

# Initial Droplet Size Distribution in Miniemulsion Polymerization

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**ABSTRACT:** The initial droplet size distribution of miniemulsions has not yet been measured. It is deduced from previous experimental results that the distribution is broad. Furthermore, the small fraction of the distribution, depending on the nonideality of the cosurfactant–monomer system, may not be stable. This may lead to a rearrangement of the distribution leading to a bimodal distribution. The stability criterion is based on the phenomenon of molecular diffusion

or Ostwald ripening. Experimental proof in support of the conclusion regarding the bimodal distribution is cited. The practical significance of the conclusion for making emulsion polymers with high solid contents is given. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 3058–3065, 2003

**Key words:** calculations; stabilization; thermodynamics

## INTRODUCTION

A relatively new process termed *miniemulsion polymerization* has been a focus of research as an alternative to conventional emulsion polymerization.<sup>1</sup> It is believed that this alternative process can lead to efficient routes to produce emulsion polymers with novel characteristics that are currently not possible through conventional emulsion polymerization. In the conventional emulsion polymerization method, monomer droplets, because of their large size (1–10  $\mu\text{m}$ ) and resultant small total surface area, are not thought to contribute to particle nucleation. In miniemulsion polymerization, the monomer is introduced in the form of small and stable droplets in the size range of 50–500 nm; they become the predominant loci of particle nucleation and subsequent polymerization (Fig. 1). This was experimentally demonstrated for the first time at Lehigh University in 1972.<sup>2</sup> The stability of these droplets was provided by a mixed emulsifier system consisting of a cosurfactant (e.g. sodium dodecyl sulfate) and a surfactant [e.g. hexadecane (HD) or hexadecanol, which is also known as cetyl alcohol (CA)].

## INITIAL DROPLET SIZE DISTRIBUTION

The droplet size distribution in miniemulsion polymerizations has not yet been measured. This distribution is determined by pre-emulsification and emulsi-

fication steps.<sup>3</sup> Variations in the emulsification steps (e.g., the type and amount of the cosurfactant and the intensity and uniformity of the energy input) have been shown to affect the polymerization kinetics and the final particle size distribution.<sup>4–6</sup> These variations result in different initial droplet size distributions, and the initial droplet size distribution, as these results demonstrate, affects the polymerization kinetics and the final particle size distributions. A direct comparison of the initial particle size distribution and the final particle size distribution has proven to be difficult because of the problem of measuring the full droplet size distribution. It was initially thought that the final particle size distribution was an exact replica of the initial droplet size distribution.<sup>2</sup> This is strictly true if all the droplets are nucleated at once and they polymerize without any redistribution of the monomer between them and the particles. It has been shown that the droplet nucleation may extend throughout the course of polymerization, and there is a continuous flux of the monomer from the droplets to the particles.<sup>7</sup> Miller<sup>8</sup> observed the effects of changes in the pre-emulsification and emulsification steps on the resulting average size of the droplet size distribution with the capillary hydrodynamic flow fractionation method.

In the absence of knowledge of the full droplet size distribution, defining the distribution in terms of analytical functions seems to be a convenient recourse.<sup>9</sup> The incorporation of information on the shape and any two size variables of the distribution (e.g., mean and standard deviation or maximum and minimum diameters) will make this representation more meaningful. For the shape of the distribution to be defined, in general, *a priori* knowledge regarding the following

