

# Relative Shear Stability of Mini- and Macroemulsion Latexes

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**ABSTRACT:** The shear stability of mini- and macroemulsion latexes is compared and quantitatively evaluated with respect to their particle-size distributions. The effect of a few externally added large particles on the shear stability of these two types of latexes was also investigated. All the latexes selected were in the colloidal size range (less than 1 micron). The original particle sizes for the macroemulsion latexes ranged from 141 to 241 nm, and those for the miniemulsion latexes ranged from 96 to 209 nm. The miniemulsion latexes were found to be more shear stable than were their macroemulsion latex counterparts over the particle-size range investigated. This trend was repeated even in the presence of a few large particles. Additionally, seeding experiments suggest that mini- and macroemulsion latexes incur different levels of shear aggregation due to inherent differences in their particle-size distributions. The shear rate used along with the particle size and number were quantitatively shown to significantly influence the aggregation process. Finally, a quantitative method for evaluating relative shear stability in emulsion polymerization was demonstrated, which, although not very rigorous, could serve as a starting point for further quantitative isolation and investigation of the various parameters that affect the shear aggregation process.  
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## INTRODUCTION

Conventional batch emulsion polymerization (referred to herein as *macroemulsion* polymerization to distinguish it from *miniemulsion* polymerization) reactions can be divided into three intervals: Interval I (particle nucleation, which involves radical entry into micelles), Interval II (particle growth in presence of a separate monomer droplet phase), and Interval III (particle growth in absence of a separate monomer phase). Nucleation of particles is assumed to take place predominantly in the micelles which are formed when the emulsifier concentration in the monomer emulsion exceeds the critical micelle concentration and

to some extent in the aqueous phase, depending on the extent of monomer solubility in water. There is assumed to be no polymerization in the relatively large (1–10 micron) monomer droplets, due to their insignificant surface area (several orders of magnitude less than that of the micelles) and consequent inability to capture water-borne free radicals.

Miniemulsion polymerizations utilize a surfactant–cosurfactant system in order to produce small (50–500 nm) monomer droplets. The small droplet size leads to a large monomer surface area, and most of the surfactant is adsorbed at the surface of these droplets. There is often not enough free surfactant to form micelles or to stabilize homogeneous nucleation as in conventional (macroemulsion) emulsion polymerization. Particle nucleation occurs primarily by radical (primary or oligomeric) entry into the monomer droplets. If a preponderance of the droplets are nucle-

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ated, there will be no real Interval II<sup>1</sup> as defined in macroemulsion polymerization.

Although miniemulsion latexes exhibit many of the properties of macroemulsion latexes, due to the difference in polymerization mechanism, there may be subtle differences in particle-size distribution (PSD) and surface characteristics. Due presumably to these differences, miniemulsions have been reported to exhibit greater shear stability than do comparable macroemulsions. The purpose of this work was to document and quantify the differences in shear stability between mini- and macroemulsion latexes. In this work, a quantitative approach was developed to address this problem, where the change in the average diameter and in the total number of particles were related to the PSD before and after shearing. In addition, an aggregation rate constant was computed to quantify shear-induced aggregation.

## EXPERIMENTAL

Two pairs of mini- and macroemulsion latexes were polymerized for this study. The macroemulsion latexes were prepared using the following reagents: methyl methacrylate (MMA) monomer (Rohm and Haas Co., inhibited with 10 ppm methyl ethyl hydroquinone), sodium lauryl sulfate (SLS; BDH Ltd., Poole, England); potassium persulfate (KPS; Fisher); dodecyl mercaptan (DDM; Aldrich); hexadecane (miniemulsions only—Fisher); and deionized (DI) water.

The inhibited monomer (MMA) was washed with 40 mL of a 5% NaOH solution, then subsequently with a saturated NaCl solution to remove the methyl ethyl hydroquinone inhibitor. The monomer was then transferred to the reaction vessel which already contained the desired SLS solution, and the flask was then submerged in a cooling water bath maintained at 60°C. A condenser was connected to the system and the entire system was purged with nitrogen for 5 min. Agitation during the reaction was provided by a paddle wheel stirrer with a rpm of  $700 \pm 100$ . This level of agitation is adequate to provide good mixing, but not sufficient to cause a significant monomer droplet size reduction. After the nitrogen purge was completed, the KPS initiator was introduced into the system through a syringe, initiating the polymerization reaction which was allowed to continue to termination at a constant temperature of 60°C.

