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High solid content latexes

A. Guyot, F. Chu, M. Schneider, C. Graillat, T.F. McKenna[*]

CNRS-LCPP/ESCPE-LYON, 43 Blvd du 11 Novembre 1918, BP 2077, 69616 Villeurbanne, France

Abstract

High solid content (HSC) latexes are of growing interest for many reason, but making this type of product entails many difficulties. Increasing the solid content (fraction of polymer relative to the continuous phase) in a reproducible manner entails the strict control of a complex particle size distribution (PSD). The PSD must be either quite broad, or multimodal in order to obtain solids contents much above 55 or 60 vol%. In addition, the viscosity of a latex is highly sensitive to the PSD near the upper limit of solids content; however, it is still not possible to predict a priori how a complex PSD will effect the viscosity. This article presents an overview of the rheology of concentrated latexes, followed by a discussion of the state of the art in the area of high solids latex production. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Emulsion polymerisation; Concentrated latex; High solid content; Latex viscosity

Contents

* Corresponding author. Tel.: +33-4-72-43-17-75.
  E-mail address: mckenna@cpe.fr (T.F. McKenna).

1. Introduction

Huge quantities of polymer latexes (several millions tons) are produced each year for a wide variety of uses. Most synthetic elastomers such as SBR, NBR, polychloroprene, a significant part of plastics including ABS and PVC, and all water-borne coatings (vinyl and acrylic paints, paper coatings, textile fibres, polymers for non-woven textiles, vinyl adhesives) are produced by emulsion polymerisation. In most emulsion polymerisation processes, the solid content (i.e. volume of particle phase to total volume of the dispersion) ranges from 40 to 55 vol%, the remaining part being water and dissolved compounds. If quality constraints allow us to do so, it is useful to 'pack' as much polymer as possible into a latex (i.e. increase the solid content) because this increases the space-time yield of the reactor, and makes product transport more efficient and less costly. In addition, a reduction in the water content of water-borne coatings allows us to reduce film-formation and drying times. Not only does this make applications more efficient, it also reduces energy load needed in some cases.

One of the main advantages of emulsion polymerisation is that this process yields a latex, i.e. a dispersion of small particles. This type of material is easy to handle because the macroscopic viscosity of the product remains much lower than that of a polymer produced in a bulk process. As we will see later, the solid content at which the viscosity becomes significant depends to a very large extent on the particle size distribution (PSD). However, in the case of typical industrial products, the macroscopic viscosity remains fairly low for solid volume contents up to 55% in the great majority of the cases. However, above this limit the viscosity can increase extremely rapidly as a function of solids content and, if special care is not taken in its formulation, the latex becomes very viscous. In addition, it can become sensitive to shear stress which can be experienced in the reactor itself, or during the pumping or handling of the latex.

For these reasons, it is important to understand the relationship between the viscosity of the latex and its solid content. How we formulate the latex will influence its solid content, PSD and thus viscosity. Thus, before looking at how high solid content (HSC) latexes are produced, we will take a brief look at the parameters governing the viscosity of latexes and colloidal dispersions in general.

2. The viscosity of colloidal dispersions

A certain number of general or review articles on this topic are available in the literature [1–3]. We will present a brief overview of some of the more important points raised in the literature in this section in order to show how the viscosity of a complex latex depends on the solid content and the PSD. Note that for some applications, for instance if we want to make caulking materials or certain types of adhesives that can be applied by hand, maintaining the viscosity as low as possible is not particularly important since the viscosity of the final product is very high anyway, and the process is designed to handle this type of product. On the other hand, there exists a wide range of applications such as coatings and films where it is essential to keep the viscosity as low as possible. Low viscosities are also important when we wish to produce new HSC recipes in existing plants since the agitators, pumps, transfer lines and product handling equipment are designed for low viscosity materials. Although we will discuss a small number of high viscosity applications later on in this article, most of the work published in the open and patent literature deals with increasing the solids content of an emulsion while maintaining the viscosity at a level as low as possible. As we will see later, the PSD is perhaps the single most important parameter in determining the relationship between solids content and viscosity in an emulsion. Correctly

formulating an HSC latex thus depends essentially on identifying the shape of the PSD required, and obtaining it in a given process. We will begin this discussion by looking at experimental work done on the relationship between the PSD, solids content and viscosity, and then turn our attention to an overview of modelling latex viscosity.

In terms of the variation of the viscosity with the solid content, typical behaviour is shown in Fig. 1 for an experimental produced latex, thought to be trimodal [4] (note that this is a multimodal latex—exactly the same type of behaviour can be seen for monomodal latexes as well [5]). A dilute latex will exhibit very low viscosities, and the viscosity, η, will slowly increase as a function of the solid content until it approaches some limiting value. As it gets close to this upper limit of the volume fraction of solids (referred to in this work as ϕ), η begins to increase very rapidly, with a small increase in ϕ leading to huge increases in η. The implications of this upper limit and attempts at predicting it will be discussed later, but it can be pointed out here that the PSD will obviously influence where it is situated.

If we consider the two arrangements of particles in Fig. 2, it is easy to see that the maximum value of ϕ, ϕ_M for the arrangement with R_1 (ratio of large to small particle diameters) will be greater than for the second arrangement. The fact that the small particles fit nicely into the interstices in the configuration to the left means that all of the particles in the system are just barely touching and we fill up a maximum amount of space with particles. In the second configuration, the small particles are larger than the interstices, and thus prevent maximum utilisation of the space in the system. It might be theoretically possible to develop a model to calculate ϕ_M as a function of R, but, as we shall see later, this is very difficult. The most straightforward way seems to be through experimental validation.

2.1. Experimental investigations

A certain number of experimental studies of the influence of bi- and trimodal PSDs on latex viscosity
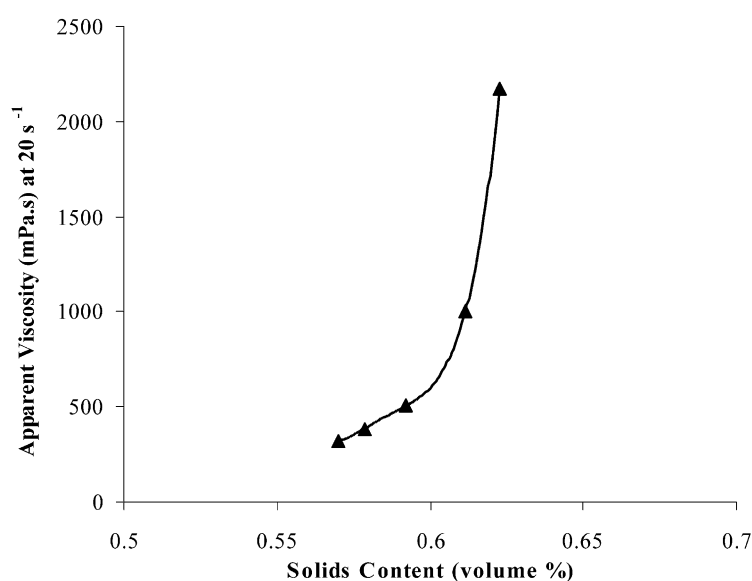

Fig. 1. Variation of the viscosity of a trimodal latex as a function of the solids content (here shown as percent volume of solid phase) at a fixed shear rate of 20 s^{-1}.
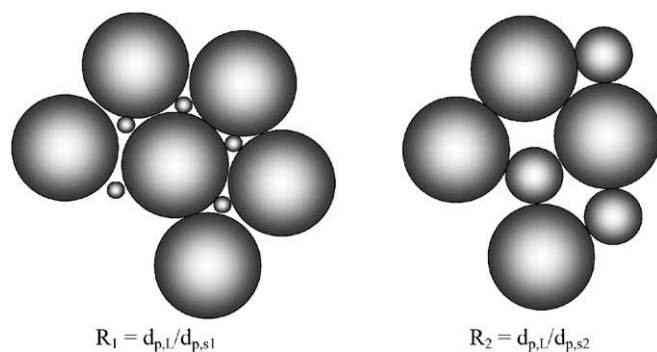
$R_1 = d_{p,L}/d_{p,s1}$ $R_2 = d_{p,L}/d_{p,s2}$

Fig. 2. A 2-dimensional representation of two different 'blends' of particles, where the ratio of large to small particles is such that $R_1 > R_2$.

have been published [4–10]. One of the more comprehensive in these are the studies by Greenwood et al. [5,6]. They used poly(methylmethacrylate) latexes [5] or poly(styrene) latexes [6] to study the effect of the ratio of the diameters of the large ($d_{p,L}$) and small ($d_{p,s}$) particles, and of the relative quantity of each population on latex viscosity. They tested different diameter ratios of $R = d_{p,L}/d_{p,s} = 2.8, 4, 5.7, 7.8$ and 11.1 and PSDs containing 25, 50 and 75% large particles (with respect to total number of particles).

The minimum value of viscosity was obtained for the R in the range $6.37–11.15$ and a volume fraction of 25% small particles. This result is easily explained in the sense that in this range of diameters, the small particles just fit into the interstitial volume between the larger ones. They can thus occupy a maximum volume, while offering a minimum amount of surface contact between the particles. Reducing the size of the small particles further allows us to make small gain in volume fraction. The results in Refs. [8,9] indicate that the minimum viscosity is obtained with a 20% volume of small particles— similar to what Greenwood et al. [5,6] found (note that in these latter works the lowest fraction of small particles considered was 25%). Interestingly enough, Peters et al. [8] showed that a latex with this same volume fraction of large to small particles will have the lowest minimum film-forming temperature at short drying times than latexes with the same composition but different bimodal PSDs.

Kemmere et al. [7] studied a range of solids content (35–44 vol%) for a single value of $R = 2.84$ and different fractions of small (38 nm) and large (108 nm) particles. They found that at 44% solids, the viscosity was lowest for approximately 35% small particles. However at these solids contents, the dependence of η on the relative amounts of small and large particles is extremely weak.

A recent study was published by Chu et al. [10] dealing with a trimodal distribution of particles. The trimodal latexes were prepared by mixing monodisperse latexes with different diameters of 75, 135, and 340 or 477 nm. The latexes were semi-rigid particles made with styrene (65%), butylacrylate (34%) and methacrylic acid (1%). The mixtures were concentrated by evaporation to various solid contents and introduced in a Couette rheometer. Mixtures of two latexes were studied first, and it was confirmed that these bimodal PSD latexes display a minimum viscosity for mixtures containing 20% of the smallest particles. For a trimodal PSD, the smallest viscosity was observed for a mixture containing 80% of large particles (477 nm), 10% of medium particles (135 nm), and 10% of small particles (75 nm). The corresponding viscosity was measured as 1077 mPa s at a shear rate of $20 \, \mathrm{s}^{-1}$. The authors demonstrated that a maximum solid contents of more than 72% can be reached in that zone of composition of a trimodal distribution for a viscosity of 1000 Pa at a shear rate of $20 \, \mathrm{s}^{-1}$. In a further paper, Chu and

Guyot [11] compared the viscosity of bi- and trimodal blends of latexes and showed that there is very little difference between the two for realistic particle sizes.

Schneider et al. [4,12] undertook a study to determine the maximum attainable solid content of blends of two or three monomodal latexes to make bi- and trimodal latexes of butylacrylate and methylmethacrylate. They investigated the relative quantities of small (60 nm) and large (607 nm) particles in a bimodal latex, and of small, medium (340 nm) and large particles in a trimodal latex. The latex that showed the highest attainable solids content (just above 70% solids) was a mixture of 15% small particles, 5% of medium-sized particles and 80% large particles (by volume), although the difference between that blend and a bimodal blend containing 15% small and 85% large particles was very small (which in turn was very close to a trimodal latex 10:10:80, small/medium/large). A summary of these results is presented in Fig. 3, where we can see that a large particle volume fraction of around 80% is optimal in terms of obtaining the highest possible solids content for a fixed viscosity. It is all interesting to note that there seems to be little to no advantage in making trimodal latexes with respect to bimodal ones under these conditions. These results are very close to those of Chu et al. [10,11], even though the ratio of the particle sizes was slightly different in the two works. This suggests that although the ratio of large to small particles is an optimisation variable, it is possible that if the large and small populations are not too similar, it is the relative fraction of the different populations that counts.

While experimental determination of the optimum PSD is a reliable means of determining the 'best' conditions for producing an HSC latex, it is an onerous and time consuming task. It would be ideal to be able to use a model to determine the relationship between the PSD, solids content and viscosity.

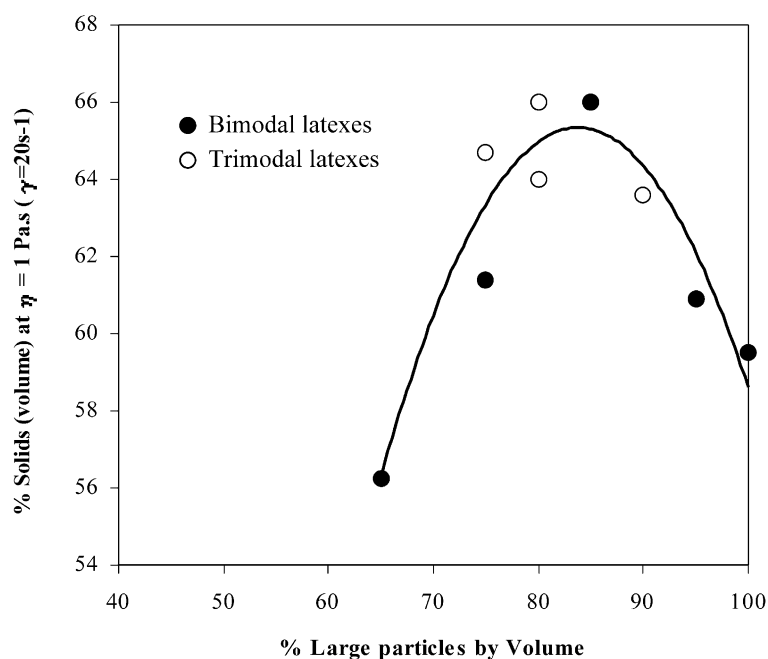Fig. 3. Experimental data from Schneider et al. [4] showing the solid contents of blends of two or three monomodal latexes that correspond to a viscosity of 1000 mPa s at a shear rate of 20 s^{-1}. $d_{p,L} = 607, d_{p,M} = 340, d_{p,S} = 60$. Bimodal blends are always of large and small particles. NB: the curve is inserted only as an indication of the trend and does not have any theoretical significance.

2.2. Modelling of latex viscosity

We will begin by looking at some of the original models for monodisperse dispersions, and then progress on to more complex situations.