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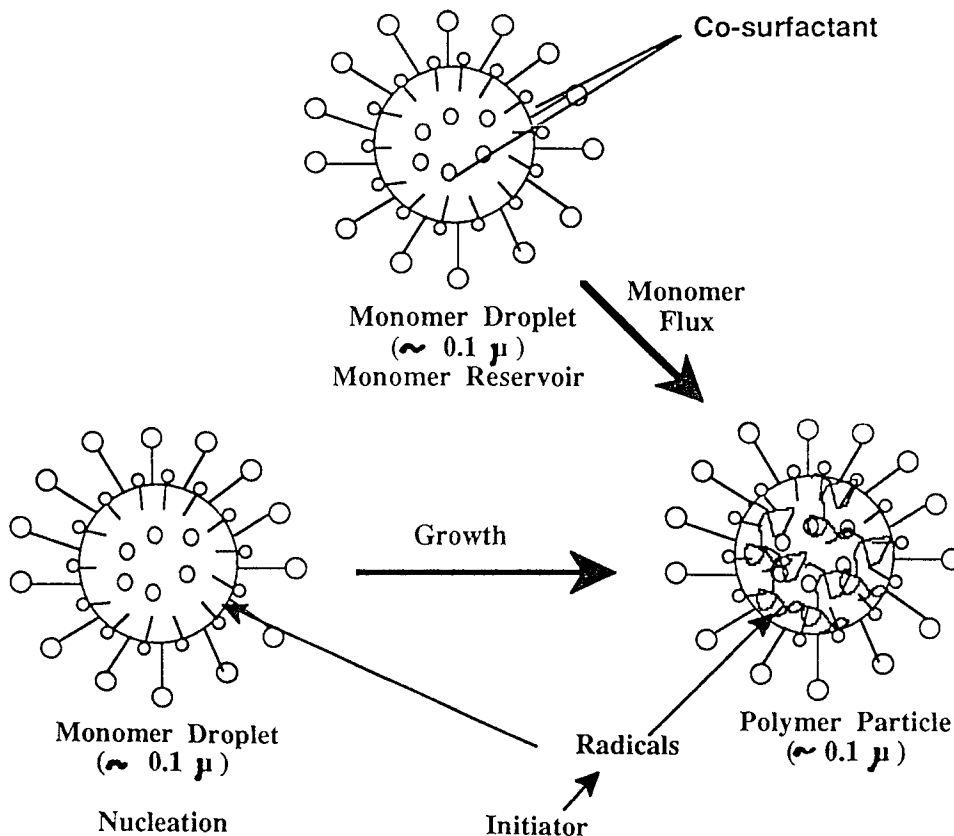


Figure 1 Schematic representation of miniemulsion polymerization.

four variables is necessary: the mean, standard deviation, skewness, and kurtosis. The mean and standard deviation provide information about the average size and width of the distribution, the skewness is a measure of the departure from symmetry or lopsidedness of the distribution, and kurtosis represents the shape of the distribution at the extreme ends or the flatness of the distribution.

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 follows:

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

where  $d$  is the size variable,  $d_m$  is the mean, and  $\sigma$  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  $d_2$ .

Because the actual distributions are rarely symmetric, and there is some evidence that the distribution obtained as a result of the mechanical subdivision of large volumes is generally positively skewed (lopsided to the left), the lognormal distribution offers a

satisfactory representation.  $P(d)$  of the lognormal distribution is expressed as follows:

$$P(d) = \frac{1}{\sqrt{2\pi}\sigma_g d} \exp\left[-\frac{(\ln d - \ln d_g)^2}{2\sigma_g^2}\right] \quad (2)$$

where  $d_g$  is the geometric mean value and  $\sigma_g$  is the geometric mean standard deviation. These are related to the mean  $d_m$  and  $\sigma$  by

$$\ln d_g = \ln d_m - \sigma_g^2/2 \quad (3)$$

$$\sigma_g^2 = \ln(1 + \sigma^2/d_m^2) \quad (4)$$

Figure 2 compares the normal (given by the solid line) and the lognormal distribution (given by the dashed line) for a narrow distribution defined by a mean diameter of 100 nm and by a standard deviation of 20 nm. There is an insignificant difference between the two. Figure 3 compares the two distributions when the droplet size distribution is broad, defined by a mean size of 100 nm and by a standard deviation of 50 nm. The differences become quite significant to the left side of the mean or for small sizes. The normal distribution is further discretized into five classes for the two cases, and the results are given in Tables I and II.

