In Situ Bimodal or Broad Particle Size Distribution Using Miniemulsion Polymerization

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ABSTRACT: Calculations for maximum volume fraction (φ_m) for a monomodal and a bimodal dispersion are given. These are extended to express the volume fraction of dispersed phase ($\varphi < \varphi_m$) for a bimodal distribution. By substituting the volume fraction, so obtained, various semiempirical laws relating relative viscosity to the volume fraction of the dispersed phase for monomodal dispersions can be extended to bimodal dispersions also. It was mathematically shown that the viscosity of a bimodal dispersion shows a minimum for a particular size ratio of small to large particles for a given relative number concentrations of small to large particles and the interspacing between the small and the large particles. Also, it was shown that an increase in the relative number concentrations of small to large particles, keeping the size ratio of small to large particles and the interspacing between the small and the large particles constant, always increases viscosity. These findings also have practical significance because they can be used to obtain high solid content dispersions with minimum viscosity. Candidate recipe and operating variables that can be varied to obtain either bimodal or very broad distributions through miniemulsion polymerization are finally identified. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 49–61, 2009

Key words: calculations; dispersions; lattice models; particle size distribution; viscosity

INTRODUCTION

Emulsions are dispersed systems with liquid monomer droplets (dispersed phase) in a liquid (continuous phase). Miniemulsion involves creating a stable emulsion of very small monomer droplets in the size range of 50–500 nm. The droplet is stabilized against Ostwald ripening (or molecular diffusion) and against coalescence by collisions. In creating a miniemulsion, diffusional stabilization is achieved by adding a small quantity of a highly monomer-soluble and water-insoluble agent, which is called a hydrophobe or costabilizer (cosurfactant in early literature). Stabilization against coalescence is provided by adding an appropriate surfactant. In miniemulsion polymerization, the polymerization process is initiated in small, stabilized nano-droplets. In 1973, Ugelstad et al.[1] were the first to publish results in which monomer droplets with sizes of less than 700 nm were nucleated, leading to polystyrene polymer particles of similar sizes and having a broad particle size distribution. Creation of miniemulsion droplets was obtained by stirring; sodium dodecyl sulfate (SDS) was used as a surfactant and cetyl alcohol (CA) was used as a costabilizer. Characteristics of miniemulsions can be summarized as follows: (1)

The creation of a miniemulsion requires high mechanical agitation or intense shear to reach a steady state given by rate equilibrium of droplet fission and fusion. (2) The osmotic stability of miniemulsion droplets results from an osmotic pressure in the droplets, which balances the Laplace pressure and thus prevents monomer diffusion. The osmotic pressure results from the addition of the hydrophobe or costabilizer, which has extremely low water solubility. Miniemulsions undergo structural changes to establish a situation of zero effective pressure. (3) The colloidal stability of miniemulsion droplets is achieved by adding a surfactant. The surface coverage of the miniemulsion droplets by surfactant molecules is not complete. The amount of surfactant required to form a polymerizable miniemulsion is small, usually between 0.5% and 25% with respect to the monomer phase. The miniemulsion polymerization process has the potential of revolutionizing the production of latexes with unusual performance characteristics. The various aspects and advantages of this polymerization process have been documented in the review papers of the leading researchers in this area.[2–6]

In this work, the potential of miniemulsion polymerization as a means to produce *in situ* bimodal or very broad particle size distribution is explored. This is based on our previous works.[7–10] In the first of these works,[7] we had found that the experimentally reported instability by Miller et al.[11,12] is due to a broad initial droplet size distribution in which,

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depending on the nonideality of the costabilizer-monomer system, the smaller fractions of the distribution may not be stable, leading to a bimodal droplet size distribution. Polymerization in such a droplet size distribution will lead to a bimodal particle size distribution as well. The stability criterion is based on the phenomenon of molecular diffusion or Ostwald Ripening and thermodynamics. In the works on the modeling of particle size distribution in miniemulsion polymerization,[8–10] we found that due to the slow and continuous nucleation period in this process, the final particle size distribution is broad as characterized by a large standard deviation and polydispersity index. The model was validated against the data of Choi et al.[13] and Miller et al.[11,14]

BACKGROUND

Durbin et al.[15] were the first to report that broad and, sometimes, bimodal particle size distributions, were obtained in some commercial processes in which the reactants were pre-emulsified prior to being charged into a reaction vessel. Fitch[16] discussed the phenomenon of diffusion degradation and how it leads to bimodal size distributions in the presence of water-insoluble components in the organic droplets. Since then, a number of workers[17–23] have reported bimodal particle size distributions formed as a result of miniemulsion polymerization. It has been experimentally found that bimodal particle size distributions can give latexes of high solid content and low viscosity.[24]

The advantages of high solid content latexes for application as Pressure Sensitive Adhesives (PSA) can be gauged from Table I, where tack and peel strength of three different PSAs having solid contents ranging from 45 to 55% are tabulated (PSAs used here were the terpolymers of vinyl acetate, 2-ethtyl hexyl acrylate and dioctyl maleate and dibutyl phthalate was used as a plasticizer) (Jubilant Organosys Ltd., Gajraula, India). It can be seen that the higher the solid content, the better the rolling ball tack and the higher the peel strength. The commercial latexes are prepared with solid contents between 40 and 55%. It will be useful to further increase the solid content as this will further increase the tack and the peel strength. Increasing the solid content also 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.[25] An increase in solid content also increases the shelf life of latexes and provides better surface coverage.

In the case of typical industrial products, the macroscopic viscosity remains fairly low for solid vol-

TABLE I
Rolling Ball Tack and Peel Strength of Pressure-Sensitive Adhesives Having Different % Solid Contents

PSA no.	% Solid content	Rolling ball tack (cm)	Peel strength (g/inch)
PSA-I	55%	7.48	870
PSA-II	50%	10.8	698
PSA-III	45%	10.9	379

ume 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. The problem of high viscosity at high solid content can be overcome by the use of bimodal particle size distribution of the dispersion[24–27] or using broad particle size distribution.[25,28–30]