The simplest model for highly dilute suspensions is probably the Einstein equation. According to this model, the relative viscosity η_r of a dilute suspension of hard, monodisperse spheres is

$$\eta_r = 1 + [\eta_r]\phi \tag{1}$$

where ϕ is the volume fraction of spheres relative to the total volume of the dispersion, and η_r is the intrinsic viscosity of the continuous phase. Note this expression often appears with $[\eta_r] = 2.5$ (dilute dispersion of rigid spheres in water). In developing Eq. (1), it was supposed that the suspension is dilute enough that there are no interactions between neighbouring spheres, and that dispersion is in a Stokes flow regime. In addition, it is assumed that the dispersing solvent is a Newtonian fluid, that the dimensions of its molecules are negligible with respect to the radius of the spheres, and that no external force is acting on the system (e.g. Brownian motion, gravity).

The Einstein expression is only valid at low to very low values of ϕ. In reality, most of the conditions mentioned earlier are not satisfied, and more complex expressions are needed to predict the viscosity of hard, non-interacting spheres. Nevertheless, as suggested by this model and the results in Fig. 1, the viscosity of a dispersion increases linearly with ϕ up to a moderate volumes fractions of about 20%. However, beyond this point, η_r can increase rapidly as ϕ increases to a maximum volume fraction ϕ_M. The results in Fig. 1 do not show this very clearly because of the scale needed to incorporate the rapid increase in viscosity near the limiting solids content mark. However, once the solids content reaches ϕ_M, the system is blocked and flow can no longer occur (i.e. $\eta_r = \infty$).

Several authors have proposed equations to describe the dependence of the viscosity on the volume fraction. One of the first approaches was developed by Vand in 1945 [13]

$$\eta_r = 1 + 2.5\phi + k_2\phi^2 \tag{2}$$

where k_2 is an adjustable constant. This second term apparently helps to account for particle–particle interactions in semi-dilute, or moderately concentrated solutions.

A very widely used model was subsequently proposed by Mooney [14] three years later:

$$\eta_r = \exp\left(\frac{2.5\phi}{1 - \phi/\phi_M}\right) \tag{3}$$

This equation has the advantage of introducing the term ϕ_M, the maximum particle volume fraction. If one can identify a value for ϕ_M, this expression allows us to relate the PSD to the viscosity. However, as we will discuss later, the maximum volume fraction is very difficult to estimate a priori for real latexes, and for multimodal latexes in particular, which means that in the sense of this equation ϕ_M remains an adjustable parameter.

In 1972, another well-known equation was suggested by Krieger and Dougherty [15] specifically for polymer latexes:

$$\eta_r = (1 - \phi/\phi_M)^{-[\eta]\phi_M} \tag{4}$$

Another slightly different model was proposed by Quemada [16] in 1978:

$$\eta_r = \left(1 - \frac{[\eta]}{2}\phi\right)^{-2} \tag{5}$$

This model has been shown to be valid for silica spheres and for hard polymer colloids (PVC).

The models presented in Eqs. (3)–(5) can all be made to fit specific, relatively well-behaved sets of data for a wide range of monodisperse, non-interacting particles [4,12]. Unfortunately, these two major conditions are rarely applicable to polymer latexes, and it is therefore difficult (if not impossible) to use these and similar models for latex viscosity without using experimental data to estimate k_2, ϕ_M, or $[\eta_r]$. As an example of some of the difficulties encountered, Schneider et al. [4] curve fit the Krieger–Dougherty model to some experimental data and found that values of $[\eta_r]$ ran from 2.7 to 4.8 for latexes that (in principle) had very similar continuous phase compositions. The results are shown in Fig. 4(a), where we can see that the prediction of this model is very sensitive to the value chosen for $[\eta_r]$, especially at HSCs. In addition, Fig. 4(b) shows just how sensitive the model is to the estimates of ϕ_M. It is clearly necessary to have very good estimates of these parameters in order to obtain reliable results from a model relating the viscosity to the solid content. (NB the changes in the parameters reported in this figure are much smaller than the experimental range of the same values noted in Ref. [4].) Note also that this model is not any more sensitive to the others available in the literature.

There are several factors that make it difficult for us to model the viscosity of a latex a priori, some of which include: most colloidal dispersions are not made of neutral, non-interacting spheres; the particles are surrounded by an electronic double layer, the size of which varies as a function of the concentration of a number of species; the PSD is very rarely perfectly monodisperse (i.e. the particles are rarely of the same size); the intrinsic viscosity of the continuous phase is effected by dissolved polymers and surfactants.

Most often polymer colloid particles are not neutral, but rather bear electric charges coming from ionic surfactants and/or initiators. Such products are often employed in the form of salts, so we will be faced with a situation where the positive/negative charges of the ionic species are partitioned on a local scale. The counter ions associated with the electrically charged active species are mostly located in a thin layer around the individual particles. This layer, commonly referred to as the electronic double layer, also includes some constituents of the continuous phase, and therefore tends to be deformable. Thus the double layer can contribute to an expansion of the effective particle diameter to an extent that depends on number of features. These features are named electro-viscous effects.

There are three kinds of electro-viscous effects. The first one, which tends to be very weak, is caused by an asymmetry of the electric field around the particle provoked by the distortion of the double layer when it is subjected to a shear stress. The second one is related to the interactions between the particles when the ionic strength is varied. When the ionic strength is weak the double layer expands. The effective radius of the particle thus increases, and the effective volume fraction occupied by the particles is larger than the geometric one. The third electro-viscous effect can be caused by the presence of polyelectrolytes in the medium surrounding the particles (serum). These components are able to penetrate inside the double layer, and can cause rather significant changes in the interactions between the particles.

In theory, one can partially account for at least the last two electro-viscous effects by replacing the volume fraction ϕ in the previous equations by an effective volume fraction ϕ_{eff} if the thickness of the

(a)

(b)
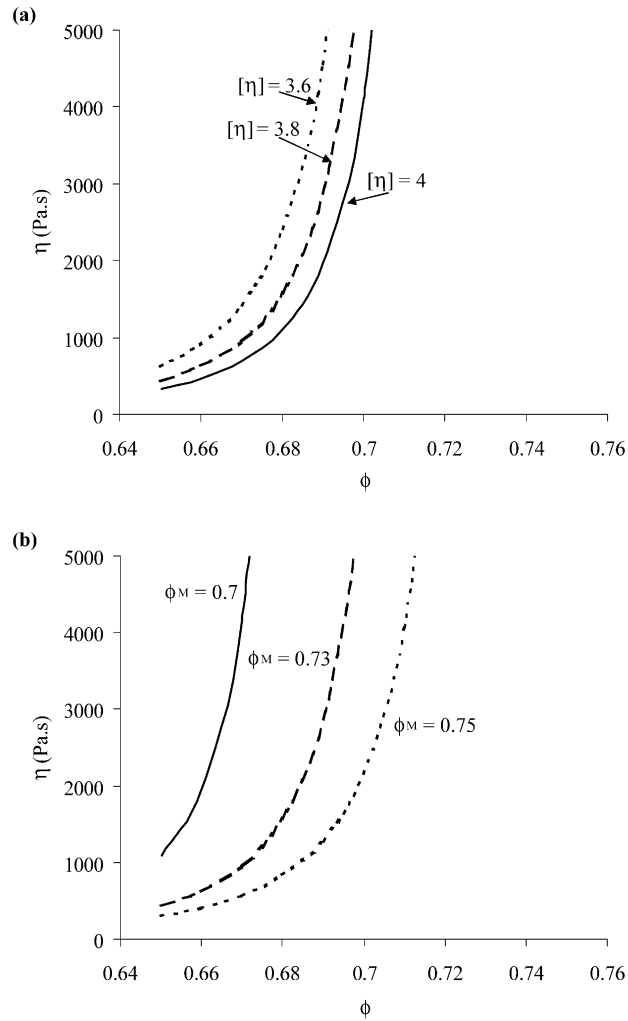
Fig. 4. Sensitivity of the Krieger–Dougherty viscosity model to small variations in the parameters $[\eta_r]$ for a value of $\phi_M = 0.73$ (a), and ϕ_M for a value of $[\eta_r] = 3.8$ (b).

double layer can be calculated

$$\phi_{\text{eff}} = \phi\left(1 + \frac{\kappa^{-1}}{d_p/2}\right)^3 \tag{6}$$

where κ^{-1} is the thickness of the boundary layer. In fact, presence of the double layer and an increase in the effective particle size also explains why the apparent macroscopic viscosity is a function of particle size, even for monodisperse latexes. It is a well-known fact that, at the same solids content, a latex with small particles will be more viscous than a latex with large particles—simply because of the effect of the

relative surface areas. The more surface area we have, the more the particles interact, and the higher the viscosity will be. The double layer, on the other hand, is essentially independent of the particle size, and its thickness can be calculated from [17]

$$1/\kappa = \sqrt{\frac{\varepsilon k_{\mathrm{B}} T}{8\pi e^2 N_{\mathrm{A}} I}} \tag{7}$$

where ε is the permittivity of water (continuous medium); k_{B}, the Boltzmann constant; T, the absolute temperature; I, the ionic strength; e, the charge of a single electron; N_{A} is Avagadro's number. Since the thickness of the layer is independent of the particle size, it will therefore have a relatively larger impact when the particles are small; i.e. a layer of 5 nm will increase the surface area of a latex with $d_{\mathrm{p}} = 50$ nm by 21%, whereas the surface area of a latex with $d_{\mathrm{p}} = 150$ nm will increase only by 6.7%. In addition, if we increase the solids content to a point where the double layers overlap (interpenetrate), we will observe massive destabilisation of the latex, i.e. the value of κ will also determine in part a value of ϕ_{M}. In order to understand how this can influence the solids content of a latex, let us consider the following example.

In practice, the ionic strength I of a latex is in the order of 10^{-3}–10^{-2} mol/l, which corresponds to double layer thickness of 9 and 3 nm, respectively (strictly speaking, we should also account for ionic species absorbed on the surface of the latex, but we will content ourselves with a simplified example here). The curves in Fig. 5 show the evolution of the distance δ between two particles for particles of 100, 250 and 500 nm as a function of the solids content [12]. The horizontal lines in this graph represent two times the double layer thickness for each of the two ionic strengths considered. When the curves $\delta(\phi)$ intersect the line $2/\kappa$, we will observe interpenetration of the double layers and see either of the latex, or a sharp increase in the latex viscosity. This phenomenon is clearly more important for small particles at a given solid content than for larger ones. This calculation shows that the interpenetration point for the 100 nm particles is at a solids content of 38% for $I = 10^{-3}$ mol/l, whereas it is equal to 57% solids for much larger particles.

Several parameters can influence the viscosity in this manner. One of the more important is the pH of
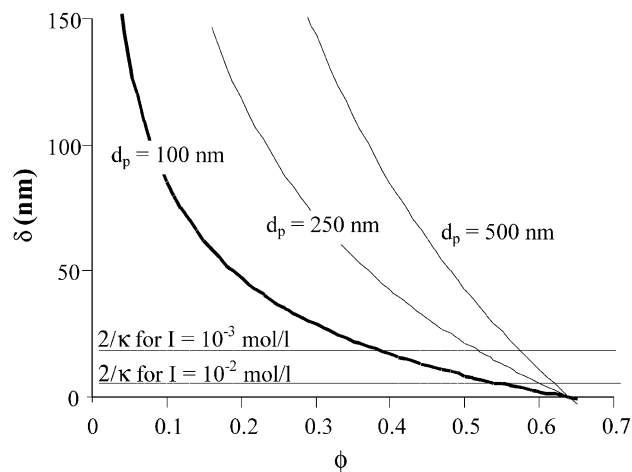

Fig. 5. Distance between particles (δ) for different particle diameters and ionic strengths as a function of the solid content ϕ.

the system when the formulation contains carboxylic acids. Increasing the pH leads first of all to an increase in the ionic strength of the latex, which contributes to a contraction of the electronic double layer, which has a certain influence on the viscosity. Secondly, and more importantly, at a pH over the pK_a (e.g. >5 for acrylic acid) any carboxylic acid chains that are on the surface of the particles will be in their ionised state and therefore extended. This unfolding of the chains at high pH leads to an effective increase in the volume fraction of the particles, which, at HSC can of course provoke a large increase in the viscosity. Similarly, if a particle contains a polymer capable of absorbing water then its effective volume will increase.

It is also possible that hydrosoluble polymers could increase the viscosity of the continuous phase, and thus of the latex. These polymers could take the form of chains polymerised in situ, or non-ionic surfactants.

Even in the event that we can accurately predict the effective particle volume, one of the major problems that remains is obviously to be able to predict the maximum volume fraction ϕ_M. Only two purely theoretical values available are that of the maximum packing of monodisperse spheres in an infinitely large container and for a single sphere in a container. In the case of monodisperse spheres in a face-centred cubic packing arrangement, $\phi_M = 0.74$. However, if the particles are packed in this manner, the latex cannot flow or the particles cannot move with respect to each other, and a value of $\phi_M = 0.74$ should correspond to an infinite viscosity (for perfectly monodisperse particles!). On the other hand, a single sphere occupies only 52% of the volume of the corresponding cube with a side equal to the particle diameter. Therefore, the value of ϕ_M for randomly packed monodisperse spheres is in between these two values. A number of attempts have been carried out in order to rigorously calculate ϕ_M for randomly packed spheres, and although convention dictates $\phi_M = 0.64$ for such a system, values up to 68% have been mentioned [18], but again the possible flow of this system was not considered.

Estimates of the maximum fraction of solids that can be packed in a monodisperse latex have been made, and, as one might expect, have been shown to be dependent on the shear rate [19]. At low shear rates, a latex is generally Newtonian when the flow regime does not show a yield point, and therefore the viscosity is independent of the shear rate. As the shear rate increases, the viscosity begins to decrease, and the latex exhibits a shear-thinning behaviour until it reaches either a point value or an initial plateau at a given shear rate. The value of viscosity at this lower limit is the result of a kind of organisation of the particles in each plane of flow. In the case where a plateau is reached, the latex will behave like a Newtonian liquid and then decrease to a second lower value as the particles are rearranged in a different manner. The solid content where these points occur will depend to a certain extent on both the PSD and the shear rate. For a fixed PSD, Talbi [19] found that maximum volume fractions (i.e. where the viscosity tended to infinity) were around 0.64 for the low shear rates, and a value of ϕ_M for a second plateau of the viscosity dependence on the shear rate near 0.71.

In a slightly different vein, Bicerano et al. [3] claim that ϕ_M can be used as an approximation for what they call the viscosity percolation threshold (ϕ^*) since they prefer to use percolation theory to understand the influence of particle size, shape and concentration on the viscosity of a dispersion of particles. ϕ^* is said to be the volume fraction of particles at which the particles in the dispersion are 'stuck' in place. They argue that viscosity should be modelled with respect to the reduced volume fraction of particles (i.e. the term ϕ/ϕ_M that appears in some of the equations earlier) rather than just ϕ. Ideally, it would be interesting to be able to attach a real physical significance to this term to help understand the limits of solid content beyond which we cannot hope to go if we wish to avoid problems with high viscosity. From the point of view of the viscosity of a dispersion of particles, and in particular

of a multimodal latex, it is intuitively obvious that the combination of particle sizes that provides the highest value of ϕ_M will also lead to the lowest viscosity for a fixed value of ϕ. For this reason, it is interesting for us to identify a value of ϕ_M for our multimodal latexes, and to find a means of quantifying the relationship between the PSD, polymer concentration and ϕ_M.