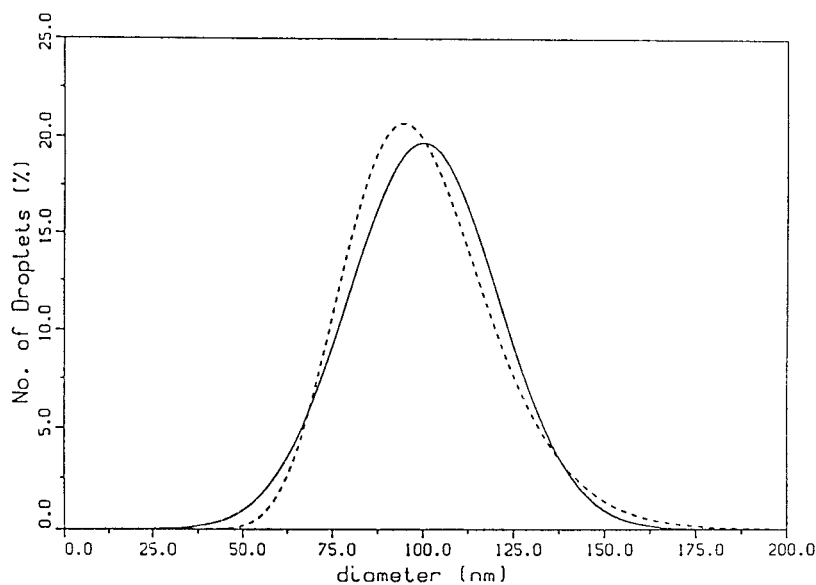


Figure 2 Comparison of narrow normal (solid line) and lognormal (dashed line) distributions.

The IMSL Math/Library version 1.1 Fortran subroutine ANORDF was used to discretize the droplet size distribution and obtain the aforementioned results. It can be further assumed that for a broad distribution, the fraction of droplets in each of the five classes is equal to 0.2.

#### STABILITY OF THE DROPLET SIZE DISTRIBUTION

Miller<sup>8</sup> found that the measured average size of the distribution, monitored over time, did not change when HD was used as a cosurfactant, whereas with CA as a cosurfactant, the average size increased up to 1.5 h and leveled off after that (Figs. 4 and 5). With an

increase in the amount of CA, the rearrangement behavior was retarded, and the final average size decreased.

A theoretical analysis reconciling the aforementioned experimental observations in terms of a suitable theoretical framework was conducted.<sup>10</sup> The instability may arise as a result of coalescence, which results from an insufficient barrier (e.g., electrostatic and viscoelastic) against contact or from molecular diffusion (popularly known as Ostwald ripening). Sodium dodecyl sulfate, an anionic surfactant, provides an electrostatic barrier against contact. In such cases, coalescence is normally called *coagulation*. The cosurfactant, HD or CA (relatively low molecular weight,

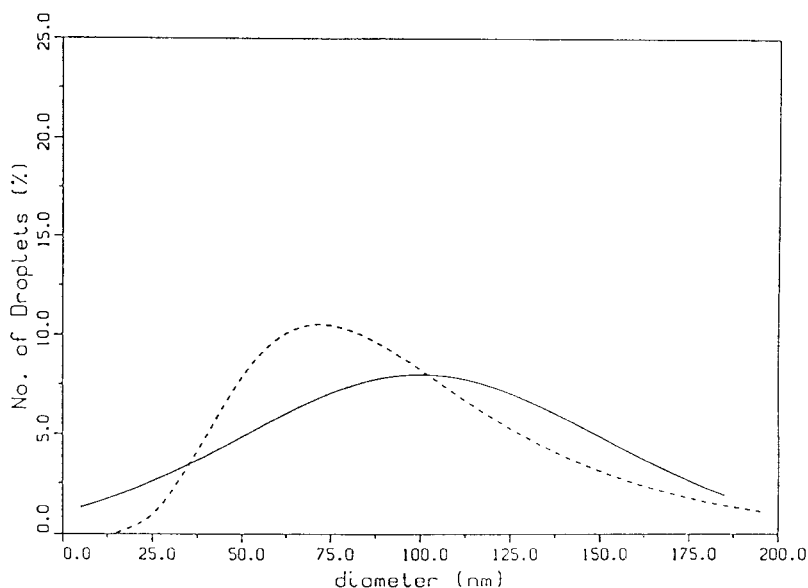


Figure 3 Comparison of broad normal (solid line) and lognormal (dashed line) distributions.