The same procedure was followed when making the miniemulsion latexes, except that a cosurfac-

tant (hexadecane) was added to the monomer before it was mixed with the SLS solution to form an emulsion. Additionally, the emulsion was sonicated at 60% power (300 W maximum) for 5 min before transferring to the reaction vessel, in order to prepare a miniemulsion, with the monomer in the range of 10–500 nm.

The latex pairs prepared had the following characteristics:

### Pair I

#### *Macroemulsion (Sample A)*

0.02 mol SLS/L aq; 0.0115 mol. KPS/L aq; 2 g DDM;  
PSD range: 141–188 nm (diameter).

#### *Miniemulsion (Sample E)*

0.02 mol SLS/L aq; 0.0115 mol KPS/L aq; 2 g DDM;  
PSD range: 96–123 nm (diameter).

### Pair II

#### *Macroemulsion (Sample H)*

0.01 mol SLS/L aq; 0.0115 mol. KPS/L aq; 4 g DDM;  
PSD range: 167–241 nm (diameter).

#### *Miniemulsion (Sample D)*

0.01 mol SLS/L aq; 0.0115 mol KPS/L aq; 4 g DDM;  
PSD range: 145–209 nm (diameter).

The macro- and miniemulsion latexes were paired based on their PSDs, i.e., each macroemulsion latex was paired with a miniemulsion latex with similar or overlapping PSD to provide a valid basis for comparison of shear stability of the two systems with respect to a given PSD. Care was also taken to ensure that the amount of surfactant used in the polymerization was the same for both latexes in a pair, since the extent of the surfactant surface coverage of the polymer particles could significantly influence the aggregation process.

## Particle Size

Particle sizes were measured by the Malvern Autosizer IIc dynamic light scattering instrument. All measurements were verified twice at 5-min intervals with no statistically significant differences being noted in the diameters. This instrument provided average diameters, standard deviations, and distributions based on mass, intensity, and number. Diameter measurements are reproducible to within less than 5%. The shift in

average particle diameters before and after shearing were compared in this analysis along with the shift in the PSD and also the change in total number of particles calculated from the average particle size and total emulsion solids.

### Shear Stability

The samples were sheared using a rotational viscometer with a coaxial cylinder system, based on the Searle-type, i.e., the inner cylinder (connected to a sensor system) rotates while the outer cylinder remains stationary. The outer cylinder surrounding the inner one was jacketed, allowing for good temperature control, and the annular gap was of constant width. Such rotational viscometers are found to be very well suited for measuring the flow behavior of high and low viscosity non-Newtonian fluids. The sensor system used was the NV type, with a rotor having a recommended viscosity range of  $2 \times 10^3$  mPa, a maximum recommended shear stress of 178 Pa, and a maximum recommended shear strain rate of  $2700 \text{ s}^{-1}$  and could work with volumes from 10 to 50 mL. Under these recommended conditions, nonlaminar flow errors caused by Taylor vortices and turbulent flow can be avoided.<sup>2,3</sup>

The optimum shear rate for each pair was arrived at by trial and error, such that the shearing produced sufficient aggregation without any deaggregation, i.e., the shear rate was not increased beyond the point at which the particle diameters stopped increasing (and maybe even started decreasing again). All the tests were conducted at  $25^\circ\text{C}$ , and time was not a variable in these tests, i.e., each miniemulsion latex within a pair was sheared for the same time interval as its macroemulsion latex counterpart. Only the change in the particle sizes were followed during these series of experiments, with the PSD as analyzed by the Malvern Autosizer IIc recorded before and after shearing for each of the shear experiments.