As we can see from the equations presented earlier, the value of the macroscopic viscosity of a concentrated dispersion will be a strong function of the particle volume fraction at a given shear rate. However, what is not clear from these models is it will also be a function of the PSD, and eventually particle morphology.

If one considers a bimodal latex composed of one perfectly monodisperse population of large particles at a solids content near ϕ_M for this population of spheres, it is easy to imagine that we could increase the solids content by adding a second population of particles small enough to fit in the interstices between the larger ones. Another possible means of increasing the maximum volume fraction is to have deformable particles instead of hard spheres, as can be the case for liquid droplets that can adopt polyhedral geometries. We will not consider this last option in what follows as it is of little interest in terms of polymer colloids.

Not surprisingly, little work has been done on modelling the viscosity of polymodal dispersions, especially given the difficulty associated with the need for ϑ_M the expressions presented earlier. This problem is definitely very complex, much more so than in the case of monodisperse latexes, where there were already an infinity of solutions for random packing.

Talbi [19] tried to apply Quemada's equation (Eq. (5)) to a mixture of two monodisperse latexes, one of large rigid spheres of polystyrene with a particle diameter, $d_p = 400$ nm, and the second of smaller and softer particles of a styrene–butadiene latex ($d_p = 80$ nm). The approach was simply to replace ϕ_{eff} in Eq. (5) by

$$\phi_{eff} = \left[k_s{}^3 (\phi_s/\phi) + k_L{}^3 (1 - \phi_L/\phi) \right] \tag{8}$$

Here $k_s = r_{s,eff}/r_s$ and $k_L = r_{L,eff}/r_L$, where $r_{s,eff}$ and r_s are the effective and geometric (i.e. not counting the electronic double layer) radii of the small spheres, respectively. $r_{L,eff}$ and r_L are the analogous quantities for the large sphere. Talbi [19] indicates the methods used for estimating the factors k taking into account the electro-viscous effects.

Farris [20] also presented a method for modelling polymodal dispersions. His model was designed for large particles (> 1 μm), but can be applied to any mixture of monodisperse particle populations. For a distribution of three populations of large (L), medium (M), and small (S) particles, the approach is as follows:

1. Define a series of volume fractions. The population of small particles (V^S) is first considered, with a volume fraction ϕ_S defined by the volume of small particles by the sum of the volumes of the continuous medium (V^c) plus that of the small particles. Then, ϕ_M is defined as the volume comprised of medium-sized particles (V^M) divided by the sum of the volumes of the small and medium particles and the continuous phase. Finally, ϕ_L is defined in a similar manner, i.e. $\phi_S = V^S/(V^c + V^S)$, $\phi^M = V^M/(V^c + V^S + V^M)$, and $\phi_L = V^L/(V^c + V^S + V^M + V^L)$.
2. Farris then considers a function $H(\phi)$ which is the relative viscosity versus the volume fraction of a

monomodal latex. For a trimodal latex, the relative viscosity is defined as

$$\eta_r = H(\phi_S)H(\phi_M)H(\phi_L) \tag{9}$$

In this representation, we can use any model we wish for each of the monodisperse populations, e.g. Mooney's equation.

In the case examined in Ref. [20], the particle populations were very large (several micrometers) with respect to the size usually met in emulsion polymerisations (tens to hundreds of nm). Furthermore, it was assumed that the particles did not interact, and the author used a viscosity function independent of the particle size. It was further assumed that the ratio between the diameter of the different particle populations is infinite. If all of these assumptions are valid, then Eq. (9) can be used to predict the minimum reduced viscosity as a function of the PSD. The results presented in Ref. [20] were as follows:

- For a bimodal distribution: 28 vol% of small and 72% of large particles
- For a trimodal distribution: 12% (v/v) of small, 28% of medium, and 60% of large particles.

Schneider et al. [4,12] attempted to adapt Farris's model in the case of bimodal emulsions, and showed once that it could be done by fitting parameters such as $[\eta]$ and ϕ_M to data sets, but, as mentioned earlier, we have no means of estimating these parameters ahead of time. However, Greenwood et al. [6] also attempted to fit their data using the Farris model, the Kreiger–Dougherty expression for the viscosity (Eq. (4)) and a value of $\phi_M = 0.71$ for a bimodal latex of PMMA spheres (25% v/v small particles, $R = 4.76$, $d_{P,s} = 78$ nm). The model seemed to give an accurate fit for solids contents of up to 20%, but beyond that point severely underestimated the experimental data, once again demonstrating the inability of existing models to describe the evolution of the viscosity of multimodal PSD latexes.

Another approach was developed in a series of papers by Sudduth [21–23] who presented and validated a generalised model to predict the viscosity of suspensions of spherical particles in a continuous medium

$$\ln(\eta_r) = \left(\frac{[\eta]}{k}\right)\left(\frac{1}{\sigma - 1}\right)\left\{\frac{1 - \left(1 - \dfrac{\phi}{\phi_M}\right)^{\sigma-1}}{\left(1 - \dfrac{\phi}{\phi_M}\right)^{\sigma-1}}\right\} \tag{10}$$

where σ is a 'particle interaction coefficient'. Sudduth [23] curve fit previously published data to estimate the particle interaction parameter σ:

$$\sigma = 773.6/D_1 + 0.750 \tag{11}$$

This model can be reduced to the Krieger–Dougherty model for $\sigma = 1$, or to the Mooney equation for $\sigma = 2$. As with some of the models presented earlier, Eq. (10) requires a value of the maximum packing fraction. Sudduth used previous studies to elaborate a model for calculating ϕ_M for a multimodal distribution of n monodisperse particle populations [22]

$$\phi_{n,M} = 1 - (1 - \phi_L)^n \tag{12}$$

where n indicates the number of populations to be considered and ϕ_L is the maximum packing fraction for a latex made up of the large particles. For instance, if $\phi_L = 0.639$ (Sudduth's value for dense random packing), then the ultimate packing fraction for a binary distribution would be 0.87. And if we consider a binary blend of particles that are loosely packed (i.e. $\phi_L = 0.589$), then $\phi_M = 0.831$. Note that this description assumes that the second population is small enough to fit into the interstices of the larger ones, it is simply intended to define an upper limit. Although the fact that we still need to know whether the particles are loosely or densely packed, and what value ϕ_L will take means that this is not truly a method for estimating ϕ_M a priori.

Nevertheless, Sudduth [22] went on to develop a model that allows us to calculate the packing fraction based on knowledge of the PSD. He defined particle size ratios D_x for a multimodal distribution in the following manner

$$D_x = \frac{\sum_{k=1}^{n} N_k D_k^{\,x}}{\sum_{k=1}^{n} N_k D_k^{\,x-1}} \tag{13}$$

and showed that the ratios D_5/D_1 and D_4/D_2 were useful in determining the packing factor for a complex, but well-characterised blend of monodisperse populations (see Section 3 for comments on characterisation). He goes on to develop an algorithm that allows one to calculate the viscosity of binary and ternary blends based on Eqs. (9)–(13).

Finally, Schneider et al. [4] recently discussed a means of at least identifying the PSD associated with the highest possible value of ϕ_M. This method, illustrated schematically in Fig. 6(a), consists of pre-defining a PSD of interest (size of particles, relative proportion of each size) and 'dropping' the particles one by one into a 'box'. A random number generator is used to choose a particle to be dropped, and another generator chooses a set of $x-y$ coordinates from where the particles will be dropped. An algorithm calculates where the particles will fall, and, if they come into contact with one or more particles, whether or not they will be displaced, in what direction the displacement occurs, etc. For more details, the reader is referred to Refs. [4,12]. The weakness of the algorithm defined here is that it does not allow us to directly calculate ϕ_M. Because the particles cannot move once they come to rest, certain 'dead spaces' are created in the box that become inaccessible to newly falling particles. This is illustrated in Fig. 6(b), where we can see that a medium-sized particle has come to rest on three larger ones. If we were dealing with a trimodal latex, the small particle shown in Fig. 6(b) would also come to rest on top of the larger ones, even though it could fit in the space formed below the three large particles. Nevertheless, these authors demonstrated that by letting enough particles fall into the box, they could calculate a limiting particle volume fraction, termed ϕ_{lim}. It was then shown experimentally the PSD that gave the highest value of ϕ_{lim} corresponded to highest possible solid content for a given viscosity. This plainly suggests the PSD that gives the highest value of ϕ_{lim} will also give us the highest value of ϕ_M. However, more work needs to be done in this direction if we hope to apply this type of approach to the direct calculation of ϕ_M.

Despite these difficulties, these last three examples of how to model the relationship between the PSD and viscosity show that if we wish to maximise the solid content while minimising the viscosity, it is essential to control the PSD. And in order to control the PSD, it is necessary to be able to measure it.

Other points that should be retained here include the intrinsic viscosity. This quantity appears in a

(a) Calculation of ϕ_{lim} for a given PSD.

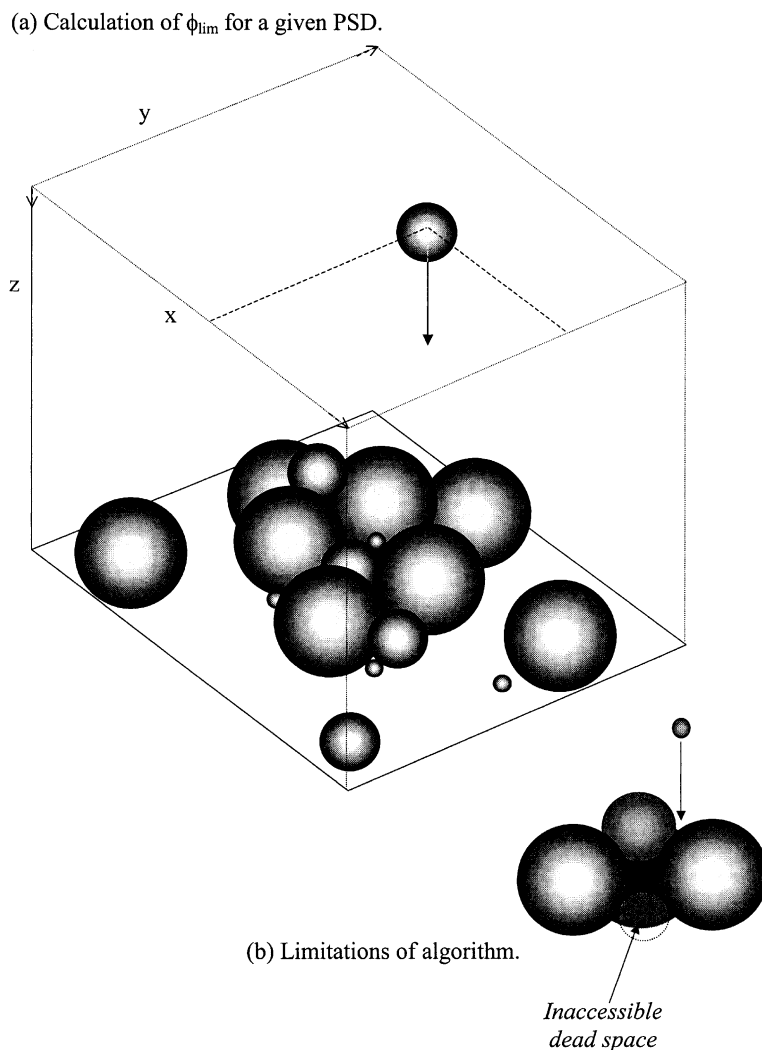
(b) Limitations of algorithm.

*Inaccessible
dead space*

Fig. 6. Schematic representation of the model proposed by Schneider et al. [4] to calculate the limiting volume fraction of particles for multimodal PSDs.

number of the correlations found in the literature, and it is logical that the viscosity of the continuous phase should have an influence on the macroscopic viscosity of a polymeric latex. Although it is common practice (or at least, so it seems) to take $[\eta_r] = 2.5$, Schneider et al. [4] showed that curve fits of their data to the Kreiger–Dougherty model (Eq. (4)) yielded values of $[\eta_r]$ closer to 4 for their latexes. Note that the latexes studied by Schneider et al. contained 2–3% by mass of surfactant, and acrylic acid and methyl methacrylate as comonomers. It is, therefore, reasonable to assume that a small amount of dissolved polymer/oligomer is present in the aqueous phase of their latexes. Unfortunately, the need to dilute the serum in order to measure the intrinsic viscosity made it impossible for them to clearly identify an experimental value of $[\eta_r]$.

In addition, non-ideal behaviour such as the formation of coagulum can also influence the viscosity. If

a number of particles agglomerate to form macroscopic coagulum, a fraction of the continuous phase is trapped inside these structures, and the effective volume fraction of the solid phase increases [24]. Such agglomerates are also not necessarily spherical, and it has been shown that they can in fact perturb the local flow fields and increase the viscosity (however, it is unlikely given the range of interfacial tension typical of emulsion polymerisation that this last problem is significant for latexes).

3. Evaluation of the particle size distribution

The PSD is an important characteristic for all dispersed media, such as emulsions, dispersions, powders as it influences, not only the rheological behaviour, but also the optical properties and the film-forming process. Of course, in the context of this review, we will only be interested in the relationship between the PSD and latex rheology. As we have seen earlier, the PSD is a key characteristic in determining the macroscopic viscosity of a latex, especially as the solids contents increase to their upper limits. It is, therefore, clear that a reliable estimate of the PSD is needed in order to correctly formulate HSC latexes. This topic has been discussed in a number of papers in the open literature [25–34]. The last two of these articles, by Elizalde et al. [33] and Schneider and McKenna [34] present recent experimental evaluations of different commercially available devices, and discuss the relative merits of microscopy, light scattering (static and dynamic), and separative flow devices (e.g. capillary hydrodynamic fractionation, CHDF; field flow fractionation, FFF) among others. The general conclusions from these two studies was that monodisperse samples were easily characterised by all techniques, but that bi- or trimodal distributions could be problematic if it is not possible to use transmission or scanning electron microscopy. Microscopic techniques are probably the most accurate methods of determining the PSD, and are often considered as a reference, due to their reliability. However, because of the high cost of instrumentation and analysis, microscopy cannot be used as a routine measurement. Nevertheless, it is highly recommended that it can be used occasionally to verify measurements obtained with more simple methods.

In terms of devices using light scattering, and/or separative methods, the question of measuring the complete PSD for complex latexes is more delicate given the complications of trying to interpret data relating to the different particle sizes at the same time. Techniques based on multiangle variable light scattering (to a lesser extent) and on separative methods seem to yield the results closest to the expected reference values. Methods based on static light scattering methods were much less satisfactory in terms of estimating the particle size and PSD than were those employing dynamic light scattering.