So far, blending (i.e., large and small particle size latex blends) and *in situ* (i.e., by either surfactant or seed addition during polymerization) methods of preparation are used in conventional or macroemulsion polymerization for high-solids bimodal latexes.[31] Blending large volumes of the order of 1–10 metric tons in which specialty latex products for applications like adhesives, paints, etc., are made, is energy intensive. Besides, a number of factors must be considered in blending latexes. The emulsifier systems should be compatible. Further, if high pH latex is blended with low pH latex, latex shock will often result and the two latexes will coagulate. Even similarity of pH does not ensure latex compatibility. These problems can be obviated by creating *in situ* bimodal particle size distribution. As already stated, *in situ* methods of preparation, by addition of surfactant or seed during polymerization, are used in conventional emulsion polymerization. Few workers have developed bimodal particle size distribution models for emulsion polymerization reactors,[32–37] which can be of help in creating such distributions. Creating *in situ* bimodal particle size distribution using conventional emulsion polymerization requires a secondary nucleation stage that must be introduced by carefully manipulating the emulsifier feed rate above that required to stabilize the growing surface area of the first population of particles. Addition of surfactant, either continuously or as a shot addition, is not only cost intensive as surfactant is a costly component of recipe but it leads to the deleterious effects on certain specific properties of polymers produced by emulsion polymerization such as optical clarity, adhesion to substrates, and weather durability, etc. There is another problem

associated with *in situ* generation of second population of particles as discussed by Boutti et al.[38] They had mentioned that this type of process is often difficult to master, with highly irreproducible results and/or significant stability problems. Solids contents produced in this manner seem to be in the order of 65–68% (v/v) at best. Most of the difficulties associated with this type of process seem to stem from the destabilization of the latex due to rapid particle generation. This generation of a large number of small particles is often worsened by the fact that a good number of the applications for which high solid content latexes are used contain (partially) water-soluble monomers such as acrylic acid, itaconic acid, methyl methacrylate, and others. This type of product obviously favors the generation of particle via homogeneous nucleation throughout the reaction. In addition, the use of persulphates, or other compounds that generate electrically charged radicals, favors the creation of such small particles. In the event that a large number of small particles (with respect to the amount of surfactant available) are created rapidly, this can provoke a rapid and disastrous redistribution of the surfactant already present on the surface of the existing particles. If this happens, the latex can coagulate (totally or partially). And even if one only experiences a partial loss of stability, it can be very difficult to control the particle size distribution with the precision necessary to maintain good rheological properties at moderate to high solid contents.

Broad distributions can be obtained in conventional emulsion polymerization by varying the initial initiator amount, initial emulsifier amount, the reaction temperature, monomer addition mode (batch or semi-batch) or monomer feed rate. A low initial initiator amount or a high emulsifier amount or low reaction temperature or addition of monomer in batch mode rather than semi-batch mode and faster addition of monomer in semi-batch mode leads to broader distributions, as found through modeling studies.[39,40] However, compared with the broadness of the distribution obtained using miniemulsion polymerization as characterized in terms of the standard deviation and the polydispersity index, the breadth of the distribution in emulsion polymerization is low.[8–11,39,40] Thus, the miniemulsion polymerization process offers a greater advantage over conventional emulsion polymerization process in obtaining very broad particle size distributions.

Thus, a means of obviating the aforementioned problems of conventional emulsion polymerization can be offered by miniemulsion polymerization in creating high-solid, low-viscosity latexes with bimodal or broad particle size distribution. Initially, the author has theoretically shown, by assuming a cubic lattice model, how bimodal distribution can
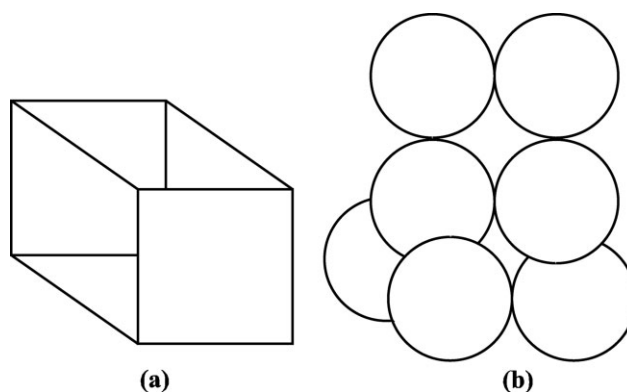

Figure 1 Simple cubic lattice of dispersion with one size fraction.

lead to high solid content and low viscosity. The previously published criterion[7] for creating bimodal distribution using miniemulsion polymerization is followed by exploration of variables that can be manipulated to yield a desired bimodal particle size distribution. The broadness of particle size distribution obtained using miniemulsion polymerization is discussed.

Bimodal distribution as a route to produce high solid content latexes

Volume fraction (φ_m) for maximum packing density is calculated, first for a monomodal size distribution (particles of one size) and then for a bimodal distribution (particles of two different sizes). It is assumed that particles of one size are packed in a simple cubic lattice occupying its eight corners, as shown in Figure 1.

If R is the radius of one particle and L is the length of one side of the cube, $L = 2R$. Each cube has eight particles at eight corners and they contribute 1/8th of their volume to a cube. So, effective particle per cube = $8 \times 1/8 = 1$ and therefore, effective particle volume per cube = $4/3\pi R^3$. Volume of cube is $L^3 = (2R)^3 = 8R^3$. So, maximum packing fraction:

$$\varphi_m = \text{Volume of particles in a cube/Volume of a cube}$$
$$= 4/3\pi R^3/8R^3 = \pi/6 = 0.523 \quad (1)$$

Now, consider a small particle of radius, r, occupying the center of cube, which is the interstitial space between large particles as shown in Figure 2. Length of the main diagonal of the cube = $D = \sqrt{(L^2 + L^2 + L^2)} = \sqrt{3}\,L$, which is also equal to $2(R + r)$. Also, $L = 2R$. Therefore, $(R + r) = \sqrt{3}\,R$, or, $r = (\sqrt{3} - 1)R = 0.732R$. There is one small particle in the cube with volume equal to $4/3\pi r^3$. There are eight large particles at the eight corners of the cube, each contributing 1/8th of its volume to the cube. So,
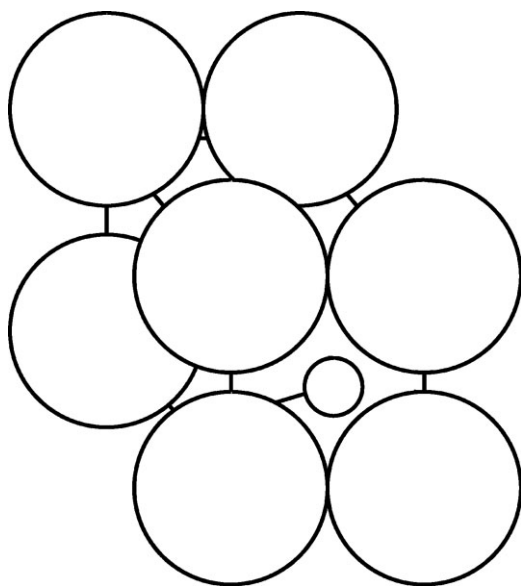
Figure 2 Body-centered cubic lattice with two size fractions.

effective number of large particles in the cube is 1 with volume $4/3\pi R^3$. Volume occupied by particles in the cube = $4/3\pi(R^3 + r^3) = 4/3\pi R^3(1 + 0.732^3)$. Volume of the cube is $L^3 = 8R^3$. Therefore, maximum closed pack volume fraction:

$$\varphi_m = \text{Volume of particles in a cube/Volume of a cube}$$
$$= 4/3\pi R^3(1 + 0.732^3)/8R^3 = 0.726 \quad (2)$$

Thus, maximum volume fraction that one can obtain from a bimodal distribution is quite high. The relative number concentration of small to large particles ($n : N$) for this high volume fraction is 1 : 1, the size ratio($r : R$) is 0.732, the volume ratio (nr^3: NR^3) is $(0.732)^3 = 0.392$ and the volume fraction ($nr^3/(nr^3 + NR^3) = 0.392/[1 + 0.392]$) is 0.282. Thus, the volume fractions of the small-sized fraction particles, the large-sized fraction particles (in the above size ratio), and the continuous phase are 0.203 (= 0.282 × 0.726), 0.523 (= 0.726 − 0.203), and 0.274 (= 1.0 − 0.203 − 0.523), respectively.

