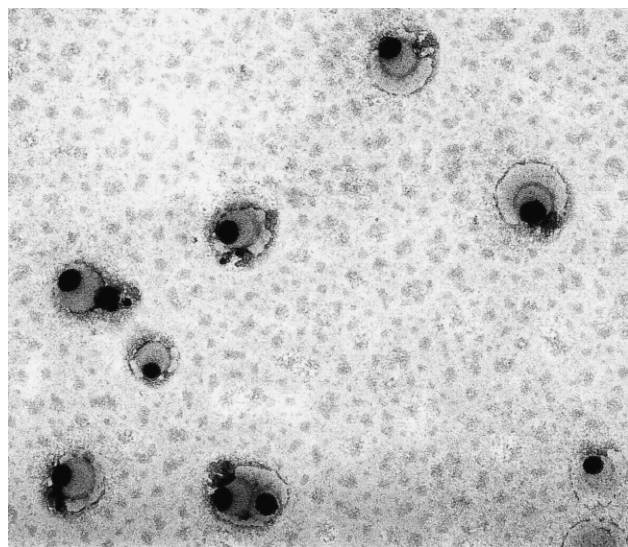


Fig. 7. TEM micrograph of latex CF:VA-ST12 after staining with uranyl acetate and ruthenium tetroxide. This shows the effect of using AIBN as initiator.

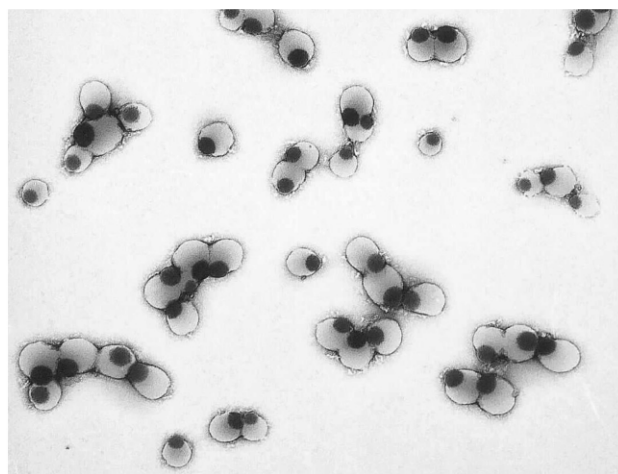


Fig. 8. TEM micrograph of latex CF:VA-ST13 after staining with uranyl acetate and ruthenium tetroxide. This shows the effect of adding sodium metabisulfite.

3.6.2. Use of hydrophilic monomers in the creation of poly(vinyl acetate) seed

The previous section discussed a way of reducing the affinity a polystyrene domain might have for the aqueous phase by eliminating charged initiator-derived endgroups. A complementary strategy is to increase the affinity of PVAc chains for the aqueous phase. This type of approach has been used to force inverse core-shell morphology to occur when the hydrophobicities of the two polymer types would naturally give a conventional core-shell morphology [43]. Charged functionality can be incorporated into PVAc by copolymerization with monomers such as the surfmer Sipomer COPS 1 (Fig. 9) and sodium vinyl sulfonate (SVS).

Recipe CF:VA4 (Table 1) was the same as recipe CF:VA2 (the seed latex with 1% DDM) except in that 1% by weight of Sipomer COPS 1 relative to the total weight of VAc was added with the initial charge of VAc. Adding the comonomer at the beginning like this may have affected particle nucleation. Indeed, if the final particle sizes given in Table 1 are accurate, then latex CF:VA4 had a slightly enhanced particle number; however this would not have been of any significance in subsequent inverse core-shell experiments. Experiment CF:VA-ST14 (Table 3) was the same as CF:VA-ST4 except for the seed latex (CF:VA4 rather than CF:VA2). The resulting latex is shown in Fig. 10, which again shows no departure from the morphology observed when no surface-active comonomer was used in PVAc seed preparation (Fig. 4A): each PS domain still appears to be located at or relatively close to a particle surface. Reasons for this are discussed below.