### Seeding with Large Particles

Varying percentages by weight (2, 5, 10, and 25%) of two larger particle-size latexes, Sample C (macroemulsion) and Sample G (miniemulsion), were added to the macro and mini latexes, respectively, used in the first part of this work, to determine the effect of the presence of a few larger particles on shear stability of polymer latexes. The size ranges of these seed latexes were as follows:

*Macroemulsion Seed Latex (Sample C)*

PSD range: 252–298 nm (diameter)

Average diameter: 276 nm.

*Miniemulsion Seed Latex (Sample G)*

PSD range: 320–380 nm (diameter)

Average diameter: 344 nm.

The same analysis approach used for the original samples was repeated, i.e., the shifts in the PSD range and average diameter and the change in the total number of particles were recorded for each experiment. It is important to note that upon mixing the small number of large particles with the original samples and measuring the PSD, a fairly sharp distinction was noted in the average particle diameters between the original particles and the small amount of large particles added.

### Quantitative Data Analysis

The mini- and macroemulsion latexes used in this work were quantitatively compared based on the change in the PSD before and after shearing. In addition, the mini- and macroemulsion latexes were compared for shear stability based on the change in the total number of particles before and after shearing, and the aggregation rate constant  $k$  was computed from these results. An important assumption made in this analysis is that each PSD can be treated as essentially monodisperse and, hence, can be represented by its average radius which is reasonable considering the polydispersities of each distribution.

One can define a rate constant for the aggregation of particles  $i$  and  $j$  of radius  $a_i$  and  $a_j$  as follows<sup>4</sup>:

$$k'_{ij} = \alpha \left( \frac{4}{3} \right) G(a_i + a_j)^3 \quad (1)$$

Assuming that

$$a_i \approx a_j \Rightarrow (a_i + a_j)^3 \approx (2a_i)^3 = 8a_i^3 \quad (2)$$

one can define an aggregation rate constant for all particles as

$$k' = 8\alpha \left( \frac{4}{3} \right) G a_i^3 \quad (3)$$

The rate of change of the number of particles due

**Table I Effect of Shear on PSD—I**

Sample	Shear Rate (s <sup>-1</sup> )	Time of Shear (s)	Initial PSD Range (Diameter) nm	Ave. Diameter Before Shearing (nm)	PSD Range After Shearing (nm)	Ave. Diameter After Shearing (nm)	% Change in Av. Diameter (nm)
A (macro)	200	1260	141–188	155	181–244	204	31.61
E (mini)	200	1260	96–123	108	106–143	121	12.04
H (macro)	200	1260	167–241	195	218–319	264	35.38
D (mini)	200	1260	145–209	168	170–223	195	16.07

to shear coagulation (assuming only binary particle interactions) can then be written as

$$\frac{dN}{dt} = -k'N^2 \quad (4)$$

If the degree of agglomeration was small, eq. (4) can be approximated as

$$\Delta N \approx -k\Delta t a_0^3 N_0^2 \quad (5)$$

where  $\Delta t$  = time of shearing (s),  $N_0$  = total initial number of particles per liter;  $N_f$  = total final number of particles per liter;  $a_0$  = initial average particle radius (experimentally measured); and  $k$  = aggregation rate constant ( $=k'/a_0^3$ ).

The aggregation rate constant  $k$ , which accounts for all effects other than particle size in the shear aggregation of the particles, can be found as follows:

$$N_0 = \frac{(\text{total volume of polymer})}{(\text{initial particle volume})} \quad (6)$$

$$N_f = \frac{(\text{total volume of polymer})}{(\text{final particle volume})} \quad (7)$$