**TABLE I**  
Discrete Narrow Normal Distribution (Mean = 100 nm,  
Standard Deviation = 20)

Size range (nm)	Mean size (nm)	Fraction of droplets
38–62	50	0.03
63–87	75	0.24
88–112	100	0.46
113–137	125	0.24
138–162	150	0.03

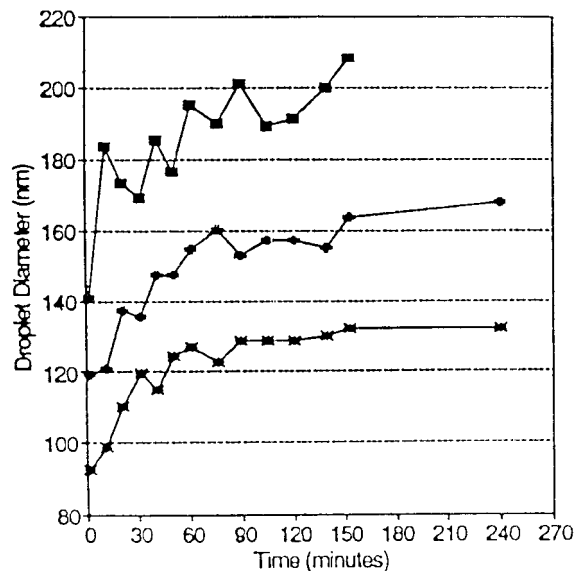
less water-soluble compounds), retards the molecular diffusion of the monomer.<sup>11</sup> The minimum surfactant coverage required to provide adequate electrostatic stabilization against coagulation has been calculated with the framework provided by the Deryaguin–Landau–Verwey–Overbeek theory.<sup>12</sup> The minimum surfactant coverage required for stability is 1–5%, whereas the actual value of surfactant coverage, for a typical recipe, varies between 18 and 20%. This value is an order of magnitude greater than the minimum value required for electrostatic stabilization. Therefore, it is concluded that the initial droplet size distribution is stable against coagulation. It can be reasoned further that the amount and nature of the surfactant are the same whether HD or CA is used as a cosurfactant, and so if insufficient stabilization provided by the surfactant is the cause of the instability, this would result in the aforementioned rearrangement for both HD and CA. Electrostatic stabilization is the more commonly used criterion for analyzing stability in an emulsion system, whereas molecular diffusion is rarely considered. We considered this phenomenon in explaining the instability seen in the miniemulsion system.<sup>10</sup> In this study, we have further extended that treatment.

### MOLECULAR DIFFUSION

Two droplets of different sizes can change their size, without coming into contact, through molecular diffusion, the smaller droplet decreasing in size and larger droplet increasing in size. This can be retarded and stopped by the addition of a low molecular weight, less water-soluble component.<sup>11</sup> In miniemul-

**TABLE II**  
Discrete Broad Normal Distribution (Mean = 100 nm,  
Standard Deviation = 50)

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

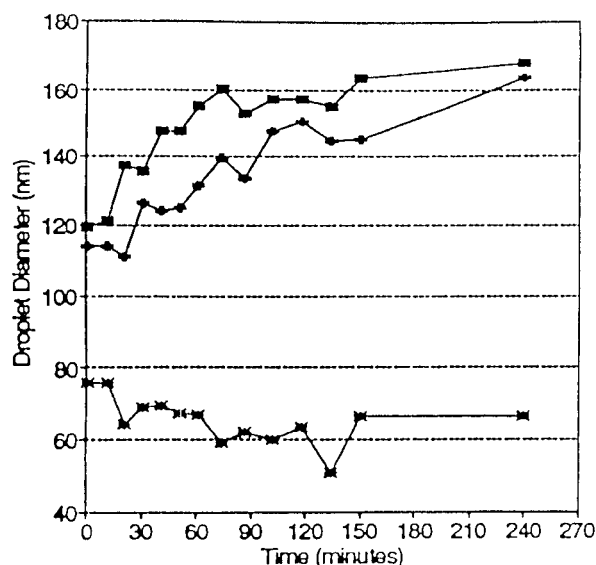


**Figure 4** Variation of the droplet diameter with time for different amounts of CA: (■) 10 mM CA, (●) 30 mM CA, and (×) 50 mM CA.<sup>8</sup>

sion polymerization, this role is played by the cosurfactant.