Seed latex CF:VB1 further explored the effect of changing the interfacial tension by incorporation of a hydrophilic comonomer, sodium vinyl sulfonate (SVS). This recipe is very close to one developed by Vandezande and Rudin [33]. Even though VAc is the predominant monomer, the recipe is reported to give a seed polymer which contains sufficient hydrophilic groups that it is found at the particle surface even after a subsequent VAc polymerization [44]. This can be explained by the fact that the CF:VB1 recipe embodies all the techniques and principles of this paper for encouraging inverse core-shell morphology formation: the use of DDM to enhance the mobility of the seed particle phase, the addition of sodium metabisulfite at the conclusion of the experiment to eliminate residual persulfate, and the use of a hydrophilic comonomer. Other aspects of recipe CF:VB1 derive from its relation to recipes used in the manufacture of surface coatings from butyl acrylate (BA) and VAc. Note that

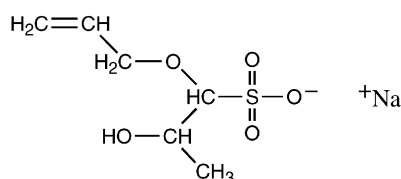


Fig. 9. Structure of surface-active monomer Sipomer COPS 1.

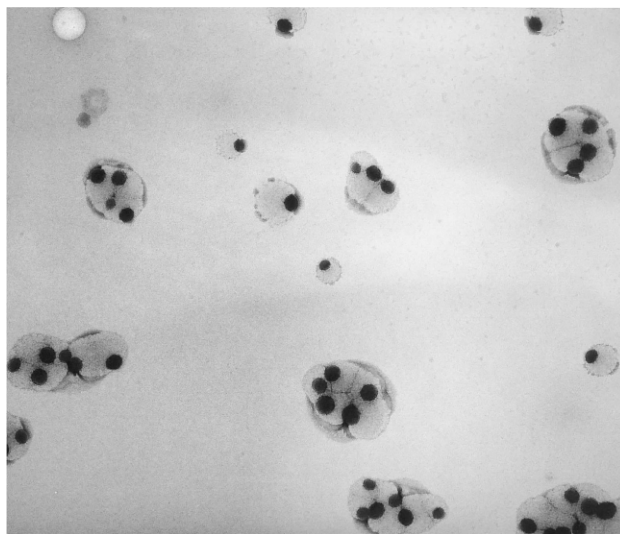


Fig. 10. TEM micrograph of latex CF:VA-ST14 after staining with uranyl acetate and ruthenium tetroxide. This shows the effect of using Sipomer COPS 1 as comonomer in PVAc seed preparation.

having BA as a comonomer would if anything hinder the formation of inverse core-shell morphology, as it is considerably more hydrophobic than VAc. Further, the presence of poly(butyl acrylate) (PBA) will promote the possibility of first-stage branching and second-stage grafting, as PBA is even more prone to chain transfer to polymer than PVAc [40,45].

Another aspect of recipe CF:VB1 is that it is designed to give a relatively large and monodisperse particle size distribution (by the standards of PVAc seeds). The anticipated radius of approximately 150 nm was confirmed by TEM, although it was impossible to be more precise because of deformation in the TEM beam and because no standard was included. This is about double the size of the CF:VA latices (Table 1).

CF:VB1 was used for second-stage polymerization with styrene: recipes CF:VB-ST1, 2 and 3 (Table 3). Fig. 11 shows latex CF:VB-ST1, made with AIBN as second-stage

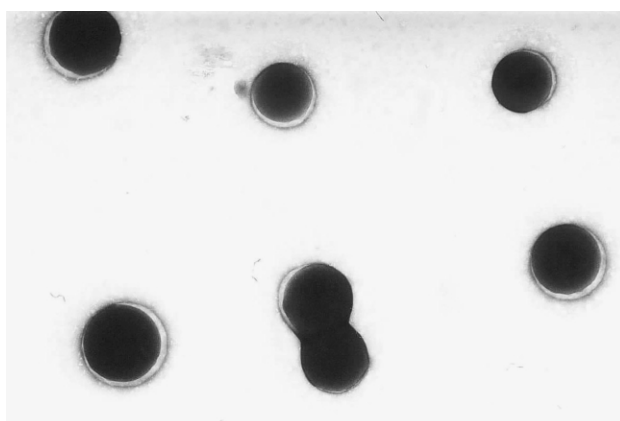


Fig. 11. TEM micrograph of latex CF:VB-ST1 after staining with uranyl acetate and ruthenium tetroxide. This shows the effect of using seed latex CF:VB1 and a relatively large amount of styrene.

initiator and a styrene to seed polymer mass ratio of almost 1:1. Despite its appearance to the contrary, the latex of Fig. 11 really does contain a significant amount of PVAc (the shell is relatively thin but of large radius). It is evident that concentric core-shell morphology is achieved in experiment CF:VB-ST1: there is one PS core per particle, always located very close to the particle centre. The central location is a consequence of the relatively large amount of PS: this domain is so big that it must be centred near the particle middle. Thus the significance of the result of Fig. 11 is that the PVAc-based copolymer always forms a continuous shell layer around the PS domain, even though this domain is large (compare Fig. 11 with all previous images of particles with a single PS domain).