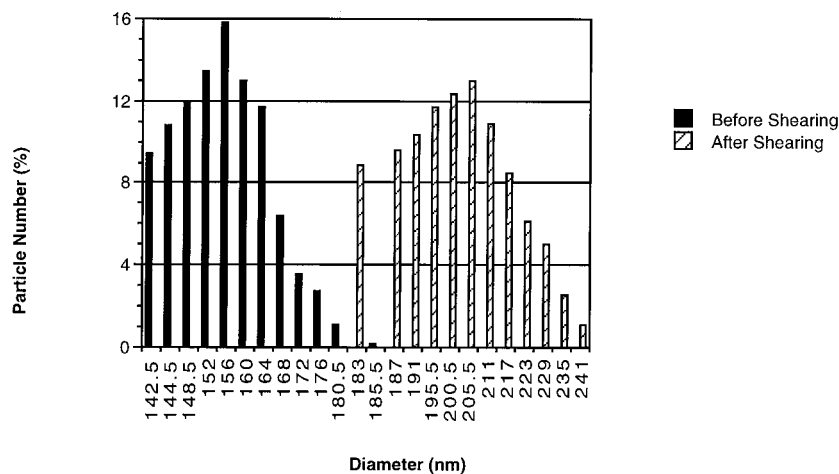
$$\Delta N = N_f - N_0 \quad (8)$$

From eqs. (5) and (8),  $k$  can be expressed as

$$k = \frac{-\Delta N}{(\Delta t a_0^3 N_0^2)} \quad (9)$$

The ratio of the total number of particles initially present to the total number of particles after shearing ( $N_i/N_f$ ) was also computed and used in this work both as a means of comparing the two types of latexes and to determine the extent of aggregation and the nature of the aggregates formed. This was done to verify that no higher, three-dimensional aggregates were involved, since these would invalidate a reasonable representation of the shear aggregation process by the simplistic analysis presented here.

It is important to reiterate that each pair of



**Figure 1** Particle size and number distribution: Sample A (macro).

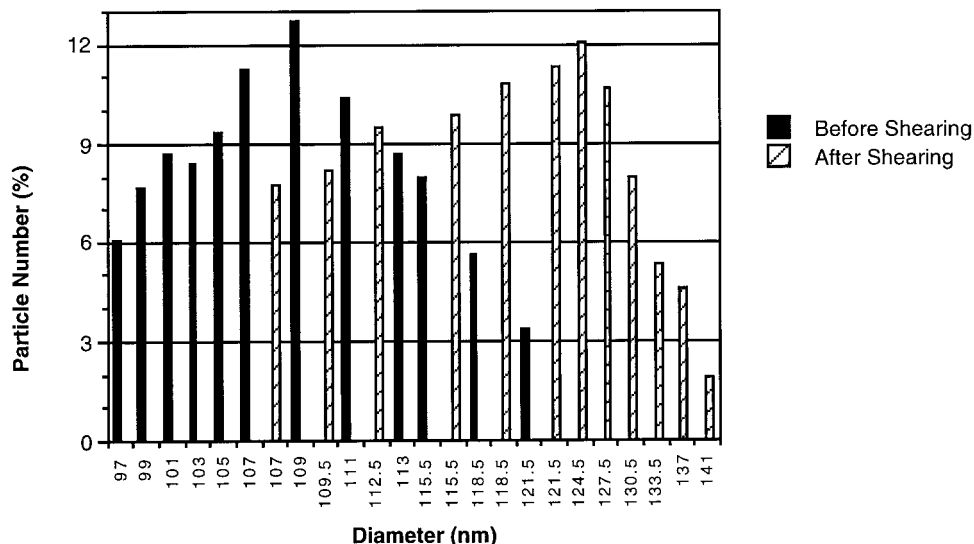


Figure 2 Particle size and number distribution: Sample E (mini).

latexes (mini and macro) was sheared under identical conditions, and the exact same method of computing the shift in average diameter and the aggregation rate constant  $k$  was used to compare them. The value of  $k$  should be viewed as a measure of the relative tendency to aggregation and not as an absolute rate constant. Also, time is not a variable in this analysis, i.e., the mini and macro latex making up each pair of samples being compared was sheared for the same time, and both the mini and macro latex samples within a pair were sheared at the same shear rate and at a temperature of 25°C. In addition, all the shear

experiments conducted were repeated at least twice for each sample sheared to verify repeatability.