Separative techniques such as FFF and CHDF tended to perform better than directly injecting a sample into a multiangle dynamic light scattering device because they allow us to separate the particles according to their size, and the particles are measured at the outlet of a column or cell on a one-by-bases. In principle (with the caveats issued earlier), a multiangle scattering technique is the most efficient technique to use at the outlet of a device because an absolute measurement of the whole PSD is possible, and, through a judicious choices of angles, one can measure a wide range of particle sizes. Although it should be possible to quantitatively analyse the whole PSD, some limitations exist due in part to slow detection dynamics. In order to determine the full PSD, each population must be detected at each detection angle. Also, since the intensity of light scattered by small particles is very low in comparison to the intensity of larger particles, and the intensity collected at small detection angle is stronger than that at high detection angle it can be difficult to find the minimum concentration of the suspension that allows

the detection of all populations at all detection angles, with no saturation of the detectors. Working with more than three detection angles may provide better results, since detection angles can then be selected such that complete signals are obtained.

However, even if these techniques allowed us to measure the average particle size of two populations in a blend, they did not provide reliable estimates of the proportions of each population—a major difficulty in rheology studies because errors of 5–10% in terms of the volume fraction of each population can have a significant impact on the macroscopic viscosity of a latex [4]. This problem should be kept in mind during the following review: on the one hand, we need to correctly formulate a latex to obtain a well-defined PSD in a highly reproducible fashion; and on the other hand, it is next to impossible to obtain an exact measurement of the full PSD!

4. Direct synthesis of high solid latexes

In this text, we will take HSC to mean latexes having a volume fraction higher than 60%. Of course, this is an entirely arbitrary limit, but experience dictates that certain precautions or special steps need to be taken at approximately this limit, if we want to increase the solids content. In addition, the viscosity of the latex begins to become sensitive to the solids content at about this point as well. While reading this and Section 4.1, try to keep in mind the difficulty associated with predicting the relationship between the PSD and the viscosity, as well as the problem we have in determining the full PSD of complex latex dispersions. This will help put the difficulty of the task at hand in perspective.

Recall that not only the PSD, but also the intrinsic viscosity of the continuous medium and the ionic strength are also very important factors in determining the relationship between the solid content and viscosity of an emulsion polymerisation. Thus the choice of initiator and stabilisation system, the use (or not) of pH buffers, the pH, the type of monomer, etc. will all play important roles in how easy of difficult it is to produce HSC latexes.

4.1. Academic studies

4.1.1. Via emulsion polymerisation

There are not a significant number of papers available in the open literature that describe the synthesis of high solid latexes, and most of the work published on this subject seem to be in the patent literature, which will be reviewed in a subsequent section.

To the best of our knowledge, the first paper to focus on producing HSC latexes was published by Kuo and Chen [35], who studied emulsion polymerisation using polymeric emulsifiers. The latexes obtained were shown to have a bimodal PSD, with small particles from 50 nm in diameter, and large particles with a broad distribution with diameters larger than 1 μm. It was suggested that these large particles were aggregated as shown by experiments of pyrene solubilisation and fluorescence.

Another study was published by the group of Asua [36,37] on the terpolymerisation of vinyl acetate–methyl methacrylate–butyl acrylate (VAc, MMA, BA) to produce high solid latexes (they defined high solids as being in the order of 55%). It was found that there was a trend for the accumulation of vinyl acetate during the process, and that secondary nucleation took place resulting in bimodal PSD. The authors observed that secondary nucleation increased upon increasing the amount of initiator and emulsifier, as expected. However, increasing the feed rates of initiator (total amount remained constant)

also lead to changes in the number of particles. Unfortunately, no clear trend emerged for this data, as increasing the feed time (i.e. decreasing the rate of addition) from 4 to 5.5 h, lead to a slight decrease in the number of particles (N_p), but going from 5.5 to 6 h lead to an increase in N_p by a factor of 2. This suggests that the nucleation of particles in situ can be a delicate point, especially in the presence of water-soluble initiators like VAc and ionic initiators such as the potassium persulphate used in Ref. [36]. An optimal strategy for obtaining a homogeneous terpolymer composition was developed, but no attempt was made to control the PSD as the authors' principle concern was to control the copolymer composition under realistic conditions rather than to increase the solids content above 55% volume. Another study from the same group on the seeded semi-continuous copolymerisation of styrene (Sty), 2-ethylhexylacrylate (EHA) and methacrylic acid (MAA), in which the effect of the type and the amounts of emulsifier on the final properties of the latexes were analysed. It was observed that when large amounts of emulsifier were used, the PSD becomes broader and the viscosity of the latexes decreased [38].

Although the solids content was limited to 50 vol% polymer, a recent study by Chern et al. [39] is pertinent since it deals directly with the issue of how to create a bimodal PSD. The authors studied the emulsion polymerisation of a mixture of 95 mass% butyl methacrylate (BMA) and 5% MAA, with a seed of the same composition with a diameter of 212 nm. The emulsifier system to produce the seed was a mixture of SDS and a non-ionic NP 40. The initial charge was a mixture of water, buffer and seed latex. An equal volume of monomer was slowly fed together with a small amount of initiator (sodium persulfate) solution. A charge of surfactant was added after a given time t_s, in order to cause a secondary nucleation. A two-level factorial design was used in which the variables are the concentration of the seed particles (2–10% based on the total monomer), the amount of SDS injected (1–3% based on total monomer) and the time t_s (5–35 min). The theoretical size which should be obtained at the end of the process assuming the number of particles initially introduced by the seed was kept constant (neither nucleation of the second crop of particles nor flocculation) was calculated. They also calculated the fraction of monomer fed to the reactor that did not participate in the growth of the seed latex, P, and found that the greater the value of P, the greater the probability of generating a second set of particles. This parameter is related to the total surface area of the seed A_s and proportional to $A_s^{1/3}$. In general, if $P > 70\%$, the final latex will be bimodal. According to their analysis, the seed concentration is the most important in determining the broadness of the PSD, followed by t_s. Surprisingly, the amount of SDS introduced after the start of the feed seems to have little influence on the PSD. Increasing the concentration of the seed and also t_s both cause the bimodal distribution to be broader, because there is a competition between the seed and the new crop of particles.

More recently, Chu et al. presented a series of articles on producing bi- and trimodal PSD latexes to obtain high solids [40–42]. In the first article [40], they used the same strategy as Chern et al. [39] to produce bi- and trimodal PSD by re-nucleating small particles in the presence of a seed emulsion polymerisation of Sty–BA–MAA (65–33–2 wt%)with an initial average, a particle size of $d_p = 130$ nm. The seeds were prepared using ammonium persulfate (APS) as the initiator and a mixture of a non-ionic nonylphenolethoxylate and an anionic surfactant of the same structure but sulphated. The feed was an emulsion of the monomers containing a mixture of surfactants with one part of anionic and five parts of non-ionic surfactants, together with a solution of initiator. Different series of experiments were carried out. In the first series, the feeding period was divided into two parts: an initial growth period during which the large particles of the seed were allowed to grow (Stage I). Once a large part (between 50 and 70%) of the emulsion in the feed reservoir was added, the second period began (Stage II), which

consisted of adding a shot of a mixture of surfactants, and feeding the remainder of the emulsion of monomers for 1–3 h. The shot of surfactants provoked the birth of a second crop of smaller particles to provide the small particle tail of the desired bimodal PSD. In this series of experiments, equal amounts of non-ionic and anionic surfactants were added but the total amount of surfactant was varied. Also the proportion of emulsion fed in the first stage was 50% in the first experiment and 70% for three other runs. The instantaneous conversion remained above 80% during all the feed periods. They observed that the number of large particles ($N_{p,L}$) remained stable during the first period, but decreased during the second stage in all of the runs. On the other hand, once formed, the size of the small particles tended to increase more rapidly than the large particles, while $N_{p,S}$ (number of small particles) decreased. Note because these particles have a T_g well over ambient temperature, Chu et al. [43] were able to use a technique based on centrifugation plus light scattering to obtain reliable estimates of the PSD. Of course, in the absence of any limited flocculation phenomena, it is normal for the small particles to grow more rapidly (in terms of $d_p(t)$) during semi-batch feed since d_p varies as the volume to the one-third power. Thus a small increase in volume is more easily noticed in terms of diameter for the small particles. As we shall see later, this is an important factor in trying to determine when to add/create the second or third populations. When the amount of surfactant added in the shot decreased, d_p of the two families increased more rapidly and N_p decreased. These two trends suggests that decreasing the surfactant concentration below some critical limit (probably around 50% surface coverage) leads to insufficient stabilisation and flocculation of the latex.

   Some data in this first series of experiments are reported in Table 1. In order to maintain the stability of the latex and to consume all of the monomer fed during the second stage for the small particles, it was necessary to add a very large quantity of surfactant (7% with respect to the final amount of monomer added). This means that there are more than 100 small particles for each of the large particles. In this series of experiments to make a bimodal PSD, the latexes with the lowest viscosity contained approximately 80% large particles (by weight, which, given the densities of the system, is very close to the volume fraction), as expected from the results discussed in the first part of this review.

   In another series of experiments (also in Ref. [40]), the amount of surfactants was limited to ≤4 wt% with respect to total monomer, and the ratio between the relative amounts of anionic and non-ionic surfactant were varied (the conditions and results are summarised in Table 2). Larger seeds ($d_p =$ 486 nm) were used at a solid contents of 53%. This enabled the authors to produce a bimodal, and possibly trimodal PSDs with large, small and medium-sized particles. The separative method presented in Ref. [43] was used to estimate the average d_p of the different latexes produced here, and showed that they contained latexes of 28–55 nm (S), 91–130 nm (M), and 507–549 nm (L). In these experiments, the average size of the three particle population was lowest at the upper limit of surfactant concentration, and the sizes increased as the surfactant concentration decreased.

   The authors claim that the trimodal distributions observed in this series of runs results from the fact that the amount of surfactant has been decreased with respect to the previous series of experiments (from 7% w.r.t. monomer down to less than 4%). The injection of the surfactant creates a second population of particles, but, because of its relative paucity, it is possible that a certain portion of the freshly nucleated small particles flocculate either onto each other, or onto the larger particles to enable the system to attain a new equilibrium. Flocculation between the smaller particles is said to lead to the creation of the third (medium-sized) population that is not found in the previous experiments. However, it cannot be explained why the 'small' particles in this series are so much smaller than the small particles in the first set of experiments (Table 1).

Table 1
Data of Chu [40] for the first series of experiments

Run	Stage 1 feed%	Surface mass% w.r.t. monomer	Final size (nm)		Final PSD (L/S)		% Monomer used for small particles[a]
			Large	Small	Weight	Number	
1	50	7	306	69	44/56	1/112	≫ 99
2	70	7	327	50	61/39	1/182	≫ 99
3	70	3.5	365	66	68/32	1/78	82
4	70	2	391	90	76/24	1/25	53

With respect to total amount of feed used in Stages I + II.

[a] With respect to number of particles.

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Table 2
Data of Chu [40] for the third series of experiments

Run	Surface % w.r.t. monomer		% Monomer Stage I/II	Size (nm)			PSD (S/M/L)		% Monomer used for small particles[a]
				Small	Medium	Large	Weight	Number	
1	2	2	70/30	26	91	507	10/0.9/89	753/2/0.96	36.3
2	2	2	60/40	38	91	531	12.2/5.7/82	365/13/0.9	44.8
3	2	0.5	60/40	36	121	538	7.1/4.2/88	248/4/0.93	28.3
4	1	0.25	60/40	36	130	549	3.2/3.5/93	113/3/0.93	16.8
5	1.5	1.5	50/50	55	101	549	10.5/9/80.5	125/17/1	39

[a] With respect to mass of particles.

The PSD was also found to be sensitive to the relative amount of anionic and non-ionic surfactant. In this series, when less non-ionic surfactant was used, it was found that the stability of the latex decreased as the size of the medium particles increased. However, these trends are not so clear, probably because it is not so easy to control the limited flocculation that leads to the creation of the medium-sized particles. It is also interesting to note that the minimum latex viscosity was observed the PSD having a relative ratio of 80/10/10. This agrees well with the domain in that corresponds to the highest solids content possible for a fixed viscosity.

A different strategy was used by Chu et al. in Refs. [41,42] to produce bi- and trimodal PSDs, respectively. These two papers dealt with the polymerisation of a mixture of two seeds of Sty/BA/MAA with a monomer feed of the same composition (65/33/2 by weight). In order to make a bimodal latex [41], the seed used in the initial charge had a diameter of 130 nm. These particles were grown by adding pre-emulsified monomer for 5 h in parallel with the addition of an initiator stream. At this point the large particles have a $d_p \approx 300$ nm. Following a finishing stage of 2 h, a second seed with an average particle size of 75 nm was added at a solid content of 50%. More pre-emulsified monomer was then added (approximately the same amount as was used to grow the large seeds) for 3 h. At the end of the process, the large particles had a diameter of $d_{p,L} \approx 400$ *nm*, and the small particles were at $d_{p,S} \approx 95$ *nm*. $N_{p,L}$ remained constant during the initial growth step, but both $N_{p,L}$ and $N_{p,S}$ decreased during the second stage (although $N_{p,L}$ seemed to decrease more quickly). This indicates that a limited amount of flocculation took place during the reaction. Surface tension measurements were also carried out, showing the absence of micelles in the serum and a partial coverage of the particles, which decreases from 80 to 50–55% during the process. This value seems to be the limit under which flocculation might take place.

In a further study, Chu et al. [42] were able to obtain a trimodal PSD by repeating the process used in Ref. [41], but adding rather significant amounts of additional surfactant. When more than 2% of additional surfactant (versus total monomers) was added with the second seed, a third family of small particles is nucleated. Their size is around 50–60 nm, while their number increases during the process up to $2.5 \times 10^{17} \, l^{-1}$. Simultaneously, the size of the large particles goes from 300 to 400 nm and their number remains stable at around $10^{17} \, l^{-1}$. The medium-sized particles are grown from the second seed, and their diameter increases from 75 to 92 nm, and their number does not change ($1.5 \times 10^{17} \, l^{-1}$). It was found that in order for the secondary nucleation to occur and to create the population of small particles, the surface coverage of the existing particles must be above 70%. If this condition is satisfied, the amount of additional surfactants seemed to have no significant effect on the size and the number of medium-sized particles. However, increasing the surfactant concentration reduced the size of large particles due to the fact that the flocculation process is less and less important.

Chu and Guyot analysed the effect of the solids content on the viscosity of either bimodal or, more often, trimodal latexes similar to the ones created in the last two papers. The experiments were carried out with latexes of the same composition than those of the previous studies, using a seed of large particles with a diameter of 477 nm, a second seed with particles of 75 nm, and additional surfactants to generate the third population of particles. Two successive growth steps were carried out, separated by the introduction of the second seed with the additional surfactants. A few typical data are reported in Table 3.