The process of molecular diffusion, in general, is governed by the difference between the chemical potential of the diffusing substance (a monomer in our case) in the two phases. The chemical potential of the monomer ( $\mu$ ) in a monomer droplet of diameter  $d$ , with the volume fraction of the cosurfactant ( $\phi_c$ ), is given as follows:<sup>7</sup>

$$\mu = \ln(1 - \phi_c) + (1 - m_{mc})\phi_c + \chi_{mc}\phi_c^2 + \frac{4\gamma V_m}{dRT} \quad (5)$$



**Figure 5** Variation of the droplet diameter with time for CA and HD: (■) CA from the gel phase, (●) CA dissolved in styrene, and (×) HD.<sup>8</sup>

where  $m_{mc}$  is the ratio of the equivalent number of the molecular segment,  $\chi$  is the interaction parameter,  $V_m$  is the molar volume of the monomer,  $\gamma$  is the interfacial tension,  $R$  is the universal gas constant, and  $T$  is the temperature. This equation is based on the Flory–Huggins lattice theory of polymer solutions,<sup>13</sup> the extension of Morton et al.<sup>14</sup> involving the addition of an interfacial energy term for spherical phases, and the further extension of Ugelstad and Hansen<sup>15</sup> for phases not involving a 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, and are used to consider the nonideality between the two constituents, the monomer and the cosurfactant.  $\chi$  provides a measure of the nonideality of the system; the larger  $\chi$  is, the greater the nonideality is. The fourth term represents the partial molar free energy of swelling. Defining  $\alpha = 4\gamma V_m/RT$  and knowing that  $\ln(1 - \phi_c) \sim -\phi_c$  for small values of  $\phi_c$ , we can reduce the previous equation as follows:

$$\mu = -m_{mc}\phi_c + \chi_{mc}\phi_c^2 + \frac{\alpha}{d} \quad (6)$$

From this equation (with some manipulation), it follows that the difference in the chemical potential ( $\Delta\mu$ ) of the two droplets of diameters  $d_1$  and  $d_2$  and cosurfactant volume fractions  $\phi_{c,1}$  and  $\phi_{c,2}$  is given by

$$\Delta\mu = \alpha(1/d_1 - 1/d_2) - (\phi_{c,1} - \phi_{c,2})[m - \chi(\phi_{c,1} + \phi_{c,2})] \quad (7)$$

In the absence of the cosurfactant ( $\phi_{c,1} = \phi_{c,2} = 0$ ), only the first term in this equation, arising from the contribution to the free energy from swelling, accounts for  $\Delta\mu$  of the two droplets.  $\Delta\mu$ , in this case, can never be diminished, as the mass transfer through the molecular diffusion of the monomer from small droplets (having higher  $\mu$  values) to large droplets (having lower  $\mu$  values) will further increase this difference. As can be seen from the equation, this irreversible change in the droplet sizes can be retarded when a cosurfactant is present. In its presence, the mass transfer of the monomer from the smaller droplets to the larger droplets changes their composition. As can be seen from the equation, this can result in the equalization of their chemical potentials, as the second term arising from the mixing of the two components compensates for the first term due to the swelling.

### EQUILIBRIUM SWELLING THERMODYNAMICS

We have solved the equations for equilibrium swelling thermodynamics for the five classes of droplets for

**TABLE III**  
Recipe Considered in the Solution of Equilibrium Swelling Thermodynamics

Recipe component	Amount
Monomer (styrene)	8 mL
Water	25 mL
Cosurfactant (CA)	10 mM (based on aqueous phase)

narrow and broad distributions. The solution requires that the chemical potential of the monomer in each of these five classes and the chemical potential of the monomer dissolved in the aqueous phase, at equilibrium, should become equal.