It is likely that the inverse core-shell transformation seen in Fig. 11 arises from the incorporation of SVS into the seed polymer chains: the inclusion of pendant sulfate groups onto PVAc chains seems likely to give highly surface-active chains which would be driven to form a continuous shell layer around a PS domain.

The latex made with Sipomer COPS 1 probably did not give continuous PVAc shells around PS domains (Fig. 10) because not enough of this surfmer was incorporated into PVAc chains. The amount used was low: 1% of VAc weight as opposed to almost 3% SVS relative to the combined weight of VAc and BA in recipe CF:VB1. Secondly, the higher level of DDM in recipe CF:VA4 compared with CF:VB1 would mean even shorter \bar{X}_n in the former latex, making it possible that many chains were simply too short to contain one or more Sipomer COPS 1 units. Thirdly, it is possible that this highly water-soluble monomer partitioned preferentially into the aqueous phase rather than the polymer phase, meaning that not very much of it was incorporated into PVAc chains. Lastly, the allylic nature of Sipomer COPS 1 perhaps means it does not readily copolymerize. Although this issue of incorporation of Sipomer COPS 1 into PVAc chains was not directly investigated, the present results certainly suggest that SVS is more effective as a hydrophilic comonomer.

In the two further inverse core-shell experiments carried out with latex CF:VB1, a much lower ratio of styrene to seed polymer was used in an attempt to form a thicker shell layer than in Fig. 11. Comparing these results (Fig. 12) with Fig. 11, the most striking finding is that the reduction in styrene amount resulted in the morphology shifting from a single PS domain per particle to one of many polystyrene domains. This could possibly be due to decreased PS mobility as a consequence of the particles being swollen with less monomer. However, it is felt more likely that one is actually starting with a ‘fruitcake’ morphology in these systems, and by having a large enough amount of styrene all these small PS domains are able to grow into each other to form a single PS domain. Whatever the reason, it is clear that morphology can depend markedly on the ratio of seed to second stage polymer. However, such an effect is not always observed,

e.g. in Fig. 4 there was always only one PS domain per particle, even as the PS:PVAc ratio was greatly changed.

Another result from Fig. 12 is that the latex made with AIBN appears to have fewer PS domains per particle than that made with BPO. The only obvious explanation for this is that BPO does indeed give rise to the formation of some chains of PVAc-graft-PS, as suggested in Section 3.5.

Finally, comparison of Fig. 12 with Figs. 4A, 7, 8 and 10 shows that while all these latices had similarly low levels of PS to PVAc, only in the present case were there multiple PS domains per particle, whereas in the earlier cases there was only one PS domain per particle. This difference is surprising given all the factors in experiments CF:VB-ST2 and 3 which are designed to promote the formation of single PS domains. One possible reason is that latex CF:VB1 is approximately double the dimensions of the CF:VA latices used until this point. Hence further PS diffusion is required to form a single domain. Another possible reason is the presence of PBA in latex CF:VB1. As explained above, this could lead to more first-stage branching and second-stage grafting, both of which would make multiple PS domain formation more likely.

3.7. Use of a large PVAc latex as seed

Upon reflection it is evident that the inverse core-shell idea of this work is general and is not restricted to particular PVAc latices. Thus it is of interest to carry out experiments with a commercial PVAc latex, not just as a more extensive proof of the chemical concept, but also as a way of creating real-world PS–PVAc core-shell latices with better material properties than the model systems used up to this point (recall the original motivation of this work, see Section 1). The commercial PVAc seed latex which was used had a solids content of 50% (by weight), necessitating a relatively high degree of dilution in inverse core-shell experiments CF:VA-ST15 and 16 (Table 3) in order to ensure colloidal stability after styrene polymerization. In both cases BPO was used as second-stage initiator. The TEM of the latices from these experiments was complicated by the presence of poly(vinyl alcohol) (PVALc), an important ingredient in commercial PVAc recipes. PVALc reacts with ruthenium tetroxide, which therefore could no longer be used as a selective PS stain. Instead osmium tetroxide was used as a PVALc-specific stain, which had the consequence that the PS domains were no longer as clearly observable as up to this point.