First of all, these data show the enormous influence of the solid contents on latex viscosity at high volume fractions (runs 1 and 2). It can also be seen that it is possible to significantly reduce the viscosity by adding a second family of small particles. Further, it is possible to get up to 69% solids content with a very reasonable viscosity, by creating a trimodal PSD by adding both a second population of small

Table 3
Viscosities and solids content of St/BA/MAA latexes

Run	% 75 nm	Surface % mass w.r.t. monomer	Particle sizes (nm)			PSD[a] L/M/S	Solid content (mass%)	Viscosity[b] (mPa s)
			L	M	S			
1	0	0	477			100/0/0	65.1	1953
2	0	0.3	509	0	0	100/0/0	61.3	78
3	0	2.1	586	128	42	91/4/5	68	525
4	5	2.1	584	121	43	86.5/10.5/3	68	161
5	10	0.3	546	122	0	83/17/0	55.6	15
6	10	2.1				83/14/3	68.6	153
7	15	2.7				79/17/4	69.1	155

[a] Relative weight fraction of each cut.
[b] Shear rate of 10 s^{-1}.

particles and enough additional surfactant to a bimodal distribution. This is true even if the distribution is not that exactly suggested by the data obtained by blending three monodisperse latexes shown in Fig. 3.

More recently, a new study on high solid latexes was made by Schneider [4,12,44–46], with a moderately water-soluble monomer mixture of BA/MMA/MAA (78/20/2), and stabilised by a mixture of anionic and non-ionic surfactants in which the hydrophobic part was composed of hydrocarbon long chains instead of nonylphenol moieties. In addition, the total surfactant concentration in this series of experiments was limited to less than 3% with respect to the final monomer content, and the target value of a 68% solids content with the lowest possible viscosity was set. Schneider et al. [44] perfected a process to create relatively monodisperse seeds with a $d_p \approx 500$ nm, and then tested the two methods used by Chu et al. to make bi- and trimodal PSDs (i.e. nucleation in situ [45], and polymerising blends of two latexes [45] with different components), along with a new process [46]. Note that because of the additional viscosity constraint imposed in this work, Schneider et al. were obliged not only to worry about the relative amounts of each population in the latex, but, unlike Chu et al., also their relative sizes.

In the initial approach, a seed containing large particles ($d_{p,L} \approx 500$ nm) at a solid content of 50% was pre-swollen and a pre-emulsified monomer mixture was fed together with surfactant, and APS until these $d_{p,L} \approx 600$ nm [45]. In the event that the authors wanted to make a trimodal latex, two seeds ($d_{p,L} \approx 500$ nm, and $d_{p,M} \approx 250–270$ nm) at a solid content of 50% were pre-swollen and grown together until $d_{p,L} \approx 600$ nm and $d_{p,M} \approx 350$ nm. In either case, this corresponded to a solid content of 59–60%. It was expected that this growth stage would take place without nucleation or flocculation. However, the presence of approximately 20% MMA in the monomer feed, coupled with a much lower surfactant concentration than used in Refs. [40–43] created a certain number of difficulties. It was observed that a significant number of small particles was nucleated throughout the growth stage. This not only caused a redistribution of the available surfactant (a problem that could be corrected through trial and error addition of different types and quantities of surfactant), but, as we saw earlier, the fact that the shape of the PSD was not of the desired form (i.e. there were too many small particles with $R > 10$) meant that the viscosity increased more sharply than would be expected. In addition, this secondary nucleation was not particularly reproducible, and seemed to be very sensitive to initiator addition among other things. For instance, it was observed that high local initiator concentrations at the feed point, caused by the

obligatorily low stirring rates and moderate viscosities, led to a certain amount of flocculation and formation of agglomerates. Efforts to avoid or significantly reduce it through modifying the feed policy for the surfactants (e.g. using only non-ionic surfactant in the pre-emulsion of the feed) were unsuccessful; however, it was found that trying to re-nucleate with only anionic surfactant invariably led to a massive loss of stability. On the other hand, it was not possible to re-nucleate with only non-ionic surfactant. Interestingly enough, once enough non-ionic surfactant was added, the amount of anionic surfactant did not seem to have an influence (provided, of course, there was anionic surfactant).

As was done by Chu et al. [40], shots of surfactant were used to nucleate a second crop of particles in the presence of the seeds once the latter had been grown to the desired size. Because of the relatively low levels of surfactants (imposed by the quality constraints related to the application of the latexes), and the presence of non-negligible amounts of monomer and/or oligomers in the aqueous phase, this nucleation procedure was found to be very sensitive to conditions in the reactor, and not particularly reproducible. In certain cases, it was possible to create a bimodal PSD with a solids content of 64% and a viscosity of 2500 mPa s at 20 s^{-1}, however, using the same recipe also led to the production of a latex with well above 50 000 mPa s under the same conditions.

In order to avoid this problem as much as possible, the strategy of growing a seed latex, blending it with another and further polymerising the mixture was adopted. A mixture of the medium and large seeds with the same composition was introduced into the reactor, swollen with monomer and initiator, and then a pre-emulsion of monomers was fed in parallel with a solution of initiator. Small amounts of a mixture of anionic and non-ionic surfactants near the end of the processes allowed the authors to successfully nucleate a small quantity of a third population without losing stability. This enabled them to increase the solids content to levels of approximately 2 or 3% higher than in the previous experiments. However, secondly nucleation remained a significant problem.

Schneider et al. [44] noted that when APS was replaced by the redox couple H_2O_2/ascorbic acid (AscA) as the initiator in the production of the seeds, the problem of secondary nucleation seemed to be all but eliminated. Although problems associated with maintaining a constant flux of radicals did not encourage them to pursue this replacement at that time, it did suggest that there were indeed ways of eliminating a significant portion of the secondary nucleation. The solution that they hit up [46] was to polymerise a blend of large and small particles, much as suggested earlier, but by replacing APS used in the growth stages by an oil-soluble initiator. The initiator chosen for this purpose was a liquid derivative of azobenzene (DEAB, diethylazobutyronitrile) with decomposition kinetics similar to those of APS. A schema of this process is shown in Fig. 7.

After the seed of large particles is fed to the reactor, it is swollen with monomer and initiator at room temperature. The temperature is increased to the desired level, and a pre-emulsified monomer solution is added to grow the seed to approximately 600 nm at a solids content of $\pm 60\%$. A second addition of the oil-soluble initiator is carried out before adding the seed of small particles (approximately 60–90 nm in diameter). The desired quantity of small seeds is added with more pre-emulsion, but, since there is no initiator in the aqueous phase, the small particles are partially swollen with monomer, but no polymerisation takes place. Once the desired solids content is attained, a solution of H_2O_2/ascorbic acid is added to the reactor. Unlike the DEAB, this is a water-soluble initiator system, so the radicals thus generated consumed the monomer in the aqueous phase, and entered the small and large particles indiscriminately, enabling high conversions to be reached at the end of the reaction. Care must be taken in choosing the size of the small seeds, the relative quantities of each population and the point at which
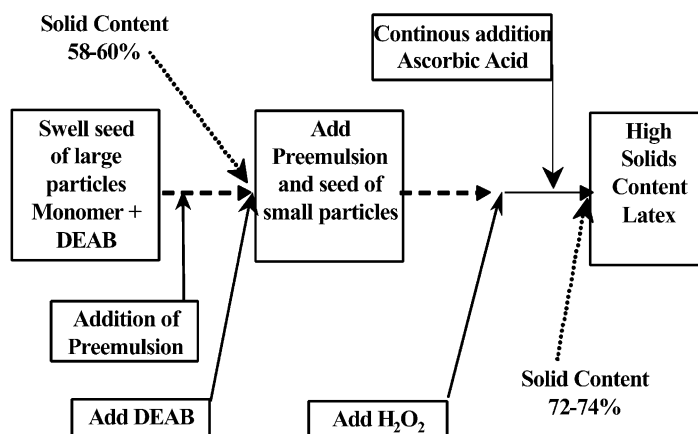
Fig. 7. Schema of the process proposed by Schneider et al. [46] to obtain HSC latexes with bimodal PSD and very low viscosity.

H_2O_2/ascorbic acid is started since doing so correctly allows us to define the right proportion of small and large particles, and to adjust the diameter ratio of each population to minimise the viscosity.

Unlike the previous process, it was found that this choice of initiator system led to highly reproducible, HSC latexes. Latexes with viscosities between 300 and 1000 mPa s at shear rates of 20 s^{-1} and with solids contents of 73% ($>70\%$ polymer) can be obtained easily. The key to these HSCs and low viscosities is a well-controlled, reproducible PSD. Some of the results of the viscosity measurements are shown in Table 4.

The data reported in Table 4 show that very low viscosity can be obtained at 70% solids even with a simple bimodal distribution if the amount and the size of the two families are well chosen. Upon comparing the new process with the more classical ones, it was observed that the localisation of the carboxylic groups at the surface of the particles has not been changed significantly.

Table 4
Properties of bi- and trimodal latexes [46]

Run	Final solids^a (mass%)	Predicted d_p (mass% of each population)	Final viscosity (mPa s at 20 s^{-1})
1	73.1	75 nm (15)	820
2	72.9	900 nm (85)	
3	72.2	110 nm (15)	300
4	72.6	900 nm (85)	
5	73.1	75 nm (15)	1200
		350 nm (5)	
		900 nm (80)	
6	73.1	75 nm (15)	700
		125 nm (5)	
		900 nm (80)	
7	71.3	75 nm (15)	900
		350 nm (5)	
		590 nm (80)	

^{a} Includes approximately 1.8–2.5% surfactant.

4.1.2. Via miniemulsion polymerisation

Miniemulsions are prepared by dissolving an anionic surfactant in water, and a cosurfactant (to stabilise the monomer droplets against Ostwald ripening) in the monomer phase [47]. The oil and water solutions are mixed with a mechanical agitator for few minutes and then in a high shear mixer (ultrasonifier, a homogeniser or a microfluidiser). This mechanical shear breaks the oil phase into sub-micron size droplets. An adequate ratio of surfactant to cosurfactant allows us to maintain adequate stabilisation of the droplets for periods up to few days, so that the risk of phase separation in the tube could be eliminated. The distribution of the droplet size generated in this manner can be either monomodal, relatively broad, or even multimodal, so the viscosity of the resulting latex is reduced compared to a typical monodisperse latex with the same solids content.

These sub-micronic particles develop a surface area large enough for the capture of the oligoradicals coming from the water phase, while Ostwald ripening of unstabilised structures in the water phase means that we have no monomer-swollen micelles, and thus no micellar nucleation of polymer particles. However, because the total surface area of the particles is much lower than that of micelles found in classic emulsion polymerisation, nucleation can take much longer in miniemulsion than in a classic emulsion polymerisation. In addition, the droplets initiated early in the polymerisation can grow much more than those initiated later on, and the longer the nucleation period, the broader the PSD is. This is one of the reasons for the interest of the miniemulsion process for the preparation of high solid latexes. Note that in this section, we will of course be focusing only on HSC-related papers.

The first approach in this direction was made by Tang et al. [48], who incidentally discovered that nucleation took place in a seeded polymerisation fed with a miniemulsion of monomers. They found that the PSD of the resulting latex was very broad, and proposed that this might be due to the fact that flocculation took place which resulted in the formation of a small amount of coagulum. However, the solids content in their study was limited to 25%.

The first results published in the area of miniemulsion applied to HSC latexes were those of Lopez de Arbina and Asua [49]. In this work, a batch terpolymerisation of Sty, EHA and MAA was carried out at a solid content of 60%, without forming any coagulum at adequately low initiator concentrations. The component of the stabiliser system was hexadecane and SDS or a sulphonated salt of an ethoxylated alkyl phenol derivative, and the miniemulsion was prepared by sonication. They observed that beyond the limit of 60% solids, both the viscosity and amount of coagulum formed increased significantly. They also compared their miniemulsion results with a classic emulsion polymerisation, and found that it was not possible to produce polymer beyond 50% solids under the same conditions, although the reaction did go faster in the classic emulsion process (smaller d_p, higher N_p and therefore rate) [50]. In terms of the PSD, it was observed that the d_p for the miniemulsion process was higher than that of the classic process, and that the PSD was broader. The latexes from miniemulsion also showed a slightly better resistance to the addition of salts, and it is suggested that there are more methacrylic acid units located on the surface of the particles in the case of miniemulsion.

This work was continued by Masa et al. [50] and extended to semi-batch processes. The initial charge used was a miniemulsion, as was the feed stream. The final solid content in this work is approximately 55% solids. The authors compared mini- and classic emulsions, and their conclusions were the same as earlier. In addition, their PSD was distinctly bimodal using this process.

Leiza et al. [51] also used a two step semi-batch polymerisation, and attempted to use reduced amounts of surfactant in order to reduce water absorption in the final product. In the first step, a seed is prepared via a semi-continuous miniemulsion polymerisation of butylacrylate in the presence of

polymer in order to aid droplet stabilisation. In the second step, the solid contents is increased up to 60–70% by feeding an emulsion of monomer containing a low amount of emulsifier (0.5% with respect to the monomer in the feed). A large number of parameters were studied, and it was observed that the shape of the impeller was important if one wishes to avoid local pools of liquid monomer. Using too little SDS resulted in a highly viscous paste-like latex with significant traces of residual monomer. The authors attempted to increase the conversion by increasing the temperature from 60 to 70 °C, increasing the initiator feed rate, and decreasing the monomer feed rate. Nevertheless, the highest attainable solids content final result was pasty latex at 64% solids. At slightly lower solids contents, the viscosity of the final product remained much more reasonable: at 61% solids, the viscosity was in the order of 6 Pa s. It should be underlined that these results were obtained with a surfactant concentration of less than 1% with respect to the total amount of monomer fed to the process—a figure much lower than the 3–7% discussed in Section 4.1.2. It was found that latexes with a broad PSD (particles ranged from 100 to 800 nm) that contained particles smaller than 300 nm were more fluid. This population of small particles resulted from secondary nucleation. When enough SDS is used, a certain amount of limited flocculation took place and a certain number of small particles remained stable, the net effect of which was to extend the PSD in both directions.

A more recent study was published by Durant [52] on the batch polymerisation of styrene in miniemulsions containing hexadecane and 60% organic phase. Very small droplets of about 100 nm were produced by sonication. The number of polymer particle initially increases, and then decrease to the initial figure. The PSD remained narrow, with sizes varying in a narrow range (120–80 nm). Full conversion was reached within 90 min. A system of double surfactants was used (dioctylsulfosuccinate + SDS). The process was applied to control radical polymerisation, using a nitroxide controller, and also to dye encapsulation.

Another study which should be mentioned is that by Ruckeinstein and Kim [53]. Although not practical from an industrial point of view, this process is interesting in so far as the authors claim to be able to produce latexes with solids contents upwards of 74%. The monomers (styrene and methacrylic acid), together with AIBN, were added dropwise into a small amount of water containing SDS. The mixture is then placed in a centrifuge tube where the polymerisation is carried out. Both the polymerisation rate and the molecular weight were higher than in bulk polymerisations, although a part of the monomers were converted under bulk conditions due to the fact that some monomer droplets agglomerated and formed a liquid phase. Furthermore, complete conversion was not obtained so the polymer solid content was lower than the expected value of about 85%. The size of the particles was reported to be in the range 200–300 nm.