One may question the use of a body centered cubic lattice for representing the geometric model of particle arrangement for latex. However, this concept is not new. Various geometric arrangements ranging from cubic to hexagonal to random spheres have been used in calculating the maximum packing efficiency of dispersions.[41] Cubic lattice has been used in other studies as well. Singh et al.[42] used a theoretical model to predict effective heat storage coefficient of multiphase systems that was applied to emulsions, suspensions, and loose granular systems by assuming spherical particles arranged in three-dimensional body centered cubic

lattice. Meyer[43] discussed the use of face centered cubic lattice and hexagonal lattice for the theoretical study of latex film formation. Goh et al.,[44] while studying the annealing effect on surface structure of latex films formed by poly(butyl methacrylate) using atomic force microscopy, found that the film surfaces were highly ordered, consistent with face-centered cubic packing in the film interior. Carbajo et al.[45] obtained assemblies of spherical particles from suspensions of polystyrene, poly[styrene-co-(2-hydroxyethylmethacrylate)], poly[styrene-co-acrylic acid], and poly[styrene-co-methacrylic acid], by elimination of the solvent in different ways—evaporation, gravity deposition, and filtration. These latex particles' packing was characterized by scanning and transmission electron microscopy and by gas adsorption to determine the efficiency of packing. The surface area, total pore volume, and pore size distributions obtained from the adsorption and desorption data were related to characteristic parameters calculated for cubic close-packed spherical particles.

Guyot et al.,[25] in their review of high solid content latexes, stated that it might be theoretically possible to develop a model to calculate the maximum packing fraction (φ_m). One serious problem associated with the application of semiempirical equations relating viscosity of concentrated fraction (as given later) is that they involve the maximum packing fraction (φ_m). However, they have further discussed that this is very difficult, and the straightforward way seems to be experimental validation. However, there is no simple method available to measure φ_m for the case of emulsions. Extrapolation of viscosity data, as is done in the case of suspensions, can give seriously erroneous results in the case of emulsions.[46] The values calculated here for monomodal and bimodal distributions can be used in these equations.

Bimodal distribution as a route to produce latexes with lower viscosity

Now, we come to the problem of finding the optimal bimodal particle size distribution that minimizes viscosity. Consider N large particles of size R and $n(<N)$ small particles of size r. These N particles are situated at the corners of N cubes. Let n such cubes have n small particles at the center interspersed between large particles with inter-space H between a large and the small particle along the main diagonal whose length = $\sqrt{3} L = 2(R + r + H)$. Now, total particle volume in such cubes is $n \times 4/3\pi(R^3 + r^3)$. We also have N-n cubes with total particle volume = $(N − n) \times 4/3\pi R^3$. Therefore total particle volume = $n \times 4/3\pi(R^3 + r^3) + (N − n) \times 4/3\pi R^3$

$= 4/3\pi(NR^3 + nr^3)$ and the total volume is NL^3 $= 8/3\sqrt{3}\, N(R + r + H)^3$. Therefore, volume fraction $\varphi = \sqrt{3}\pi/2(R^3 + n/Nr^3)/(R + r + H)^3 = \sqrt{3}\pi/2\,[1 + n/N(r/R)^3]/(1 + r/R + H/R)^3$. Defining $C_1 = \sqrt{3}\pi/2$ and $C_2 = (1 + H/R)$, and $x = r/R$, we have

$$\varphi = C_1(1 + n/Nx^3)/(C_2 + x)^3 \qquad (3a)$$

For $n > N$, the expression can be derived as follows. Again the total particle volume will be $4/3\pi(NR^3 + nr^3)$. The total volume in this case will be $nL^3 = 8/3\sqrt{3}\, n(R + r + H)^3$. Therefore, volume fraction, $\varphi = \sqrt{3}\pi/2(N/n\, R^3 + r^3)/(R + r + H)^3 = \sqrt{3}\pi/2\,[N/n + (r/R)^3]/(1 + r/R + H/R)^3$, or:

$$\varphi = C_1(N/n + x^3)/(C_2 + x)^3 \qquad (3b)$$

Note that for $n = N$, both the expressions reduce to the same expression. A number of empirical or semiempirical correlations have been proposed relating the relative viscosity of the dispersion to its volume fraction. These have been reviewed by Guyot et al.[25] and Pishvai et al.[41] Figure 3 plots the data for viscosity of polyvinyl acetate (PVAc) emulsion at different volume fractions of polymer particles dispersed in water. The first sample was obtained by emulsion homopolymerization of vinyl acetate monomer in the presence of "mixed emulsifier system" consisting of the steric stabilizer polyvinyl alcohol and anionic emulsifier sodium dodecyl sulfate with potassium per sulfate as the initiator and di-ionized water as the dispersion medium, in a 50-L pilot plant reactor.[47] The solid content of this sample was determined gravimetrically. 200 g of this sample was diluted by adding di-ionized water ranging from 4 to 10 g incrementally and thus various other samples were obtained. Their solid contents were also measured gravimetrically. The viscosity of these samples was measured by Brookfield viscometer. The solid content (X) was changed into volume fraction (φ) by using the following formula:

$$\varphi = (X/100)/[(\rho_p - (\rho_p - \rho_w)x/100] \qquad (4)$$

Here ρ_p is the density of polyvinyl acetate ($= 1.15$ g/cm^3) and ρ_w is the density of water ($= 1$ g/cm^3).