The equation for the chemical potential, now expressed in terms of the volume fraction of the monomer, becomes

$$\mu_i = \ln \phi_{m,i} + (1 - m_{mc})(1 - \phi_{m,i}) + \chi_{mc}(1 - \phi_{m,i})^2 + \frac{\alpha}{d_i} \quad (8)$$

The chemical potential of the monomer in the aqueous phase is given by

$$\mu_w = \ln \phi_{m,w} + (1 - m_{mw})(1 - \phi_{m,w}) + \chi_{mw}(1 - \phi_{m,w})^2 \quad (9)$$

There are 11 variables in these two equations, the 5  $\phi_{m,i}$ , 5  $d_i$ 's, and  $\phi_{w}$ . The equality of the chemical potentials gives 5 equations. If the cosurfactant does not diffuse from the droplets (zero solubility in the aqueous phase being implied), its amount in a droplet will remain the same and equal to the initial amount. Therefore,

$$(1 - \phi_{m,i})d_i^3 = (1 - \phi_{om,i})d_{oi}^3 \quad (10)$$

The initial sizes of the droplets are known, and the initial volume fraction of the monomer in them can be taken as that in the initial recipe because the monomer is sparingly soluble in the aqueous phase. This relation gives 5 more equations. The overall material balance for the monomer provides the 11th equation. These 11 equations can be solved for the 11 variables. IMSL MATH/LIBRARY version 1.1 Fortran subroutine NEQNF was used to solve these nonlinear algebraic equations. The recipe considered is given in Table III.<sup>16</sup> The results are given in Tables IV and V for narrow and broad distributions, respectively. The values of the parameters used in the simulations are given in Table VI.

Rearrangement leading to an equality of the chemical potentials leads to barely perceptible changes between the initial average diameter and the final diameter. As required by molecular diffusion (or Ostwald

**TABLE IV**  
Results of Equilibrium Swelling Thermodynamics  
for the Narrow Distribution

Fraction of droplets	Initial diameter (nm)	Final diameter (nm)
0.03	50	38
0.24	75	67
0.46	100	97
0.24	125	127
0.03	150	157
Average diameter (nm)	100	97

ripening), the smaller droplets decrease in size, the larger droplets increase in size, and the average diameter remains nearly the same. Therefore, the large change in the droplet diameter, approximately 40–60 nm, as monitored by Miller,<sup>8</sup> cannot be explained.

#### MINIMUM STABLE DIAMETER

In the presence of a cosurfactant, as stated earlier, compensation of the swelling effect by the mixing effect takes place. In the absence of a cosurfactant, the chemical potential of a small droplet, given by  $\alpha/d_1$ , is always larger than the chemical potential of the large droplet, given by  $\alpha/d_2$ . In the presence of a cosurfactant, the equality of the chemical potentials will require that the chemical potential of the small droplet decrease and the chemical potential of the large droplet increase as their sizes change because of molecular diffusion. Mathematically, this criterion requires that the chemical potential should be an increasing function of size,<sup>17</sup> or

$$\frac{d\mu}{dd} > 0 \quad (11)$$

Considering the equation for the chemical potential of the monomer, expressed in terms of  $\phi_c$ , and noting that for the first three terms, it is convenient to write  $d\mu/dd$  as  $d\mu/d\phi_c \times d\phi_c/dd$ , and further noting that  $\phi_c d^3 = \phi_{co} d_o^3$  (the cosurfactant amount in a droplet remains unchanged), we can write  $d\phi_c/dd = -3\phi_{co} d_o^3/d^4 = -3\phi_c/d$ , which gives the following:

**TABLE V**  
Results of Equilibrium Swelling Thermodynamics  
for the Broad Distribution

Fraction of droplets	Initial diameter (nm)	Final diameter (nm)
0.2	50	38
0.2	75	66
0.2	100	95
0.2	125	125
0.2	150	155
Average diameter (nm)	100	96

**TABLE VI**  
Values of Parameters Used in the Simulations<sup>6</sup>

Parameter	Value
MW <sub>m</sub>	104.4
MW <sub>c</sub>	242.4
$m_{mc}$	0.41
$m_{mw}$	1.29
$\chi_{mc}$	1.69
$\chi_{mw}$	7.97
$\gamma$ (dyn/cm)	3.41
$\rho_m$ (g/cm <sup>3</sup> )	0.860
$\rho_c$ (g/cm <sup>3</sup> )	0.818

$$d\mu/dd = [-1/(1 - \phi_c) + (1 - m_{mc}) + 2\chi\phi_c](-3\phi_c/d) - \alpha/d > 0 \quad (12)$$

or

$$\alpha/d < [-1/(1 - \phi_c) + (1 - m_{mc}) + 2\chi\phi_c](-3\phi_c) \quad (13)$$