4.1.3. Silicone polymers or polysiloxanes

Silicone latexes have been very sparsely studied, but play an important role in a number of industrial applications. A few academic studies have been devoted to the cationic synthesis of silicon latexes via ring opening of dimethylcyclosiloxanes (most often D_4), using an alkyl benzene sulphuric acid surfactant for both the initiation of the polymerisation and the stabilisation of the latex particles [54,55]. Anionic polymerisation of D_4, initiated with sodium hydroxide, and stabilised by an hydroxide derivative of a cationic surfactant was described by De Gunzbourg et al. [56], and more [57]. However, these kinds of polymerisation do not lead to high solid latexes. High solid silicone latexes can be obtained upon emulsifying silicone oil, as described in a rather old patent [58]. In this patent, more than 20 examples of HSC silicon latexes were described where silicon oil was thoroughly mixed in an

aqueous solution of surfactants, sometimes in the presence of a water-soluble thickener such as cellulose derivatives. Solid contents in between 72 and 95% are obtained with sizes from 300 to 2500 nm, most often with a bimodal PSD. A variety of surfactants, or surfactant mixtures were used, and it was observed that the average size decreased when the duration of the malaxing process increased. Examples are shown using reactive silicon such as vinylsilane derivatives.

4.1.4. Conclusions from academic studies

Although the number of groups looking at the production of HSC latexes is rather limited for the time being, a number of points should be clear from the preceding discussion.

- There are two basic means of creating a multimodal concentrated latex:
  2.1. *Process 1*. Mixture of two or three monomodal seeds with well-defined PSD, followed by a period of growth in a semi-batch reactor.
  2.2. *Process 2*. Creation of a seed latex, with growth of the seed latex particles during a semi-batch reaction followed by one or two nucleations of secondary (and eventually tertiary) populations.
- The most important point seems to be reproducible control over the PSD of the latex. Creating too many small particles leads to irreproducibility, high viscosity and eventual loss of latex stability. Secondary nucleation in the presence of water-soluble monomers must be suppressed. This can be done by using non-ionic initiators or oil-soluble initiators.
- Miniemulsions seem to be useful for making HSC emulsions, but no serious attempts have been made to go beyond the 60–64% mark.

4.2. Patents on HSC latex synthesis

Due to the practical interest of producing HSC latexes in the industrial world, most of the earlier studies appeared as patent applications.

As early as 1971, a patent was given to Celanese Corp. [59]. They claimed to achieve solid contents of 50–70%, with reasonable viscosities in the order of 5000–20 000 mPa s (note a Brookfield RVT viscosimeter was used for these measurements, and no shear rate or rotational speed was provided. It is, therefore, not possible to compare these results with the ones reported earlier). A simple semi-batch process has been used, with the feed of a concentrated pre-emulsion (75–94%) of rather water-soluble monomers (MMA, VAc) and perhaps of a crosslinker. A batch nucleation step is used to create a seed of unspecified dimensions that consumes 10–25% of all the monomer used in the process, and that has a solid content of 50–75% (according to the patent, although it is unlikely that this figure is much above 50%). It is possible that the favourable solid contents and rheological properties of the final latexes are due to a homogeneous nucleation of secondary population taking place throughout the process, which creates a broad PSD. This is likely given the results of Schneider et al. [45]. Unfortunately, no characterisation of the PSD was presented in the related patent.

The creation of very broad PSD for obtaining HSC latexes were described in 1978 in a patent assigned to Union Carbide Co. [60]. This is a complex process which consists of an initiation step. This step lasts for 1–2 h, and, once the nucleation process has begun, a portion of the seed latex is continuously withdrawn at the same time as a concentrated pre-emulsion plus initiator is fed into the reactor. In one of the examples, the reactor is fed with monomer, surfactant, initiator (buffered APS) and water at a rate of 3.15 g/min, and the contents are withdrawn via a siphon at 2.5 g/min. The result is a storage tank

containing 160 ml of a latex with a solid content of 25% and 135 ml of a latex with a solid content of 40 wt%. Given the operating procedure, both the stored seed and seed in the reactor will probably have a broad PSD—this is doubly true in the examples given in the patent because the monomer mixtures contain 50–70 MMA and a trace of MAA, both of which will provoke severe secondary nucleation [45]. Once enough seed has been stored, the feed rate of monomer and catalyst is adjusted, and the seed in the original reactor is grown by semi-batch polymerisation for 1–2 h, while more seed is continuously withdrawn and sent to the storage tank. At this point the reactor contains a latex with a solids content approaching 60 vol%, and the storage tank contains a latex at 40% (v/v) solids. In the final step, the latex in the storage tank is fed to the reactor along with monomer for two to two and a half hours. The final result of the two examples were latexes with a solid volume content of 67% and a viscosity of 3600 mPa s in one case, and a solid content of 68% (v/v) and a viscosity of 925 mPa s in the other (Brookfield viscosity with spindle No. 3 at 6 rpm). Note that the slightly higher solid content and lower viscosity were obtained with a redox initiator in the second case. No information was provided on the PSD, but it is safe to say that it must be extremely broad (some of the particles will have remained in the reactor for the entire process, others for half, while still others are probably nucleated near the very end of the reaction), and might indeed exhibit a multimodal shape.

In the patent granted to Rohm [61], two seeds are used to produce latexes with a bimodal PSD, and, as stressed in the objectives of the patent, this is to be done in a reproducible manner. The authors claim a solids content in the order of 60–70 wt%. This process is much like those described earlier in Refs. [41, 42,45,46], where two seeds are blended and polymerised together to make a concentrated latex. These seeds are of different sizes and can be of different compositions. For instance, one of the families of seed is composed with MMA (54%), BA (45%), and MAA (1%), and another contains 64% MMA, 34% BMA and 2% MAA. Their sizes range from 54 to 838 nm in the examples (although an upper limit of 4000 nm is specified in the claims).

In the examples, the seeds are prepared ahead of time and stored. Another seed is prepared in the reactor according to a pre-specified recipe, and one of the stored seeds is then added to the reactor. The seed prepared in situ is adjusted so that we have 10 parts (w/w) of large for one part of small seed, and the ratio of $R = d_{p,L}/d_{p,S}$ ranged from just above 2–11.2. The blend is fed of a mixture of monomers with a fixed composition is then added for 3 h. This feed time should be sufficient to significantly narrow the difference between the average diameters of the two particle populations. In the examples, the final latexes had solids contents going from 64.3% (w/w) with a viscosity of 112 mPa s, up to 69.5% with a viscosity of 9400–12 600 mPa s (viscosities measured on a Brookfield viscometer with different spindles and rotation rates so it is difficult to know the shear rate). Unfortunately, the light scattering equipment available to the authors of this patent was not able to furnish a full PSD, so there is no absolute proof of the bimodality of the latexes. Nevertheless, given the process described here, plus the fact that we are dealing with partially water-soluble monomers like MMA, it is likely that an observable number of small particles were nucleated during the reaction as well, thus contributing to the multimodality of the PSD.

The company that seems to have taken out the largest number of patents in this area is BASF. The patents appear in two large series, and although there are some earlier ones, most of the patents that interest here appear in 1990s. A initial series of patents were granted to BASF in 1994 and 1995 [62–65]. Of these four, the first three are very similar, and the last one differs essentially in how the initial dispersion is made. The objectives of these patents seem to be to produce latexes with solids contents of between 50 and 65% (closer to 65%), while maintaining the viscosity and production time as low as

possible. Reading between the lines in these patents shows that particular emphasis is placed on understanding how the PSD evolves and controlling it as much as possible through the use of well-adapted monomer addition.

In the first patent [62], no claims are made concerning the macroscopic latex viscosity, final solids content (although a solid content of 62% (w/w) is given in one of the examples) or PSD (it is simply stated that a broad PSD helps to increase the solid content), although the monomer composition seems to be an important parameter (55–90% BA, 10–40% MMA and 0–10% water-soluble carboxylic or other functional monomer such as AA or MAA). The semi-continuous process relies on the creation of a monodisperse seed, to which additional monomer (and perhaps seed) is added during the concentration stage of polybutylacrylate (PBA) was prepared in the conventional manner, using a redox initiator system of H_2O_2/AscA and Dowfax 2A1 (sodium alkyl diphenylsulphonate diphenylether) as stabiliser to prepare a latex with a solid contents of 30% and a diameter of approximately 30 nm. Some of this seed is withdrawn and mixed with surfactant, water and initiator.

The preparation of the high solids latex involves a semi-batch process using two or three streams: one contains the monomer(s) in water with a mixture of surfactants, the second (optional) stream contains a redox initiator in aqueous solution, and the third contains the seed plus emulsified monomer. The exact composition and feed rate of these streams are the objective of precise description, and it appears that a variable feed rate is used to maintain monomer, surfactant and radical concentrations at precise levels. As we suggested earlier, this seems to be in order to precisely control the PSD, and to reproduce events such as homogeneous nucleation of MMA, MAA, AA, etc. (partially or totally water-soluble monomers) as closely as possible. The final latex contained 62% solids, and seems to be used for paints.

In the second patent [63], delivered the same day as the previous one [62], solids contents go from 61 to 72 wt%. In this patent, two seeds are mixed and polymerised together. The first seed of PBA is produced using a redox initiator to yield particles of approximately 30 nm at a solid content of 30% (like in the previous patent). The second seed was more complex, had a solids content of 61–66% (w/w), and a well-defined PSD where d_p was centred on 350 nm. This seed is similar to the medium seed prepared by Schneider et al. [45], with one of the examples giving a composition of 85% BA, 12.5% MMA and 2.5% AA with a buffered sodium persulphate (NaPS) initiator and the very precise addition policy defined in this patent might be intended to circumvent some of the reproducibility problems observed earlier. The final latex was produced through the semi-batch addition of a two streams. One stream contained an emulsified mixture of monomers, similar in composition to that used for seed 2, and the other contained seed 2 (or a blend of seeds with d_p centred on 350 nm, that can have a more or less broad PSD and perhaps slightly different compositions) plus monomer, surfactant and initiator. The first stream can be augmented by a third stream where BA is added 'as-is'. The initiators used for the semi-batch concentration are redox systems (either ferrous sulphate or water-soluble peroxides plus AscA). This avoids the addition of the $SO_4^{\cdot-}$ radicals that are generated by the persulphate initiators and that can stabilise the polymer chains created in the aqueous phase due to the presence of water-soluble monomers. This reduces the risk of uncontrollable homogeneous nucleation. The solid contents of the final latexes were 71–73 wt% (66–67 vol%), with viscosities between 290 and 750 mPa s as measured at 23 °C and a shear rate of 489 s^{-1}. The PSD once again broadly contained particles larger than 800 nm and smaller than 200 nm. Note that the shear rate used here is much higher than the ones used to evaluate the latexes made by Chu et al. and Schneider et al. Since this type of HSC latex is shear thinning, care should be taken when comparing the viscosity data. For instance, Fig. 8 shows the shear thinning
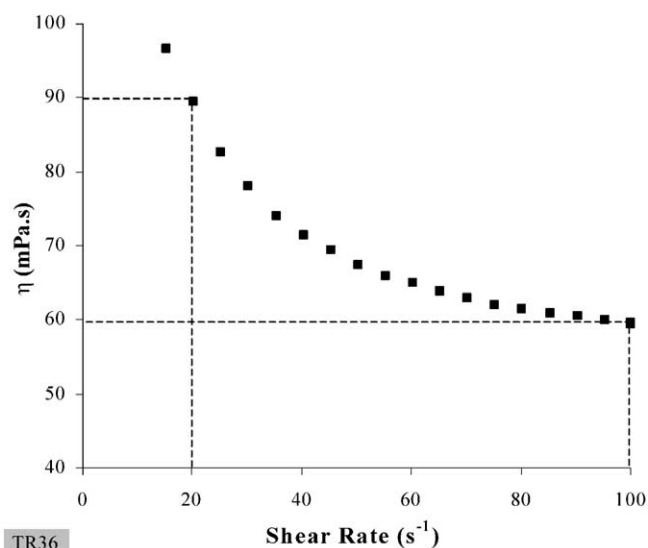
Fig. 8. Shear thinning behaviour of a latex produced by Schneider [12].

behaviour of a latex from Ref. [12]. We can see that the apparent viscosity drops from just under 90 mPa s at $20\ \mathrm{s}^{-1}$ to 59 mPa s at $100\ \mathrm{s}^{-1}$.

A third patent, delivered the same year [64] claims latexes with 75–76 wt% solid contents (67–68% v/v), and viscosities of 375–510 mPa s at a gradient of $487\ \mathrm{s}^{-1}$. The process is very similar to that outlined in Ref. [62], where a stream of monomer (majority BA, with lesser amounts of one or more of MMA, EHA or ethyl acrylate, and traces of AA) is added along with a stream containing a seed identical to the reactor heel plus a stream of water and NaPS. The products have a very broad PSD, and a complicated addition schema, illustrated in Fig. 9. The PSD claimed is also shown in this figure.

In the last patent from BASF in this series [65], a set of seeds were prepared again using a mixed Dowfax + non-ionic surfactant stabilising system, a redox initiation system of H_2O_2/AscA at 60 °C, and the same monomers as in the previous patents. It is similar in nature to Refs. [63,64], but more complex in so far as it claims a process that uses a complicated mixture of seeds with different particle sizes ranging from 40 to 283 nm. These seeds were mixed in different proportions and these different mixtures were used as the starting seed at a solid content in the order of 40%. In the final growth step, streams of monomer and initiator (same redox system) were added continuously for 3 h; however, unlike the previous examples, no particles were added during this stage. The PSD issued from one of the examples in Ref. [65] is shown in Fig. 10. The solid contents were in between 65 and 71 wt%, and, after dilution to a solid contents of ~60%, the viscosities were in the range 21–50 mPa s at a shear rate of $487\ \mathrm{s}^{-1}$. Once again, control over the PSD through variable addition policies is stressed in the text and examples of this patent.