Fig. 13 shows latex CF:VA-ST15. The polydispersity of the system is because the commercial PVAc seed was polydisperse. The most important result from Fig. 13 is that no new PS particles were created, i.e., all styrene polymerization was in the seed particles. Further definitive conclusions regarding morphology are unfortunately not possible. Stained poly(vinyl alcohol) chains are evident on the surfaces of the particles, but their internal structure is not revealed by Fig. 13. However, Fig. 13 shows no hint of

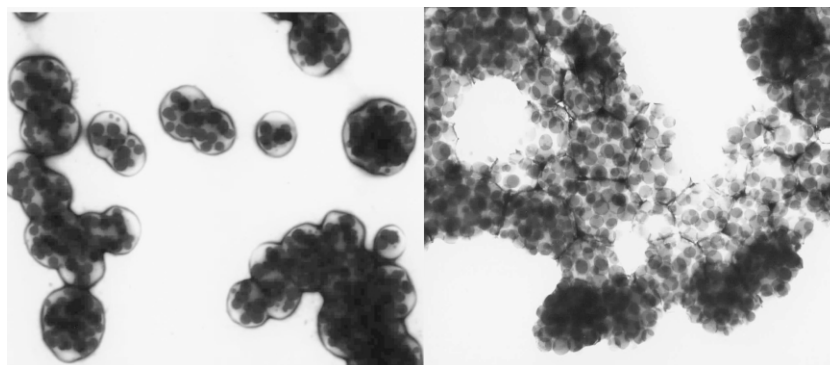


Fig. 12. TEM micrographs of latices CF:VB-ST2 (left) and CF:VB-ST3 (right) after staining with uranyl acetate and ruthenium tetroxide. This shows the effect of using a lower amount of styrene and of type of initiator (AIBN left, BPO right).

acorn morphology and it looks very much like TEM images of the seed latex (not presented). These facts suggest the likelihood that the PS domains are (relatively) central.

Experiment CF:VA-ST16 was the same as CF:VA-ST15 except in that VAc rather than styrene was used as second-stage monomer. TEM examination of CF:VA-ST16 (results not presented) first of all showed that no new particles were visible, consistent with all initiation by BPO being intra-particle (any aqueous phase initiation would result in new particle formation [26,30]). Also of interest were indications that the second-stage PVAc appeared to be located in a single domain in the centre of each particle. This surprising finding—admittedly not conclusively established—is perhaps a result of the poly(vinyl alcohol) or some other ingredient acting to keep the first-stage PVAc chains in shells.

3.8. Further considerations

This paper has relied on TEM to discern particle morphology. Now, a TEM micrograph is not an in situ image of a latex particle: morphology change can occur during TEM sample preparation. For the present work the most obvious concern in this regard is that particles are no longer surrounded by water once they are prepared for TEM. The thermodynamic driving force arising from

hydrophilicity and hydrophobicity of the different polymer phases no longer exists with the water removed. Morphology could thus change as a sample dries on a TEM grid, possibly exacerbated because ruthenium tetroxide staining involved heating a sample to about 40 °C [30]—above the glass transition temperature of PVAc. Methods to overcome these problems include [46,47] drying and viewing the sample at cryogenic temperatures, the use of embedding techniques, and some form of crosslinking of shell polymer. However, each of these procedures presents considerable difficulties in the current context. Therefore one might also consider using techniques other than TEM in order to gain information about morphology of the present composite latices, for example scattering techniques, the soap titration method, or micromechanical analysis of the resulting films.