After inversion, we get

$$d > \frac{\alpha}{[1/(1 - \phi_c) - (1 - m_{mc}) - 2\chi\phi_c](3\phi_c)} \quad (14)$$

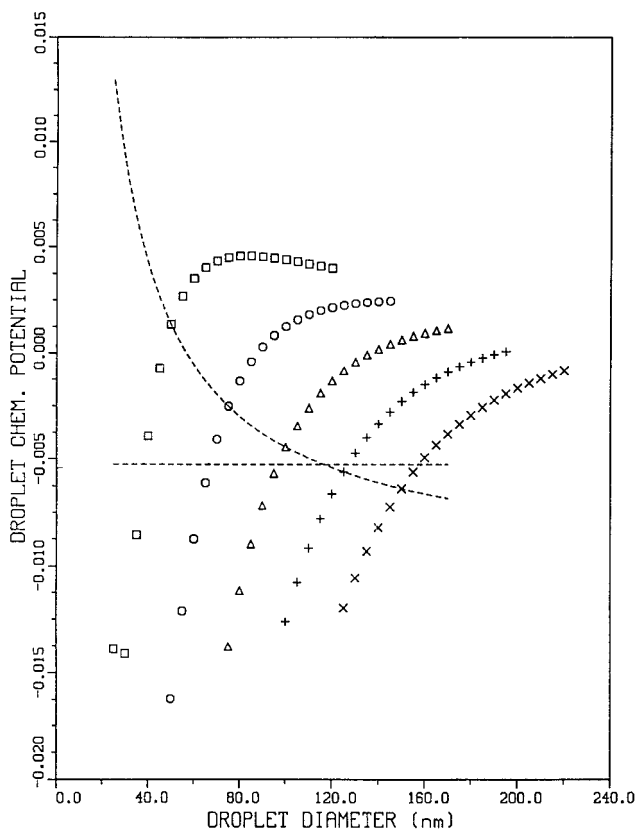
Therefore, droplets with a diameter greater than the minimum stable diameter, given by the equality in this equation, fulfill the requirement for stability,  $d\mu/dd > 0$ . This equation is a more rigorous version of the equation given in our previous publication.<sup>10</sup> We have calculated the minimum stable diameter for two cases in Table VII, which are for the ideal case ( $\chi_{mc} = 0$ ), that is, for HD and for CA ( $\chi_{mc} = 1.69$ ) for different amounts of the cosurfactant.

For a given system, for a particular amount of a cosurfactant, depending on the nonideality between the monomer and the cosurfactant, droplets with a diameter less than that given in Table VI cannot be stable in the system. Therefore, for a cosurfactant amount equal to 10 mM, for CA, droplets smaller than 63 nm cannot be stable. Because HD [CH3(CH2)14CH3] is less nonideal than CA [CH3(CH2)14CH2OH] with styrene [CH2CH(C6H5)]; the presence of the OH functionality in CA makes it nonideal, the minimum stable