Another set of patents were given to BASF, all from the same group of authors [66–68]. All were concerned with high solid latexes with low viscosity and used Dowfax as surfactant in the nucleation stage to make a PBA seed, the same mixed surfactant systems and redox initiators as earlier, and similar monomer systems. The said processes use one or two seeds with quite differing size to get latexes with particle sizes ranging from 200 to above 1000 nm for solids contents between 60 and 76%. Once again,

T=85°C

Stream 2
160 g H₂O
10 g NaPS

Stream 2

26% S3   54% S3   88% S3

Stream 3
549 g Seed 1

Stream 1
1915,2 g ABu
114 g AE
114 g A2EH
114g MMA
22,8 g AA
3,4 g tertdodecyl mercaptan

4% S1   8%S1   88% S1

0 h   1 h   2 h   3 h   4 h   5 h   6 h

160 g H₂O
11,2 g TA
11 g Seed1

ES=75,3%
375 mPa.s (shear rate =487 s⁻¹)
PSD :   **20% weight < 200 nm**
            40% weight < 400 nm
            72% weight < 600 nm
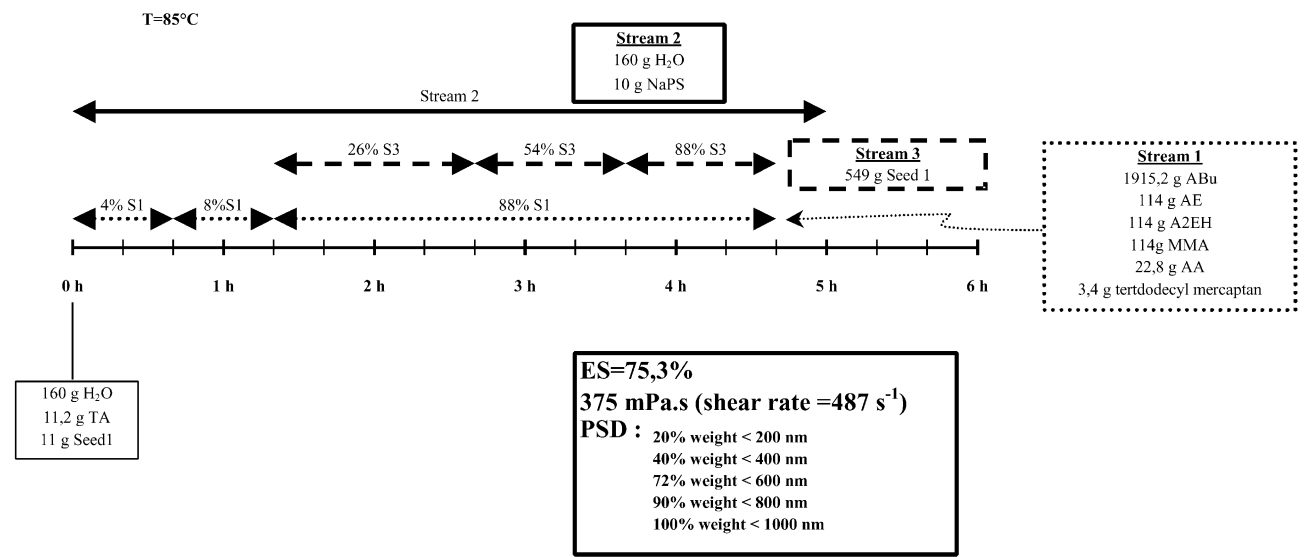   **90% weight < 800 nm**
            100% weight < 1000 nm

Fig. 9. Schema of addition of process streams and of reaction times for the HSC latex produced in one of the examples in Ref. [64]. Also shown is the PSD claimed for this example.
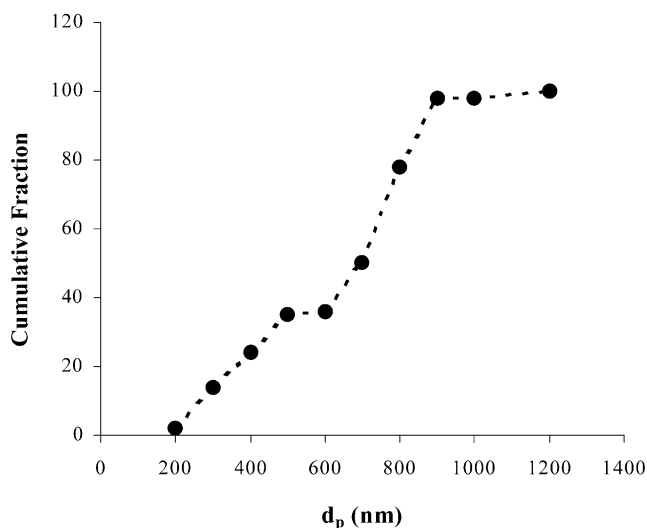
A. Guyot et al. / Prog. Polym. Sci. 27 (2002) 1573–1615

1603

Fig. 10. Cumulative PSD of a bimodal latex issued from Ref. [65].

the viscosities go from 190 to 500 mPa s at 487 s^{-1}. These patents are very similar to the first four, with the differences being subtle variations in the feed policies to get slightly different PSDs.

At the same time as these last three BASF patents, Goodrich took out a patent on high solid latexes for a different purpose [69]. The purpose of this patent was to describe high solid acrylic latexes for use as sealants with solids contents in the range 70–92 vol%, and containing a variety of additives (inorganic particles, biocides, viscosity improvers, adhesion promoters, etc.). The latexes are prepared from an initial acrylic latex that already has a preferably bimodal PSD with $d_p < 4$ μm (yes, micrometers), a solids contents of 40–68%, and has been stabilised with anionic surfactants. It appears that the extremely large particles of the seed latex are formed by coagulation and are non-spherical with aspect ratios preferably above 2. The seeds are typically commercially available acrylics (they cite in particular one of their own latexes 'carbobond'), and the monomers added in the examples are limited to hydrophobic species, in particular BA and EHA. The second monomers are fed along with anionic surfactants only, and although the authors claim that they can use any type of initiator, all of the examples are limited to t-butyl hydroperoxide (tBHPO). The final latexes have solid contents of 75–90% and very broad PSDs composed of 5–30% of particles with $50 < d_p < 700$ nm, 20–70% in the range $700 < d_p < 4000$ nm, and finally 5–75% in the range $4000 < d_p < 20\,000$ nm. It was observed that, during the initial steps of the feeding period new particles are formed, but later on, the number of particles is decreased due to coagulation. The viscosities of the different latexes are in the range 1000 to more than $50\,000$ mPa s depending on the solid contents which went from 57 to 85% (note shear rate not given). Some variations include the composition and the amount of the monomer mixture, the use of transfer agents, and the nature of the initiator system (often redox based on tBHPO), but all of the recipes cited are very similar.

The earlier work of Goodrich was continued in two additional patents [70,71] on the polymerisation of acrylic and vinylic monomers in the presence of a pre-fabricated HSC latex. The first five examples of patent [70] are in fact identical to the examples in Ref. [69]. The major difference is that [70] it gives examples where the original seed latex is a PVC latex, a polyurethane latex, a PVdC latex, and carboxylated Sty–Bd or nitrile rubber latexes. The patent in Ref. [71] seems to be identical to Ref. [69]

for all intents and purposes, and is probably just intended to add additional protection to their invention in the United States.

Another patent granted in 1996 was given to Zeneca [72], and covers the production of HSC latexes for coating applications, and more specifically for printing inks with low viscosities and fast drying times. Such applications do not require typically require extremely high solid products, but it appears that as cited in Ref. [8] (who not incidentally co-authored the patent in question), a bimodal PSD leads to favourable minimum film-forming temperatures and drying times (this in fact appears to the central purpose of this patent). The solid contents of the latexes described in this patent rarely exceed 60%. The invention describes the synthesis of a latex with a bimodal PSD from a seed latex mixed with an oligomer with a weight average molecular weight (M_w) in the range 10 000–20 000 that contains a high percent of acrylic or methacrylic acid. The process consists of preparing a conventional latex of small seeds via semi-batch polymerisation. This seed is set aside and the reactor is charged with the same monomers to begin making a second, larger feed. Once the appropriate size of the second feed is attained, the first seed is added to form a bimodal latex (i.e. we blend two latexes). The feed is composed of a pre-emulsion of styrene (52%), EHA (45%) and MAA (3–5%), which is the same composition as the seed. The oligomer can be introduced in various ways, but is usually produced in situ in a final step once the bimodal latex is ready, although it can be added as a blend from a special product synthesised before hand. A bimodal latex for this type of application is typically composed of 50–55 wt% of particles of 40–85 nm, and 45–50% of particles with a diameter of 300–325 nm.

The oligomer is chiefly adsorbed onto the surface of the particles of the latex. The carboxylic acid in the oligomer imparts a high hydrophilicity to it mainly at high pH. This means that the viscosity of the latex is pH dependent, and it will go, for instance, from 12 cP at pH 3.7 to 800 cP at pH 8.5. This phenomenon is referred to as 'reversibility'.

A Canadian patent granted to Gencorp [73] describes a method for producing moderate solids content latexes of Sty, butadiene (BD) and AA for paper coating applications. The solids contents are limited to approximately 50 wt% and a bimodal latex is made in situ, where an initial latex is formed and then grown to a desired size, and a second population of particles is nucleated in situ by adding monomer and a mixed ionic–non-ionic emulsifier. Interestingly enough the initiator used, NaPS, is added at the beginning of the reaction, and no other initiator seems to be added during the polymerisation. A stripping operation is subsequently carried out to ensure that the residual monomer content is less than 50–100 ppm since conversion is limited to 98–99%. The patent owners claim that this process result a latex with excellent strength properties, controlled gel contents, and good printability. However, the solid contents is not particularly high (50%), and the Brookfield viscosity is 200 mPa s (no shear rate or analytical conditions specified). The PSD is measured using CHDF, and is composed of two families of particles with diameters of ∼ 70 nm (25 wt%) and ∼ 160 nm (75%). The patent puts great emphasis on the properties useful for a coating paper application, and a variety of these properties are measured.

Yet another series of patents BASF appeared in 1998–2000 [74–78]. These patents are different from the previous ones cited earlier as they do not involve a seeding procedure. The first patent of this new series [74] has points in common with Ref. [78] in so far as it underlines the stability of the latex during deodorising operations, and describes high solid latexes (above 65%) designed for self-adhesive labels with a T_g between 0 and −60 °C. It is interesting to note that the process described in Ref. [74] does not rely on the use of pre-defined seeds. The reactor is simply charged with an aqueous solution of redox initiator and buffer, and then a pre-emulsion of monomer mixture composed essentially of MMA and ethylhexylacetate, together with a small amount of styrene and eventually vinyl acetate is fed into the

reactor at a variable flow rate: moderate during the first 6 min, then more rapidly for the next 40 min, then even faster for the last 4–5 h. In addition, a solution of NaPS is also fed for 5 h after the addition of the pre-emulsion. A final finishing step is carried out, using a redox of t-Bu OOH and a disulphite. The result is said to be coagulum-free latex with 70% solids. In order to produce a latex without any odour, a final stripping step is carried out. In the claims, some emphasis is given to the use of redox systems and of a selection of surfactants. Also the use of vinylsulphonate as comonomer is mentioned. No analysis of the PSD was reported, but there are data on the Brookfield viscosity which is said to be in between 600 and 3500 mPa s at their typical shear rate of 487 s^{-1} and solids contents in the order of 70 wt%. If this data is reliable, it should be clear that the PSD is well controlled.

In the following patent [75], the authors describe the production of bimodal latexes with 65–75% solids, a seed is used, together with three feed streams as shown in Table 5. The seed and some water are loaded into the reactor heated to 90 °C. A stream of initiator (NaPS) is then added for 4 h 5 min after the beginning of the addition of initiator, a stream of monomers (BA 49 parts, AA 1 part), emulsified with various surfactants, is also fed for 4 h. Sodium hydroxide is added to the reactor at a given time during the feed process (usually 30–60 min after start-up). The introduction of soda provokes a change in the pH of the medium, and causes the acidic groups on the surface of the particles to become charged. While this is true, it can nevertheless be expected that the population of the smallest particles is nucleated when the shot of soda, because without that shot addition, one would expect that without it only large particles are present (last run of Table 5). However, it is not easy to explain what the nucleation mechanism is because the influence of the parameters (amount of soda, time of its addition, and amount of seed) does not seems to have been clearly established (at least not in the patent text at any rate). It can be observed that the minimum viscosity values are observed for high concentrations of large particles. Finally, a finishing period of 1 h at 90 °C is used to eliminate residual monomer. The patent also covers the addition of an acid as well as a base, possibly in several steps, to adjust the pH. In this patent, the viscosity is claimed to be lower than 1000 cP, while the PSD is claimed to be bimodal.

The patent in Ref. [76] is concerned with the production of latexes with bimodal PSDs and $T_g <$ 50 °C which are used as additives to reinforce concrete. These latexes include copolymers with some amount of partially water-soluble functional monomers of the family of acrylamide (or methacrylamide), together with alkyl acrylate. The solid contents are normally in the range 55–65% lower than claimed in the previous BASF patents. This is possibly due to the higher water solubility of the monomers used in this process, which make the control of the PSD somewhat trickier. In this process, a redox initiator system is used, based on hydrogen peroxide and ascorbic acid. The totality of the H$_2$O$_2$ is added at the beginning of the reaction and the ascorbic acid is fed progressively together with an emulsion of acrylic monomers. The feed is added in three successive steps as shots 1, 2, then 3% of the total charge, before addition of the remainder in a continuous stream in 4 h. The functional monomer is mixed with the other monomers. The somewhat lower solid content (55–60%) means that the viscosities are very low (17–95 mPa s at 487 s^{-1}), but, as can be seen from the data in Table 6, the PSD is very broad, in the range $20 < d_p < 900$ nm. However, if we compare Figs. 10 and 11, we can see that, generally speaking, the BASF patents claim very similar PSDs in most cases.

The last patent in this series is quite different from the others in the sense that addition of monomer miniemulsions are involved [77]. In this process, a polystyrene seed with $d_p = 28$ nm and a solid content of 33% solids is heated in the reactor. Monomer (99% BA, 1% AA) emulsified with Dowfax surfactant is then added together with a stream of NaPS. Ten minutes later, a miniemulsion with $d_p = 130$ nm prepared containing a few grams of PBA in its monomer plus a solution of SDS is added. The result is a

Table 5
Data from BASF Patent WO98/16560 [75]

| | Composition | | | | | | | | | | η_{app} 23 °C 250 s^{-1} (mPa s) | PSD[a] | | | |
| | Initial charge | | Feed stream 1 | | | | Feed stream 2 | | Feed stream 3 | | | Small particles | | Large particles | |
	H_2O (g)	ID[b] (g)	H_2O (g)	Surfactants[c] (g)	BA (g)	AA (g)	H_2O (g)	$Na_2S_2O_8$ (g)	NaOH (g)[d]	Time (min)		d_p (nm)	% mass	d_p (nm)	% mass
1	104.5	40.8	292.4	53.3 A	980	20	89.9	3	8.0	30	320	143	60	468	40
2	104.5	40.8	327.9	17.8 B	1000	0	89.9	3	2.9	30	270	196	50	532	50
3	125.0	20.4	275.6	53.3 A	980	20	89.9	3	4.7	30	190	195	55	618	45
4	125.0	20.4	266.4	53.3 A	980	20	89.9	3	16.7	30	320	167	62	552	38
5	125.0	20.4	271.5	53.3 A	980	20	89.9	3	10.0	60	260	113	59	572	41
6	104.5	40.8	288.4	53.3 A	980	20	89.9	3	8.0	60	61	131	31	533	69
7	104.5	40.8	305.7	40.0 C	980	20	89.9	3	2.9	30	180	263	11	600	89
V8	104.5	40.8	307.9	40.0 C	980	20	89.9	3	0	–	620	–		600	100

[a] Measured by ultracentrifugation [42].
[b] Initial dispersion: solids content 49% weight, 99% BA-1% AA, d_p 169 nm.
[c] Surfactants A: sodium isododecylbenzenesulphonate 15% in aqueous solution; B: Dowfax 2A1 45% in aqueous solution; C: sulphonated sodium salt of octyl phenol ethoxylate (25 EO).
[d] NaOH 25% in aqueous solution.