RESULTS AND DISCUSSION

Relative Shear Stability of Mini- and Macroemulsion Latexes

The particle-size range and average particle diameter before and after shearing and the shear rate and time of shear used for each of the sample

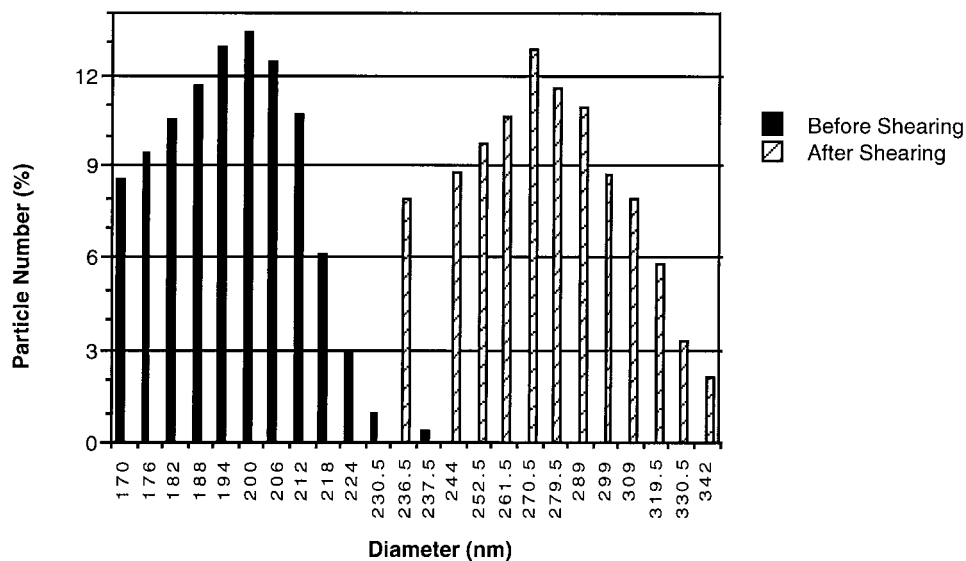


Figure 3 Particle size and number distribution: Sample H (macro).

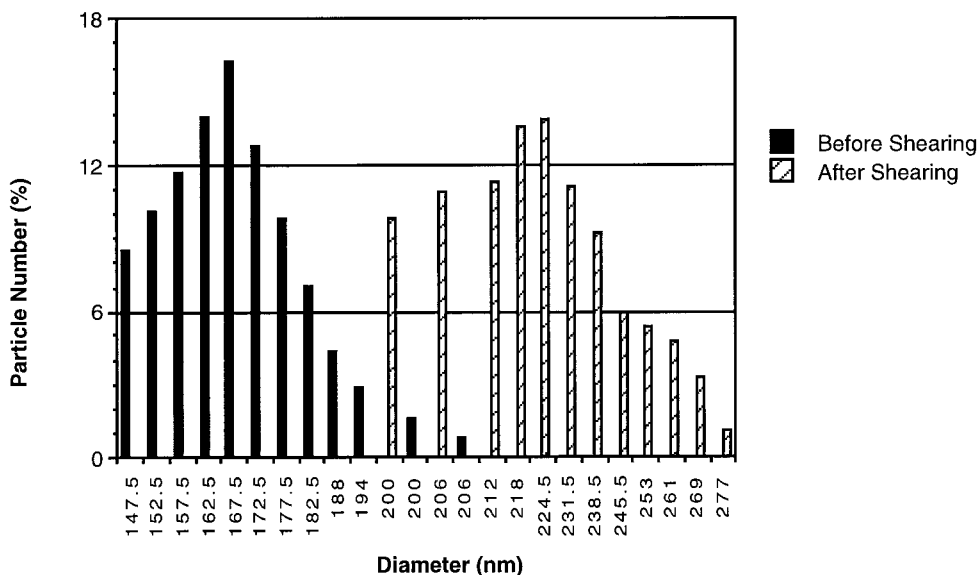


Figure 4 Particle size and number distribution: Sample D (mini).

pairs are shown in Table I. PSDs before and after shearing are shown in Figures 1–4. For both pairs, the shift in the particle-size range and in the average diameter are substantially greater for the macroemulsion latex than for the corresponding miniemulsion latex. In all cases, the PSD broadened after shearing under the conditions in Table I. The percentage change in the average diameter is greater for the macroemulsions as well.