As can be seen, the plot is a parabola. Let us choose the relation:

$$\eta_r = 1 + a\varphi + b\varphi^2 \qquad (5)$$

for relative viscosity ($\eta_r = \eta_{\text{emulsion}}/\eta_{\text{continuous phase}}$), which also gives parabolic dependence of viscosity versus volume fraction. The relationship was given by Vand[48] in 1945 and assumes hard sphere dispersions. Here $a = [\eta] = 2.5$, where $[\eta]$ is the intrinsic viscosity and b is an adjustable parameter. Also, it can be seen from the graph, if one extrapolates
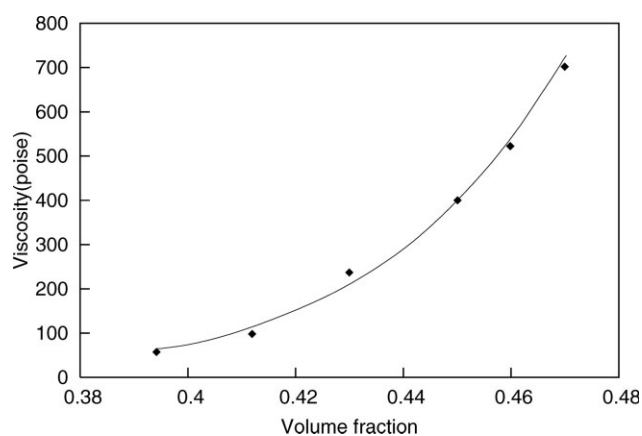

Figure 3 Variation of viscosity of emulsion with volume fraction.

this graph beyond volume fraction of 0.47, the viscosity will become infinity at volume fraction close to 0.523, the maximum volume fraction for a monomodal distribution that we have calculated. Although the full distribution was not measured, the average particle size of this sample was 1.97 μm, as measured using disc centrifuge combined with light scattering. The distribution was obtained through a combination of homogeneous-coagulative nucleation mechanism[47] and is expected to be narrow and monomodal. Pishvaei et al.[49] experimentally determined that for latex of polystyrene homopolymer produced in a semi-batch reaction that lasted for 12 h, using Disponil® 3065 (mixture of linear ethoxylated fatty acids) as the nonionic surfactant, $\varphi_m = 0.553$, which is close to the theoretically developed value of 0.523, determined in this work for monomodal distribution.

To account for the feature that as $\varphi \rightarrow \varphi_m$, $\eta \rightarrow \infty$, we can modify eq. (5) as follows:

$$\eta_r = (1 + a\varphi + b\varphi^2)/(1 - \varphi/\varphi_m) \qquad (6)$$

For our purpose, we will use eq. (5). Substituting the value of φ obtained in eqs. (3a) and (3b) in eq. (5), we obtain:

$$\eta_r = 1 + a[C_1(1 + n/Nx^3)/(C_2 + x)^3] \\ + b[C_1(1 + n/Nx^3)/(C_2 + x)^3]^2 \qquad (7a)$$

$$\eta_r = 1 + a[C_1(N/n + x^3)/(C_2 + x)^3] \\ + b[C_1(N/n + x^3)/(C_2 + x)^3]^2 \qquad (7b)$$

This is the model for viscosity of bimodal dispersions based on the cubic lattice model. Here, the

relationship given by Vand is used.[48] For hard-sphere systems, the volume fraction dependence on the relative viscosity given by other semiempirical equations, as given later, could have been used. Thus the relative viscosity is a function of parameter a, b, $C_2(= 1 + H/R)$, n/N and $x = r/R$. In experimental studies, one is interested in finding the effect on viscosity of dispersion of relative proportion of small to large particles (n/N) keeping their relative size constant (i.e., x = constant) and inter-space distance constant or of relative size of small to large particles (x) keeping their relative proportion constant (i.e., n/N = constant) and inter-space distance constant. Let us see the effect of each of these variables individually, keeping the other constant.

For minimum viscosity, $d\eta_r/dx = 0$ and $d^2\eta_r/dx^2 > 0$ (keeping n/N and H/R constant).

$$d\eta_r/dx = d\eta_r/d\varphi \times d\varphi/dx \qquad (8)$$

Now, $d\eta_r/d\varphi > 0$ (relative viscosity always increases with increase in volume fraction as seen experimentally) and therefore, $d\varphi/dx = 0$ that gives after some algebraic manipulations:

$$x^2 = (r/R)^2 = 1/(C_2 n/N) = 1/[n/N(1 + H/R)] \qquad (9)$$

Differentiating both eqs. (3a) and (3b) will give us the same result as in eq. (9). Thus, the above relation defines the optimum size ratio that gives minimum viscosity that is a function of relative numbers of the two sized particles (n/N), distance between the small and large particles (H), and the size of large particles (R). This analysis shows that an optimum bimodal size distribution does exist that can give minimum viscosity. That bimodal particle size distributions can lead to minimum viscosity is considered as a rule of thumb[26]; however, mathematical proof of this concept using a very simple model is presented.

Now let us look at the effect of n/N on viscosity.

$$d\eta_r/d(n/N) = d\eta_r/d\varphi \times d\varphi/d(n/N) \qquad (10)$$

Again, $d\eta_r/d\varphi > 0$ and $d\varphi/d(n/N) = C_1 x^3/(C_2 + x)^3$, which is always positive, can never be equal to zero. Thus, $d\eta_r/d(n/N) = d\eta_r/d\varphi \times d\varphi/d(n/N)$ is a positive number. Hence, we deduce that increasing the proportion of small particles (fines) relative to large particles (coarse) (keeping their size ratio constant) will always increase the viscosity, and no minimum will be seen. This is also a rule of thumb that increasing the proportion of small particles (fines) relative to large particles (coarse) increases the viscosity. It has been stated by Boutii et al.[38] that one must avoid creating fines in the reactor, as this would increase the viscosity and complicate the problem. Here, mathematical proof in support of

this well-known fact is provided. Here, eq. (3a) is used for φ. If we use eq. (3b) for φ, and differentiate with respect to N/n, again we will see that $d\eta_r/d(N/n) = d\eta_r/d\varphi \times d\varphi/d(N/n)$ is positive. So if $n > N$, increasing the proportion of larger particles compared with smaller particles will increase the viscosity.

Let us come to see the effect of inter-space distance on viscosity. Differentiating η_r with respect to H/R is same as differentiating with respect to C_2. We have:

$$d\eta_r/dC_2 = d\eta_r/d\varphi \times d\varphi/dC_2 \qquad (11)$$

Again $d\eta_r/d\varphi > 0$ and $d\varphi/dC_2 = -3\varphi/(C_2 + x) < 0$. Therefore, $d\eta_r/dC_2$ is negative, which implies that on increasing inter-space distance, the relative viscosity will decrease and vice versa. This is intuitively sound.