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Table 6
Characteristics of latexes produced in Ref. [76]

Run	% Solids (w/w)	η (mPa s)	Cumulative fraction of particles (%) less than particles of d_p (nm)								
			<200	<300	<400	<500	<600	<700	<800	<900	<1000
1	57.5	95	23	24	40	55	65	74	82	87	94
6	56.7	95	33	35	48	60	67	74	79	84	88
7	55.5	17	15	22	38	88	98	99	100	–	–
8	55.1	20	13	17	23	55	92	99	100	–	–
9	55	55	33	38	48	70	83	92	95	97	99
10	55.2	21	9	17	22	50	85	96	98	100	–
11	55.4	19	15	19	23	45	81	95	98	100	–

bimodal latex with 13 wt% of small particles (186 nm) and 87% of larger ones (286 nm). Various formulations were described to prepare the miniemulsion, citing the use of hexadecane, styrene–butadiene block copolymers, and different grades of PBA as the hydrophobe. Some variations in the composition of the monomer mixtures are also described. The solid contents of the final latexes are in the range 60–70% and the viscosities are from 180 to 660 mPa s (at shear rate 250 s^{-1}).

Another group of authors from BASF claims a process for making high solid latexes based on the semi-batch feed of pre-emulsified monomer plus a seed [78]. The final latexes are most often with a solids content higher than 70% and viscosities in between 350 and 500 mPa s. They are said to be all coagulum-free with no visible bits in films made from them. However, with the exception of the exact feed flows, this patent is similar to a lot of the others taken out by BASF.

5. Modelling of high solid content latexes

As we have seen, HSC latexes are generally composed of either very broad or multimodal PSDs. If we
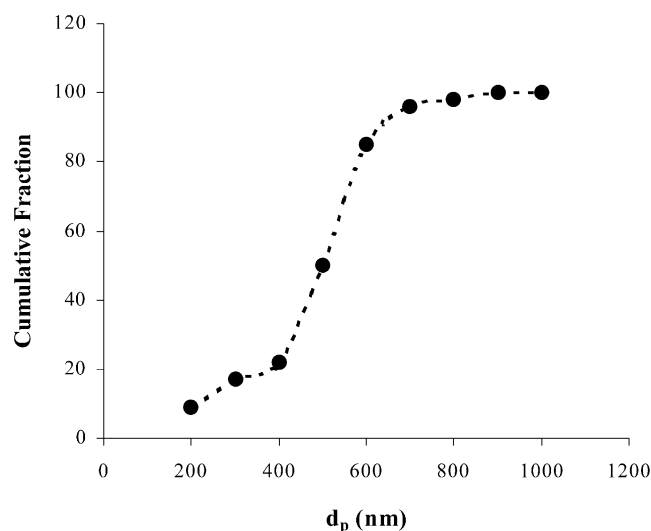

Fig. 11. Cumulative PSD of a bimodal latex: run 10 issued from Ref. [76] (Table 6).

accept for the moment that models of monodisperse latexes, then modelling HSC systems is 'simply' a matter of accounting for the influence of particle size on kinetics (and vice versa). The rate of homopolymerisation in an emulsion can be written as follows:

$$R_p = k_p[M_p] \sum_{n=0}^{\infty} \left(\frac{n}{N_A} N_n \right) \tag{14}$$

Here, the rate of reaction R_p is generally expressed in terms of moles of monomer consumed per litre of emulsion per second, N_n is the total number of particles per litre of reactor containing n radicals, N_A is Avagadro's number, and $[M_p]$ is the concentration of monomer in the growing particles. For monodispersed latexes, Eq. (14) is generally simplified to

$$R_p = \frac{k_p[M_p]N_p\bar{n}}{N_A} \tag{15}$$

where $N_p = \sum N_n$ is the total number of particles per litre of emulsion, and the average number of radicals per particle $\bar{n}$ is defined as:

$$\bar{n} = \frac{1}{N_p} \sum_{n=1}^{\infty} N_n n \tag{16}$$

Generally, it is the calculation of N_p and $\bar{n}$ that makes it more difficult to model the kinetics of emulsion polymerisation, especially when we are dealing with more complex systems. However, if we look at what determines the value of n, the number of radicals in a given particle, it will be clear that in systems with broad or multimodal PSDs, the notion of a single $\bar{n}$ for a given polymerisation has no sense. n will depend on the relative rates of the entry of radicals into the particle, on the rate of exit from the particle, and on the rate of termination inside it. The exact mechanisms of entry and exit are still open for discussion, and will depend on a number of chemical (i.e. number and concentration of monomers, surfactants, initiators, etc.) and physical (particle size, temperature, etc.) parameters. However, at the risk of oversimplifying things, the larger the particle, the higher the number of radicals it can accommodate (all other things remain constant). As an example, let us consider the approximation of general Stockmayer–O'Toole solution proposed by Ugelstad and Hansen [79]

$$n = (0.25 + \alpha_a/2)^{1/2} \tag{17}$$

where $\alpha_a = \sigma V_p N_A / k_t$. σ is the radical absorption rate; k_t, the termination rate inside the particles; V_p is the volume of a swollen polymer particle. Using the parameters given in Ref. [80] for a polymer weight fraction of 0.8 in the particles (interval III), we calculate the evolution of $\bar{n}$ for a styrene/polystyrene system at 50 °C that is shown in Fig. 12. This cannot, of course, be generalised to all polymerising systems, but serves to illustrate why the simplified approach of Eq. (2) is poorly adapted to HSC systems.

Depending on the PSD, there are different ways of approaching the modelling problem. Strictly speaking, the best approach to this problem is to use full population balance equations (PBE), which basically integrate the rate of polymerisation in particles of every size to calculate the rates of reaction, and thus particle growth. Different applications of these approaches have been discussed in the literature [81–83]. In the event that we are dealing with very broad PSD (monomodal or otherwise), this is probably the only technique that will allow us to model the evolution of the particle size and polymer concentration.
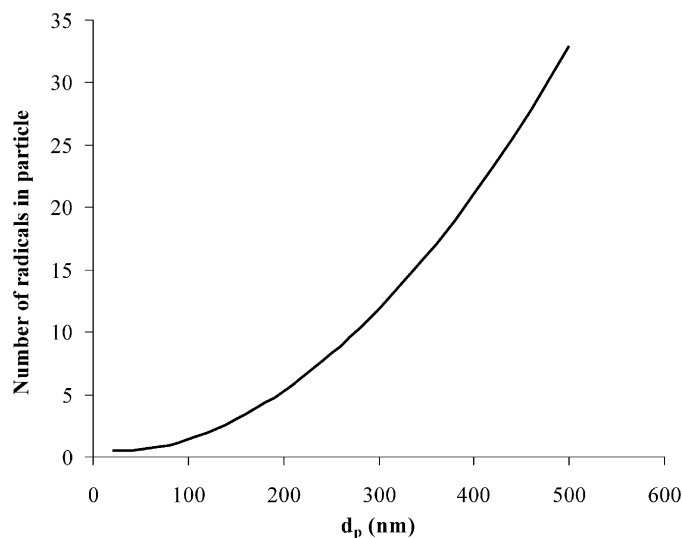
Fig. 12. $\bar{n}$ as a function of d_p for the emulsion polymerisation of styrene at 50 °C and using the parameters given in Ref. [80].

On the other hand, if we have a polymodal PSD which is composed of two or more well-defined, fairly narrow populations, it is probably sufficient to treat each population distinctly, and to assume that they will grow independently of the other populations. In this case, if we know the value of N_p for each population, we can use Eqs. (2) and (4), along with a mass balance to follow the evolution of particle size and the rate of polymerisation. This is what we have done in Fig. 13, where we see the evolution of the ratio of the diameters of large to small particles in a bimodal PS latex. The evolution of d_p for each
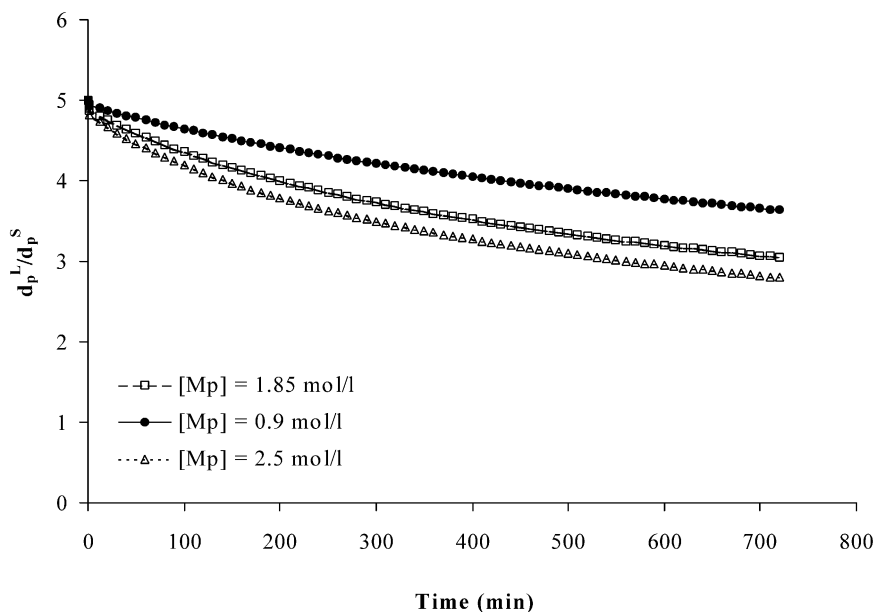

Fig. 13. Competitive growth of small and large particles of a bimodal PS latex with original particle sizes of 50 and 250 nm for different concentrations of monomer in the particles (all starved conditions), using $\bar{n}\,(d_p)$ shown in Fig. 12.

population was calculated using the parameters in Ref. [80] at 50 °C at slightly different monomer concentrations in the particles (it was assumed that $[M_p]$ was equal and constant for both populations). This figure shows that all other things being equal, the small particles tend to grow more quickly than the larger ones.

However, regardless of whether one chooses to use the full PBE approach, or the more simplified version, it is absolutely necessary to have accurate quantitative knowledge of the PSD in order to properly integrate the model equations. Even if one begins the reaction with a well-characterised seed (or blend of seeds), phenomena such as secondary particle formation via homogeneous or micellar nucleation, or particle flocculation/agglomeration can occur in many circumstances and cause the PSD to change by means other than simple particle growth due to polymerisation. In addition, it is entirely possible that quantities such as the concentration of monomer in the particles will also be a function of particle size, especially if we are dealing with systems that contain significant fractions of particles of different sizes (e.g. in Ref. [46], latexes commonly contained particles of 900 and 100 nm). It is, therefore, important to include the effect of particle size in a model for HSC latexes as well.

6. Concluding remarks

In spite of the practical interest of the synthesis of latexes with HSCs, such preparations remain more an art than a real science. It is possible to synthesise latexes with solid contents as high as 75 wt% with moderate viscosities, and mechanical emulsification processes are able to reach a polymer contents up to 95% with liquid polymers such as silicones. Even if many authors claim to possess reproducible procedures for this purpose, it is clear that a quantitative description of most of the parameters influencing the PSD remains outreach for now.

Nevertheless, it seems to be clear that in order to obtain high solid latexes with moderate or low viscosities, it is necessary to prepare latexes with multimodal or at least very broad PSD. In terms of relationship between PSD and viscosity, studies looking at blends of uniform particles have helped to lay down some rules concerning 'optimal' (or at least good) bimodal PSDs. Some indications also are known concerning trimodal blends for which the region of minimum viscosity in a ternary diagram has been located. In general, we want a PSD where the ratio between the large and small populations is between 6 and 8, and where the latexes contain 80 vol% of the large particle population (Fig. 3).

If we consider the synthesis of multimodal latexes, it seems clear that the easiest way to obtain the goal is to start with a blend of well-defined seeds, and to grow the particles to the desired size and concentration by feeding either emulsified or pure monomer into the reactor. A second, third, or fourth population of particles can be created by adding as many seeds as needed. These kinds of addition can be either shots or continuous streams (although experience dictates that it is easier to control latex stability when components, including seeds are added continuously, even for a short duration, rather than as shots). In the later case, one has a good chance of producing a broad PSD, especially if partially water-soluble monomers are part of the feed streams, as water-soluble species provoke homogeneous nucleation. This is essentially the same as continuously adding a seed of very small particles if the stabilisation system is good enough. However, as we discussed earlier, this can also be problematic since this type of secondary nucleation is difficult to control and reproduce reliably.

Of course, it is also possible to create second or third populations of particles in situ by adding enough surfactant, monomer and eventually initiator and soda to provoke the nucleation of small particles in the

presence of larger particles. This process is even harder to control than that based on blending and growing multiple seeds for a number of reasons that were presented earlier.

From a quantitative point of view, it is very difficult to know how to adjust the reaction parameters (monomer, initiator, surfactant concentration, buffer or no, etc.) in order to obtain a multimodal latex with well-defined PSD. There are many reasons for this, but they essentially turn around the problem of stabilisation and particle growth. At the present time, it is still not possible to adequately measure or model the particle stability of complex systems. This, coupled with a lack of information on particle nucleation and PSD characterisation, makes the task of knowing how to adjust the PSD without massive experimental work is extremely difficult. Only some trends can be safely stated, for instance, that a non-ionic surfactant is more useful to stabilise particles through a steric stabilisation mechanism than a anionic surfactant, which, in turn should be preferably used for provoking the nucleation of a new family of particles (but never alone—always with a certain amount of non-ionic surfactant.) For that reason, most academic studies do not describe examples of reproducible data on the synthesis of bimodal PSD latexes. Only the process reported by Schneider et al. [46] seems to have surmounted this problem, essentially by eliminating as much as possible the stabilisation of homogeneously nucleated particles. In other words, this process gives us complex, yet reproducible PSDs.

With the exception of the patents from BASF, most of the patent literature remains vague on the relationship between PSD (and how to create it), solids content and viscosity. The relatively large number of seemingly similar patents from BASF have a number of points in common: they often rely on the use of peroxide/AscA redox pairs (thereby reducing the stabilisation of homogenously nucleated particles), they have extremely precise and complex instructions for the addition of all types of process components (thus probably controlling the particle nucleation and growth stages as much as possible), and they all lead to extremely broad, or bimodal PSDs (in the case of bimodal PSDs, the ratio of the d_p of the large to small particles seems to be at least 4 in most cases). A large amount of effort seems to have gone into defining the feed protocols to adjust the final PSD (which are also claimed in the inventions) according to the type of monomers used and the final particle size desired.

It would seem that a number of points need to be mastered before we can pretend to be able to produce HSC latexes with complex PSDs.

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