Surfactant is another consideration which should be mentioned. It was deliberately not added in second-stage polymerizations in order to minimize any role it plays in determining morphology. Nevertheless, different surfactants were used in preparing the various seeds which were used: a mixture of MA 80 and OT 75 in the case of the CF:VA seeds (Table 1), sodium dodecyl benzene sulfonate for CF:VB1 (Table 2), while the commercial PVAc latex contained PVAlc and undoubtedly other emulsifier(s). Obviously it cannot be excluded that these different seed surfactants played a part in giving some of the morphology differences observed in this work, especially given in Section 3.6.2 establishes that polymer–water interfacial tension is important in determining morphology. Nevertheless, we doubt that surfactant was a major factor in any of our results, because it should always reside at the polymer–water interface, and thus it should stabilize whichever polymer is at this interface (as opposed to determining which polymer is there), it should not affect the energetics of PS–PVAc interfaces within particles, and it should not affect PS and PVAc mobility. In short, surfactant stabilizes whatever domains are on the particle surface, as opposed to determining how domains are distributed within a particle. Of course the reasoning here is crude and is undoubtedly oversimplified, but it does suggest that in our experiments at least, the seed surfactant type would not have played a major

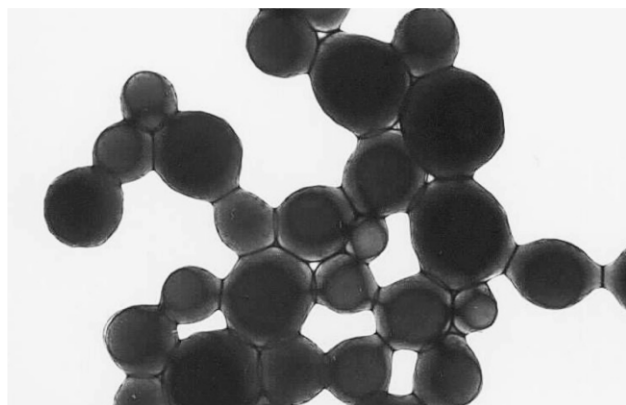


Fig. 13. TEM micrograph of latex CF:VA-ST15 after staining with osmium tetroxide vapour. This shows the effect of using a large PVAc latex as seed.

role in determining morphology. However, this possibility cannot be excluded, and so should be borne in mind in assessing our results.

4. Conclusion

With styrene being so hydrophobic and VAc so hydrophilic, one would anticipate that this system would readily give inverse core-shell polymerization with a single PS domain, but in actuality this is frequently not the case. It would seem that PVAc mobility is the most crucial factor in obtaining a single PS domain per particle, while the incorporation of a surface-active comonomer into PVAc chains is the most significant factor in obtaining continuous shells around PS domains. It is also noteworthy that a particular variable can be of changing impact, for example the styrene to PVAc ratio was seen to be of little morphological significance in one case (Fig. 4) and of much greater consequence in another (Section 3.6.2). Unlike core-shell morphology obtained by second-stage polymerization without inversion, with inverse systems there is no driving force for the hydrophobic core to be in the centre of the particle.

The data of this paper may prove a fertile ground for testing of various theories for latex particle morphology [15–23].