Validation of the minimum viscosity relationship

Let us test eq. (9). The work of Schneider et al.[50] has shown that latexes composed of 85% (v/v) of large particles and 15% (v/v) of small particles offer satisfactory results when the ratio of the diameters of large to small particles is between 4 and 8. Thus, $v_{small}/v_{large} = nr^3/NR^3 = 0.15/0.85$ or $n/N = (0.15/0.85)(R/r)^3$. Using the value of R/r as 4, we get $n/N = 11.3$. Substituting this value in eq. (9) and assuming $H \ll R$ (a valid assumption at high volume fraction of the dispersed phase), we get $R/r = 3.36$, which is quite close to 4. Similarly, using the value of R/r as 8, we get $n/N = 90.4$. Substituting this value in eq. (9) and assuming $H \ll R$, we get $R/r = 9.5$, which is quite close to 8. Greenwood et al.[51] studied the effect of composition (i.e., the volume of small particles compared with the volume of large particles) on the rheological properties of a bimodal dispersion using two monodisperse polystyrene lattices. The diameter ratio of these lattices was 4.76. The relative high shear rate viscosity and dynamic viscosity of these bimodal dispersions were measured using the Bohlin VOR. First, the rheology of the two monomodal dispersions was measured as a function of volume fraction, then 10 compositions ranging from 10 to 35% small particles by volume were prepared and again the rheology was followed as a function of volume fraction. A minimum in the relative high shear rate limiting viscosity was found in the range 15–20% by volume of small particles and another minimum was also found at 20% by volume of small particles for the dynamic viscosity measurements. Thus, it was concluded that reductions in viscosity can be achieved with a bimodal dispersion with the small particles occupying 20% of the total volume fraction. This was in agreement with other

TABLE II
Optimum Value of Various Parameters for Minimum Viscosity of a Bimodal Distribution

R/r	n/N	v_{small}/v_{large}	v_{small}/v_{large} (%/%)
2	4	0.5	33.3/66.7
3	9	0.333	25/75
4	16	0.25	20/80
5	25	0.2	16.67/83.33
6	36	0.167	14.3/85.7
7	49	0.143	12.5/87.5
8	64	0.125	11.11/88.89
9	81	0.111	10/90
10	100	0.1	9/91
15	225	0.067	6.25/93.75
20	400	0.05	4.76/95.24
50	2,500	0.02	1.96/98.04
100	10,000	0.01	1/99

studies. Thus, here $v_{small}/v_{large} = nr^3/NR^3 = 0.2/0.8$ or $n/N = (0.25)(R/r)^3$. Using $R/r = 4.76$ as used by them, we find $n/N = 26.96$. This, when substituted in our relation for optimum size ratio, gives $r/R = 5.19$, which is close to 4.76. Also, we can deduce that for small particle volume fraction (relative to large particles) greater than 39.2% (the maximum closed pack volume fraction of small particles relative to large particles for close pack body centered cubic lattice, as calculated in the section above, is 0.392), we would not see a minimum in viscosity for any size ratio. This was found by Greenwood et al.[52] in another experimental study in which they did not see a decrease in viscosity of bimodal dispersion compared to the viscosity of constituent monomodal dispersions for any size ratio for 50 and 75% composition (small particles by volume relative to large particles). The decrease in viscosity was seen only for bimodal dispersion with 25% composition.

For hard-sphere systems, the volume fraction dependence on the relative viscosity given by the semiempirical Krieger-Dougherty equation[53] [eq. (12)] or by the modified Quemeda equation[54] [eq. (13)] could be used:

$$\eta_r = (1 - \varphi/\varphi_m)^{-[\eta]\varphi_m} \tag{12}$$

$$\eta_r = (1 - \varphi/\varphi_m)^{-\varepsilon} \tag{13}$$

$[\eta]$ is the intrinsic viscosity (which is equal to 2.5 for hard-sphere systems), and ε is an adjustable parameter which usually remains in the range 1.4–3.[55] Again, we can see that $d\eta_r/d\varphi \neq 0$ and we would reach to the same conclusions as was reached above using eq. (5). The Krieger-Dougherty equation is the most popular and widely quoted equation for concentrated solids-in-liquid suspensions. It has also been used for emulsion systems.[56,57] The above relation assumes hard sphere dispersion. Thus, the optimum ratio defined by eq. (9) is independent of the semiempirical relation used for expressing viscosity (or relative viscosity) as a function of volume fraction. It is based on the principle of minimization of dispersed phase volume fraction (φ) with respect to the size ratio of the small and large particles (x) or $d\varphi/dx = 0$, for a given relative number concentrations of small to large particles (n/N) and the interspacing between the small and the large particles (H/R). Table II gives the various optimum parameters that would give minimum viscosity. For the optimum size ratio, R/r, $n/N \approx (R/r)^2$ [assuming $H \ll R$] and $v_{small}/v_{large} = nr^3/NR^3 = r/R$. Also, $v_{small} < 39.2\%$. In Figure 4, $y = \ln(\eta_r)$ versus $x = \ln(1 - \varphi/\varphi_m)$ is plotted using the data given in Figure 3. The value of φ_m is taken as 0.523, which is calculated for monomodal particle size distribution and viscosity of continuous phase, taken as 1 poise.[47] The continuous phase here consists of de-ionized water with dissolved monomer, which was vinyl acetate, poly (vinyl alcohol), sodium dodecyl sulfate, and potassium persulfate. The slope of the straight line, passing through the origin gives the value of ε, which in our case is $2.9672 \approx 3$.

Electro-viscous effects

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 are faced with a situation in which 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
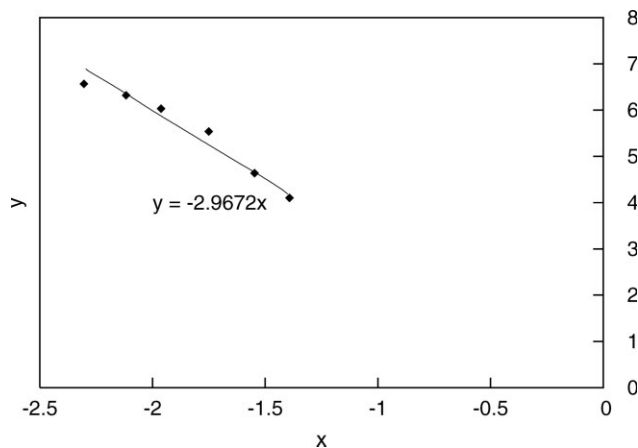

Figure 4 Plot of $y = \ln(\eta_r)$ versus $x = \ln(1 - \varphi/\varphi_m)$.
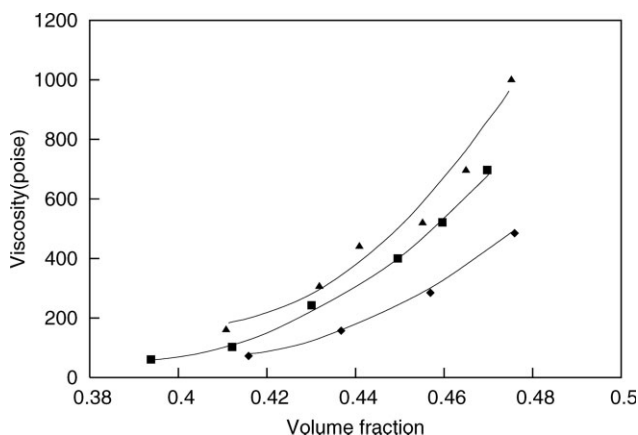
Figure 5 The variation of viscosity with volume fraction for latexes with different particle sizes particle size = 1.94 μm (triangle), particle size = 1.97 μm (square), particle size = 2.0 μm (diamond).

the effective particle diameter to an extent that depends on number of features. These features are called electro-viscous effects.[25]

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 double layer can be calculated[25]:

$$\varphi_{eff} = \varphi(1 + \kappa^{-1}/R)^3 \tag{14}$$

where κ^{-1} is the thickness of the double layer. 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 inter-particle distance. The smaller the particle size, the more the particles, and hence, the smaller the inter-particle distance and therefore, the higher the viscosity will be. Figure 5 plots the viscosity versus volume fraction curves for latexes with three different particle sizes. The polymer used

was polyvinyl acetate with polyvinyl alcohol as stabilizer.