The values of the aggregation rate constant “ $k$ ” for the latexes are shown in Table II. The ratio of the initial total number of particles to the final total number of particles after shearing ( $N_0/N_f$ ) is also presented here for each latex. The aggregation rate constant for each of the macroemulsion latexes is greater than its corresponding miniemulsion latex. Since  $k$  incorporates all aggregation effects except particle diameter, these results reinforce the observations from Table I that macroemulsion latexes have a greater tendency toward shear aggregation than do miniemulsion latexes. Additionally, Table II shows an increase

in  $k$  with an increase in the original average diameter for all the four latexes. This indicates that eq. (1) is not entirely successful in accounting for particle-diameter effects, i.e.,  $k$  is not entirely independent of the particle diameter. Since  $k$  is a function of shear rate, the  $k$  value for each latex was divided by the shear rate,  $G$ . With the effects of particle diameter and shear rate removed, the values of  $k/G$  should be relatively constant. They are not, indicating again that this simplistic analysis does not capture all the features of the aggregation mechanism. However, the value of  $k$  will be used as a relative measure of shear aggregation tendency.

It is clear that the macroemulsion latexes showed a greater shear instability. The ratio  $N_0/N_f$  gives an indication of the extent of aggregation in each of the latexes; an  $N_0/N_f$  ratio of two would indicate that average aggregation up to doublet formation has taken place and so on. It can be seen from Table II that in all the latexes aggregation has taken place essentially up to doublet formation, with there being a slightly higher aggregate for-

Table II Effect of Shear on PSD—II

Sample	% Solids	$N_i/N_f$	$k$	$k/G$
A (macro)	27.2	2.28	6.86E-03	3.43E-05
E (mini)	25.9	1.41	3.71E-03	1.85E-05
H (macro)	20.9	2.87	7.30E-03	3.65E-05
D (mini)	24.8	2.43	5.20E-03	2.60E-05

**Table III Effect of Seeding on Particle Size Distribution After Shear—I**

Sample	Shear Rate (s <sup>-1</sup> )	Shear Time (s)	Initial PSD Range (Diameter (nm))	Av. Diameter Before Shear (nm)	PSD Range After Shear (nm)	Av. Diameter After Shear (nm)	% Change in Av. Diameter
A (original—macro)	200	1260	141–188	155	181–244	204	31.61
A (2% big C)	200	1260	143–310	170	194–334	228	34.12
A (5% big C)	200	1260	144–317	176	208–358	249	41.48
A (10% big C)	200	1260	143–312	182	202–344	246	35.16
A (25% big C)	200	1260	143–308	199	196–333	250	25.63
E (original—mini)	200	1260	96–123	108	106–143	121	12.04
E (2% big G)	200	1260	102–372	118	114–380	153	29.66
E (5% big G)	200	1260	103–379	124	124–389	168	35.48
E (10% big G)	200	1260	106–384	131	130–397	177	35.11
E (25% big G)	200	1260	105–377	140	123–394	186	32.86
H (original—macro)	250	1740	167–241	195	233–348	277	42.05
H (2% big C)	250	1740	169–323	199	236–352	290	45.73
H (5% big C)	250	1740	171–338	207	264–388	324	56.52
H (10% big C)	250	1740	170–333	212	253–369	305	43.87
H (25% big C)	250	1740	170–312	222	242–355	297	33.78
D (original—mini)	250	1740	145–209	168	197–281	226	34.52
D (2% big G)	250	1740	149–370	179	224–377	247	37.99
D (5% big G)	250	1740	151–374	193	233–381	266	37.82
D (10% big G)	250	1740	154–373	208	242–399	284	36.54
D (25% big G)	250	1740	155–375	226	237–389	305	34.96

mation in the macrolatexes than in the minilatelaxes as evidenced by their correspondingly higher  $N_0/N_f$  values.