Acknowledgements

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References

- [1] Goulding TM. In: Pizzi A, editor. Wood adhesives: chemistry and technology. New York: Marcel Dekker; 1983. p. 364.
- [2] Niezette J, Desreux V. J Polym Sci, Part A-1 1971;9:3595.
- [3] Lane J, Tabner BJ. Eur Polym J 1991;27:247.
- [4] Lee S, Rudin A. J Polym Sci, Polym Chem Ed 1992;30:2211.
- [5] Lee S, Rudin A. In: Daniels ES, Sudol ED, El-Aasser M, editors. ACS Symp Series—Polymer Latexes—Preparation, Characterization and Applications, Washington DC: American Chemical Society; 1992. p. 234.
- [6] Lee S, Rudin A. J Polym Sci Part A: Polym Chem 1992;30:865.
- [7] Min TI, Klein A, El-Aasser MS, Vanderhoff JW. J Polym Sci, Polym Chem Ed 1983;21:2845.
- [8] Merkel MP, Dimonie VL, El-Aasser MS, Vanderhoff JW. J Polym Sci, Part A: Polym Chem 1987;25:1219.
- [9] Merkel MP, Dimonie VL, El-Aasser MS, Vanderhoff JW. J Polym Sci, Part A: Polym Chem 1987;25:1755.
- [10] Lee DI, Ishikawa T. J Polym Sci, Polym Chem Ed 1983;21:147.
- [11] Kirsch S, Doerk A, Bartsch E, Sillescu H, Landfester K, Spiess HW, Maechtle W. Macromolecules 1999;32:4506.
- [12] Hergeth WD, Schmutzler K, Wartewig S. Makromol Chem, Macromol Symp 1990;31:123.
- [13] Dimonie VL, El-Aasser MS, Vanderhoff JW. Polym Mater Sci Engng 1988;58:821.
- [14] Dimonie VL, Daniels ES, Shaffer OL, El-Aasser MS. In: El-Aasser MS, editor. Emulsion polymerization and emulsion polymers. London: Wiley; 1997. p. 293.
- [15] Sundberg DC, Casassa AP, Pantazopoulos J, Muscato MR, Kronberg B, Berg J. J Appl Polym Sci 1990;41:1425.
- [16] Winzor CL, Sundberg DC. Polymer 1992;33:4269.
- [17] Winzor CL, Sundberg DC. Polymer 1992;33:3797.
- [18] Durant YG, Sundberg DC. J Appl Polym Sci 1995;58:1607.
- [19] Durant YG, Sundberg DC. Macromol Symp 1995;92:43.
- [20] Stubbs J, Karlsson O, Jonsson J-E, Sundberg E, Durant Y, Sundberg D. Colloids Surf A 1999;153:255.
- [21] Gonzalez-Ortiz LJ, Asua JM. Macromolecules 1995;28:3135.
- [22] Gonzalez-Ortiz LJ, Asua JM. Macromolecules 1996;29:4520.
- [23] Gonzalez-Ortiz LJ, Asua JM. Macromolecules 1996;29:383.
- [24] Lovell PA. Macromol Symp 1995;92:71.
- [25] Gilbert RG. Emulsion polymerization: a mechanistic approach. London: Academic Press; 1995.
- [26] Ferguson CJ, Russell GT, Gilbert RG. Polymer 2002;43:4557.
- [27] Morrison BR, Gilbert RG. Macromol Symp 1995;92:13.
- [28] Maxwell IA, Morrison BR, Napper DH, Gilbert RG. Macromolecules 1991;24:1629.
- [29] Fitch RM, Tsai CH. In: Fitch RM, editor. Polymer colloids. New York: Plenum Press; 1971. p. 73.
- [30] Ferguson CJ, Russell GT, Gilbert RG. Polymer 2002;43:6371.
- [31] De Bruyn H. PhD Thesis, University of Sydney; 1998.
- [32] De Bruyn H, Gilbert RG, Ballard MJ. Macromolecules 1996;29:8666.
- [33] Vandezande GA, Rudin A. ACS Symp Ser 1992;492:114.
- [34] Hergeth WD, Schmutzler K. Acta Polym 1985;36:472.
- [35] Hergeth WD, Bittrich HJ, Eichhorn F, Schlenker S, Schmutzler K, Steinau UJ. Polymer 1989;30:1913.
- [36] Sudol ED, El-Aasser MS, Vanderhoff JW. J Polym Sci, Polym Chem Ed 1986;24:3515.
- [37] Huang NJ, Sundberg DC. J Polym Sci 1995;33:2551.
- [38] Huang NJ, Sundberg DC. J Polym Sci 1995;33:2571.
- [39] Huang NJ, Sundberg DC. J Polym Sci 1995;33:2587.
- [40] Britton D, Heatley F, Lovell PA. Macromolecules 1998;31:2828.
- [41] Christie DI, Gilbert RG, Congalidis JP, Richards JR, McMinn JH. Macromolecules 2001;34:5158.
- [42] Perepelitsa VA, Naumova TV. Kinet Katal 1988;29:1252.
- [43] Vandezande GA, Rudin A. J Coatings Tech 1994;66:99.
- [44] Vandezande GA, Smith OW, Bassett DR. In: Lovell PA, El-Aasser MS, editors. Emulsion polymerization and emulsion polymers. London: Wiley; 1997. p. 563.
- [45] Ahmad NM, Heatley F, Lovell PA. Macromolecules 1998;31:2822.
- [46] Shaffer OL, El-Aasser MS, Vanderhoff JW. In: Bailey GW, editor. Proceedings of the 41st Annual Meeting of the Electron Microscopy Society of America, San Francisco: San Francisco Press; 1983. p. 30.
- [47] Subramaniam N, Monteiro MJ, Taylor JR, Simpson-Gomes A, Gilbert RG. Macromol Symp 2000;152:43.