The double layer, on the other hand, is essentially independent of the particle size, and its thickness is κ^{-1}. The square of the inverse double layer thickness is given by:

$$\kappa^2 = \frac{2\pi e_L N_A I_e}{\varepsilon_0 \varepsilon_r k_B T} \tag{15}$$

where e_L is the electronic charge, N_A is the Avogadro's number, ε_0 is the permittivity of vacuum and ε_r is the dielectric constant of the dispersion medium, k_B is the Boltzmann's constant, and T is the absolute temperature. The double-layer thickness is a sensitive function of the concentrations and valancies of the ions of the medium, which is expressed in terms of ionic strength I_e of the dispersion medium. The ionic strength is given as

$$I_e = \frac{1}{2}\sum_{j=1}^{n}\left(C_{+j}Z_{+j}^2 + C_{-j}Z_{-j}^2\right) \tag{16}$$

where C is concentration of ions and Z is the valency.

The subscripts $+j$ and $-j$ stand for the positive ion of component j and the negative ion of component j in the dispersion medium, respectively. For aqueous solutions at $T = 300$ K, the equation for κ^2 is given by:

$$\kappa^2 = 10.822\, I_e \;\left(\mathrm{nm}^{-2}, I_e \text{ in } M\right) \tag{17}$$

The highest value of the ionic strength in a miniemulsion reactor is 10 mM (8 mM arising from 2.66 mM of initiator potassium persulfate (highest initiator concentration used),[8–11,13,14] whereas the surfactant dissolved in the aqueous phase contributing the remaining 2 mM). Substituting this in the above eq. (15), we get $\kappa^{-1} = 3.04$ nm. Table III shows the calculated effect of κ^{-1}/R on φ_{eff}. As can be seen, the contribution of κ^{-1}/R to effective volume fraction, φ_{eff}, cannot be neglected for the range of droplet or

TABLE III
Effective Volume Fraction

R (nm)	κ^{-1}/R	φ_{eff}
5	0.608	4.158φ
10	0.304	2.217φ
15	0.203	1.174φ
20	0.152	1.523φ
25	0.122	1.411φ
30	10.4	1.134φ
40	0.076	1.246φ
60	0.050	1.160φ
80	0.038	1.118φ
100	0.030	1.094φ
250	0.0122	1.037φ

particle sizes obtained in miniemulsion polymerization, and it becomes very significant for smaller radii. The highest ionic strength is considered. Since κ^{-1} varies inversely with the square root of ionic strength, this effect will be even more significant for low ionic strengths (or initiator concentrations).

In the case of a steric stabilizer such as polyvinyl alcohol, the particles are coated with a thin layer of adsorbed stabilizer. If we recalculate the effective volume fraction, φ_{eff}, based on the adsorbed layer thickness, Δ, using the following equation[58]:

$$\varphi_{eff} = \varphi(1 + \delta/R)^3 \qquad (18)$$

Again, we will see that the effect of adsorbed layer cannot be neglected if $\delta \approx 3$ nm or higher.

Miniemulsion polymerization as a route to produce bimodal distribution

As already stated, in our previous work,[7] we had shown that the experimentally reported instability by Miller et al.[11,12] is due to a broad initial droplet size distribution where depending on the nonideality of the costabilizer monomer system, the smaller fractions of the distribution may not be stable leading to a time-varying bimodal droplet size distribution. Polymerization in such a droplet size distribution will lead to a bimodal particle size distribution as well. The stability criterion is based on the phenomenon of molecular diffusion or Ostwald Ripening and thermodynamics. These were presented earlier. The derivation of the minimum stable diameter which is defined as the cutoff diameter is given again; droplets having diameters above this diameter will be stable against degradation by molecular diffusion and the droplets having diameters below this diameter will be unstable. Thus, depending on the system parameters (which will be discussed further), two populations of droplets are created. Polymerization in these two populations will lead to bimodal distributions that have been reported by a number of workers.[15,17–23]

The process of molecular diffusion, in general, is governed by the difference between the chemical potential of the diffusing substance (monomer in our case) in the two phases. The chemical potential of monomer, μ, in a monomer droplet of diameter, d, with volume fraction of costabilizer, φ_c, is given by[59]:

$$\mu = \ln(1 - \varphi_c) + (1 - m_{mc})\varphi_c + \chi_{mc}\varphi_c^2 + \frac{4\gamma V_m}{dRT} \qquad (19)$$

where m_{mc} is the ratio of equivalent number of molecular segment, χ is the interaction parameter, V_m is the molar volume of the monomer, γ is the interfacial tension, R is the universal gas constant, and T is

the temperature The above equation is based on Flory-Huggins Lattice theory of polymer solutions[60] and extension of Morton et al.[61] involving addition of an interfacial energy term for spherical phases, and further extension of Ugelstad et al.[62] for phases not involving polymer as one of their components. The first three terms in this equation represent the partial molar free energy of mixing with the first two terms representing the entropy of mixing and the third term representing the enthalpy of mixing to take into account the nonideality between the two constituents, the monomer and the costabilizer. The interaction parameter, χ, provides a measure of the nonideality of the system; the larger the value of χ, the greater the nonideality. The fourth term represents the partial molar free energy of swelling. Let us define $\alpha = 4\gamma V_m/RT$.