### Effect of Large Particles

The effect of a few externally added large particles on shear stability of mini- and macroemulsion latexes was also investigated. This was done to determine if the greater shear instability of the macroemulsion latexes (as evidenced in the first part of this work) was due to the presence of a few large particles, possibly formed by droplet nucleation during the synthesis of the latexes themselves. To test this, portions of a larger particle-size Rohm and Haas macroemulsion (Sample C) were added to the two macroemulsion latexes (Samples A and H), and portions of a larger miniemulsion (Sample G) were added to the two miniemulsion latexes (Samples E and D) used in the first part of this analysis. The percentages by weight of the larger particle-size latexes used were 2, 5, 10, and 25% of the total sample weight. The latexes were then sheared, and the shift in

the PSD range and average particle diameter, the percent change in this average diameter after shearing, and the average  $k$  and  $k/G$  values were determined for both these sets of samples. These results are shown in Tables III and IV.

Table III shows that for all the four samples analyzed the percent change in average diameter increases with the fraction of larger particles, reaches a maximum, and then decreases. In all cases, the maximum shear aggregation occurs at approximately 5–10% large particles. This supports (but by no means proves) the hypothesis that macroemulsion latexes are more susceptible to shear coagulation than are miniemulsion latexes due to the presence of a small fraction of large particles originating from droplet nucleation. It is important to remember that in all the four latexes used here the size differential between these latexes and the two latexes used as large particles (Samples C and G) is not very large. Therefore, the particles that qualify as large particles by definition lie at the upper end of the PSD of Samples C and G, i.e., only a small fraction of the externally added larger latex actu-

**Table IV Effect of Seeding on PSD After Shear—II**

Sample	% Solids	$N_i/N_f$	$k$	$k/G$
A (original—macro)	27.2	2.28	6.86E-03	3.43E-05
A (2% big C)	27.1	2.41	7.18E-03	3.59E-05
A (5% big C)	26.9	2.83	8.00E-03	4.00E-05
A (10% big C)	26.7	2.47	7.41E-03	3.70E-05
A (25% big C)	26.2	1.98	6.29E-03	3.14E-05
E (original—mini)	25.9	1.41	3.71E-03	1.85E-05
E (2% big G)	25.7	2.18	7.01E-03	3.50E-05
E (5% big G)	25.6	2.49	7.75E-03	3.87E-05
E (10% big G)	25.3	2.47	7.80E-03	3.90E-05
E (25% big G)	25.2	2.34	7.59E-03	3.79E-05
H (original—macro)	20.9	2.87	7.50E-03	3.00E-05
H (2% big C)	21.1	3.09	7.72E-03	3.09E-05
H (5% big C)	21.2	3.83	8.40E-03	3.36E-05
H (10% big C)	21.2	2.98	7.54E-03	3.02E-05
H (25% big C)	21.3	2.39	6.58E-03	2.63E-05
D (original—mini)	24.8	2.43	5.72E-03	2.29E-05
D (2% big G)	24.9	2.63	5.95E-03	2.38E-05
D (5% big G)	25.3	2.62	5.88E-03	2.35E-05
D (10% big G)	25.5	2.55	5.73E-03	2.29E-05
D (25% big G)	25.6	2.46	5.39E-03	2.16E-05

ally functions as large particles in terms of influencing shear stability.

The results shown in Table IV support the observations drawn from Table III. For all the latexes, there is an increase in the  $k/G$  value with an increase in the percent of externally added large particles, up to approximately 5–10% by weight of large particles. Any further addition of large particles decreases the  $k/G$  value. Inspection of the  $N_0/N_f$  values shows that aggregation occurred on the average, up to doublet or triplet formation. (Whether these result from homo- or heteroflocculation is unknown.)

## SUMMARY AND CONCLUSIONS

Under controlled shearing conditions, miniemulsions have been shown to be more shear stable than are similar conventional or macroemulsions. The effect has been quantified through the use of a very simplistic kinetic model. A hypothesis has been presented that the shear instability of mac-

roemulsions results from the presence of a small number of large particles (derived from droplet polymerization) which act as seeds for aggregation. Intentional seeding of mini- and macroemulsions with larger particles has induced increased shear instability, supporting the hypothesis. Other explanations such as differences in surface characteristics between mini- and macroemulsions may also contribute to the measured difference in shear stability.

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