In the presence of costabilizer, the equality of chemical potential of droplets of two sizes will require that the chemical potential of the small droplet should decrease and the chemical potential of the large droplet should increase as their size change due to molecular diffusion. Mathematically, this criterion requires that the chemical potential should be an increasing function of size,[63] or:

$$\frac{d\mu}{dd} > 0 \qquad (20)$$

Considering the equation for chemical potential of monomer(expressed in terms of the volume fraction of the costabilizer, φ_c), and noting that for the first three terms, it is convenient to write $d\mu/dd$ as $d\mu/d\varphi_c \times d\varphi_c/dd$, and further noting that $\varphi_c d^3 = \varphi_{co}d_0^3$ (costabilizer amount in a droplet remains unchanged), where φ_{co} is the initial costabilizer volume fraction and d_0 is the initial droplet diameter, we can write $d\varphi_c/dd = -3\varphi_{co}d_0^3/d^4 = -3\varphi_c/d$, which gives:

$$d\mu/dd = [-1/(1 - \varphi_c) + (1 - m_{mc}) + 2\chi\varphi_c](-3\varphi_c/d)$$
$$- \alpha/d^2 > 0 \qquad (21)$$

or:

$$\alpha/d < [-1/(1 - \varphi_c) + (1 - m_{mc}) + 2\chi\varphi_c](-3\varphi_c) \qquad (22)$$

After inverting, we get:

$$d > \frac{\alpha}{[1/(1 - \varphi_c) - (1 - m_{mc}) - 2\chi\varphi_c](3\varphi_c)} \qquad (23)$$

Thus, droplets with diameter greater than the minimum stable diameter, given by the equality in the above equation, fulfill the requirement for stability, $\partial\mu/\partial d > 0$ and will be stable; droplets with diameter less than the minimum stable diameter will not be stable.

TABLE IV
Discrete Broad Normal Distribution (Mean: 100 nm,
Standard Deviation: 50 nm)

Size range (nm)	Mean size (nm)	Fraction of droplets
38–62	50	0.23
63–87	75	0.175
88–112	100	0.2
113–137	125	0.175
138–162	150	0.23

Effect of system parameters on minimum stable diameter

Let us see the effect of each of the system variables on the value of minimum stable diameter. As can be seen from eq. (23), a low value of φ_c, a low value of $T(\alpha = 4\gamma V_m/RT)$, high value of γ, high value of $V_m(= MW_m/\rho_m)$, high value of m_{mc}, and high value of χ_{mc} will increase the minimum stable diameter and a greater proportion of droplets below this diameter will be unstable. For the sake of discussion, we assume a broad normal distribution characterized by a mean diameter of 100 nm and a standard deviation of 50 nm. The normal or Gaussian distribution is by far the most commonly used, and it arises when a large number of purely random factors are responsible for the distribution. The probability density function, $P(d)$, of the normal distribution is expressed as:

$$P(d) = \frac{1}{\sqrt{(2\pi)}\sigma} \exp \frac{[-(d - d_m)^2]}{2\sigma^2} \qquad (24)$$

where d is the size variable, d_m is the mean, and σ is the standard deviation The fraction of the droplets between sizes d_1 and d_2 is given by $\int P(d)dd$, integrated from d_1 to d_2. The normal distribution is further discretized into five classes for the above case i.e. $d_m = 100$ and $\sigma = 50$ nm, and the result is given in Table IV. IMSL MATH/LIBRARY version 1.1 Fortran subroutine ANORDF (Absoft Corporation, Rochester Hills, MI) was used to discretize the droplet size distribution and obtain the above results. It can be further assumed that the fraction of droplets in each of the five classes can be taken equal to 0.2. Let us consider the recipe given in Table V in creating the droplets. The relevant parameters of this sys-

TABLE V
Recipe for Miniemulsion Polymerization

Ingredient	Amount
Styrene (monomer)	5.66 mL
Water	17.69 mL
Sodium dodecyl sulfate (surfactant)	10 mM[a]
Hexadecanol (costabilizer)	30 mM[a]

[a] Based on water.

TABLE VI
Values of Parameters

Parameter	Value
MW_m	104.4
MW_c	242.4
m_{mc}	0.41
χ_{mc}	1.69
γ	3.41 dyne/cm
ρ_m	0.860 g/cm^3
ρ_c	0.818 g/cm^3

tem are given in Table VI. For this system $V_m = MW_m/\rho_m = 104.4/8.860 = 121.4$ cm^3/mol. With $T = 298$ K (25°C), $\alpha = 4\gamma V_m/RT = 0.6154 \times 10^{-7}$ cm. Let us vary the costabilizer amount from 5 to 30 mM for these base parameters. We see from Table VII that for costabilizer amounts between 15 and 30 mM, the entire discretized distribution is stable but for costabilizer amount of 10 mM, 20% of the droplets are unstable and costabilizer amount of 5 mM, 60% of the droplets are unstable. Let us now vary the temperature from 5 to 25°C for the costabilizer amount of 30 mM and all the other parameters having value given in Table VI. As we see from Table VIII, changing the temperature does not have much effect on minimum stable diameter (however, γ and χ are also functions of temperatures). Let us now vary the interfacial tension, which can be varied in practice by varying the surfactant amount, from 3.49 to 40 dynes/cm, keeping other parameters same. The interfacial tension of styrene with water (at 25°C) is around 40 dyne/cm. As can be seen from Table IX, until 5 dyne/cm, the distribution is stable; at 10 dyne/cm, 20% of the droplets will become unstable; at 20 dyne/cm, 60% droplets will become unstable; and at 30 dyne/cm and above, the entire distribution will be unstable. Let us now see the effect of interaction parameter on the minimum-stable diameter. We choose two values, 0 and 1.69. The value of 0 corresponds to an ideal monomer costabilizer system and the value of 1.69 corresponds to a nonideal one. As can be seen from Table X, at high costabilizer amount, the nonideality has no effect on the stability of the droplets but at low costabilizer amounts, the nonideal system is more unstable

TABLE VII
Minimum Stable Diameter and % Unstable Droplets as a
Function of Costabilizer Amount

Costabilizer amount (mM)	Volume fraction	Minimum stable diameter (nm)	% Unstable droplets
5	0.00461	110.8	60%
10	0.00918	57.2	20%
15	0.01370	39.4	0%
20	0.01820	30.5	0%
30	0.02700	20.5	0%

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TABLE VIII
Minimum Stable Diameter and % Unstable Droplets as a Function of Temperature

Temperature (°C)	Minimum stable diameter (nm)	% Unstable droplets
5	21.9	0%
15	21.2	0%
25	20.5	0%

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TABLE IX
Minimum Stable Diameter and % Unstable Droplets as a Function of Interfacial Tension

Interfacial tension (dyne/cm)	Minimum stable diameter (nm)	% Unstable droplets
3.41	20.5	0%
5.0	30.0	0%
10	60.2	30%
20	120.7	60%
30	180	100%
40	240	100%

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compared to the ideal one. Similarly, we can see that a monomer with high molar volume (high molecular weight and low density) and a monomer-costabilizer system with high value of m_{mc}, the ratio of equivalent number of molecular segment, will make the droplets more unstable. From the above analysis, it emerges that the two parameters that can be varied to get a desired number of droplets to become unstable are the costabilizer amount and the interfacial tension (by varying the surfactant amount).

Broad distributions using miniemulsion polymerization

Most industrial dispersions of practical interest are neither monomodal nor bimodal blend distributions, rather they are simply broad distributions. Considerable work has been done on the rheology of monomodal and bimodal systems. It is now recognized that broadening the particle size distribution can increase the maximum packing. However, there have been few fundamental experimental studies of the rheology of polydisperse particulate assemblies, and especially the effect of polydispersity on the rheology of these systems. In one such study,[30] the rheological properties of aqueous polystyrene latex dispersions from three synthetic batches, with nearly the same *z*-average particle sizes, 400 nm, but varying degrees of polydispersity, 0.085, 0.301, and 0.485, respectively, were systematically investigated using steady-state shear and oscillatory shear measurements. Results from steady-state shear measurements show that the viscosities of the systems exhibit shear-thinning behavior at high solid frac-

tions. However, the degree of shear thinning depends on the breadth of particle size distribution, with the narrowest distribution suspension exhibiting the highest degree of shear thinning. The relative viscosities as a function of volume fraction data were compared, and it was found that the broadest distribution suspension had the lowest viscosity for a given volume fraction. Thus, it can be concluded that a broad distribution should be preferred over a narrow distribution. Latex particle size distribution is probably the most important variable in designing low-viscosity concentrated aqueous polymer dispersions.[25] Results show that a broad particle size distribution is favored over a narrow particle size distribution, and that the presence of large particles is highly recommended.[29] Therefore, when attempting to produce highly concentrated latexes with low viscosity, the particle size distribution is an important process variable to be mastered.[28]

The author developed models for the particle size distribution in conventional emulsion[39,40,64] as well miniemulsion polymerization processes.[8–10] The distribution in miniemulsion polymerization, due to continuous and slower nucleation, compared with conventional emulsion polymerization, is inherently broader with relatively large number of large particles as compared with small particles. Table XI shows a comparison of the standard deviations obtained at the end of reaction for different initiator concentrations, using our model for miniemulsion polymerization[8,9] with the data of Miller et al.[11,14] The reaction temperature was 70°C and the means

TABLE X
Minimum Stable Diameter and % Unstable Droplets as a Function of Interaction Parameter and Costabilizer Amount

Costabilizer amount (mM)	Volume fraction	Minimum stable diameter for $\chi_{mc} = 0$ (nm)	% Unstable droplets	Minimum stable diameter for $\chi_{mc} = 1.69$ (nm)	% Unstable droplets
5	0.00461	117	60%	187	100%
10	0.00918	47.6	0%	62.6	20%
15	0.01370	38.5	0%	43.0	0%
20	0.01820	28.6	0%	33.5	0%
30	0.02700	18.9	0%	23.9	0%
40	0.03570	14.0	0%	19.1	0%
50	0.04426	11.0	0%	16.4	0%

TABLE XI
Comparison of Predicted[8,9] and Experimental
Values[11,14] of Standard Deviations for Different
Initiator Concentrations

[I] (mM)	Standard deviation (nm)^{model}	Standard deviation (nm)$^{Miller\ et\ al.}$
2.66	15.6	18.04
1.33	17.3	20.4
0.665	19.7	22.7
0.333	22.3	23.9
0.133	27.7	41.6

of creating the droplet size distribution was micro-fluidizer. The microfluidizer generates uniform shear and is known to give narrow droplet size distribution, and therefore, the droplet size distribution was considered to be monodisperse. It can be seen that by lowering the initiator amount, the standard deviation of the final particle size distribution can be increased. Lowering the temperature of the reaction will have the same effect. Similarly, a broader particle size distribution will be obtained by starting with a broader droplet size distribution.

CONCLUSIONS

Advantages of miniemulsion polymerization over conventional emulsion polymerization in creating bimodal particle size distribution have been discussed. Calculations for maximum volume fraction (φ_m) for a monomodal and a bimodal dispersion are given, by assuming a cubic lattice model. The value of φ_m obtained for monomodal distribution is 0.523. Experimental support for this value has been given. The value of φ_m obtained for bimodal distribution is 0.726. This value is higher than that obtained for the monomodal distribution. Thus, it was mathematically shown that by using bimodal distribution, higher volume fractions can be achieved. The values calculated here for monomodal and bimodal distributions can be used in the various equations representing the variation of relative viscosity of dispersion with volume fraction.

This was extended to express the volume fraction of dispersed phase ($\varphi < \varphi_m$) for a bimodal distribution. By substituting the volume fraction, so obtained, various semiempirical laws relating relative viscosity to the volume fraction of the dispersed phase for monomodal dispersions, can be extended to bimodal dispersions also. It is mathematically shown that the viscosity of a bimodal dispersion will show a minimum for a particular size ratio of small to large particles, for a given relative number concentrations of small to large particles and the interspacing between the small and the large particles. Also, it is shown that increase in the relative number concentrations of small to large particles,

keeping the size ratio of small to large particles and the interspacing between the small and the large particles constant, will always increase the viscosity. So far, these have been considered as rules of thumb. The mathematical proof has been given in this work for the first time. Experimental support of the relationship derived for the optimum size ratio was given. It was shown that presence of double layer around the droplets and particles in miniemulsion can not be neglected and one should use the effective volume fraction instead in the viscosity–volume fraction relationships.

Based on the criterion for stability of the droplet size distribution, an expression for minimum stable diameter as derived earlier was given. It was shown that in order to create bimodal particle size distribution using miniemulsion polymerization, the costabilizer amount should be lowered. Also, the interfacial tension should be increased by lowering the surfactant amount. Further, low initiator amount, low temperature and a broader initial droplet size distribution will give broader particle size distribution.

NOMENCLATURE

a	limiting viscosity number (intrinsic viscosity)
C_1	$\sqrt{3\pi}/2$
C_2	$1+H/R$
d	diameter
e_L	electronic charge
H	inter-space between a large and a small particle
I_e	ionic strength
k_B	Boltzmann's constant and
L	length of one side of the cube
m	ratio of equivalent number of molecular segments
MW	molecular weight
n	number of small particles of size r
N	number of large particles of size R
N_A	Avogadro's number
P	probability density distribution function
R	radius of a small particle
R	radius of a large particle
R_G	universal gas constant
T	temperature
V	molar volume
x	r/R
X	solid content

Greek letters

η	viscosity
η_{rel}	relative viscosity
φ	volume fraction
φ_{eff}	effective volume fraction
φ_m	maximum closed pack volume fraction

ε_0	permittivity of vacuum
ε_r	dielectric constant of the dispersion medium k_B is the Boltzmann's constant and T is the absolute temperature
α	$4\gamma V_m/RT$
χ	interaction parameter
γ	interfacial tension
μ	chemical potential
ρ	density
σ	standard deviation
δ	adsorbed layer thickness

Subscripts

c	costabilizer
m	monomer
p	polymer
w	water

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