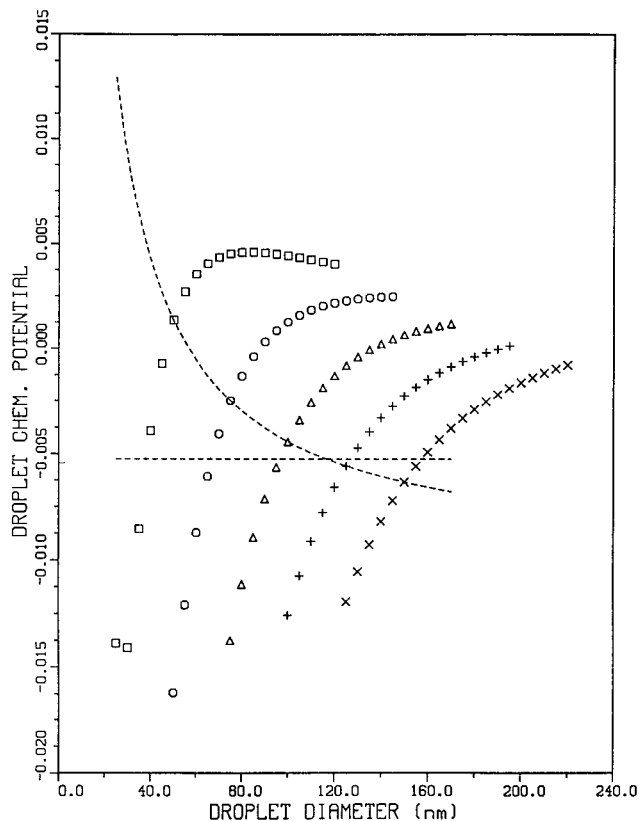
**TABLE VII**  
Minimum Stable Diameter

Cosurfactant amount (mM)	Volume fraction	For $\chi_{mc} = 0$ (HD; nm)	For $\chi_{mc} = 1.69$ (CA; nm)
5	0.00461	117	187
10	0.00918	47.6	62.6
15	0.01370	38.5	43.0
20	0.01820	28.6	33.5
30	0.02700	18.9	23.9
40	0.03570	14.0	19.1
50	0.04426	11.0	16.4

diameter in its case is smaller, and so small droplets can become stable with HD as a cosurfactant, and no rearrangement is seen. Similarly, with an increase in the cosurfactant amount, the minimum stable diameter decreases, and this leads to a smaller rearrangement. Now, if the distribution is narrow, as considered in Table I, only 3% of the droplets will disappear with time, and this will cause a very small change in the average diameter. However, if the distribution is broad, as given in Table II, then 23% of the droplets will disappear, and the average diameter of the distribution will shift from 100 to 112.5 nm; this change is significant. Therefore, it can be concluded that the initial droplet size distribution is broad with a significant fraction of small droplets. It has been shown that in the presence of a cosurfactant, the droplets do not completely lose their monomer and can exist as small droplets.<sup>7</sup> Therefore, a result of the instability is a bimodal distribution consisting of these smaller droplets that cannot attain stability and larger droplets that can attain stability. In Figures 6 and 7, we have plotted the chemical potential of the droplets as a function of their diameter and initial position and the path that they would take to attain equilibrium for narrow and broad distributions, respectively.



**Figure 6** Chemical potential as a function of the droplet diameter (initial and final equilibrium positions) for the narrow distribution. ( $\square$  = 50 nm;  $\circ$  = 75 nm;  $\triangle$  = 100 nm;  $+$  = 125 nm;  $\times$  = 150 nm)



**Figure 7** Chemical potential as a function of the droplet diameter (initial and final equilibrium positions) for the broad distribution. ( $\square$  = 50 nm;  $\circ$  = 75 nm;  $\triangle$  = 100 nm;  $+$  = 125 nm;  $\times$  = 150 nm)

Experimental proof for this conclusion can be found in the work of Pan,<sup>18</sup> who reported a bimodal distribution for miniemulsion polymerization for a recipe involving 10 mL of styrene, 30 mL of water, 0.3 wt % sodium dodecyl sulfate (surfactant; surfactant/cosurfactant = 1:3), potassium persulfate (initiator; 1.5 mM), and a temperature of 70°C. It was reported that the final distribution consisted of two groups with diameters of 260 and 600 nm. It was also reported that these two groups developed at early stage and that at a 4.4% conversion, the diameters were 100 and 300 nm. It can be concluded that these two group arose because of the polymerization of small and large droplets that were formed as previously mentioned. Miller<sup>8</sup> also reported bimodal particle size distributions.

There is a practical significance to the aforementioned behavior for the practitioners of emulsion polymerization. It can be used to formulate recipes leading to solid contents as high as 70% in which smaller particles can exist in the interstitial spaces between the larger particles.<sup>19</sup>

## CONCLUSIONS

The full initial droplet size distribution in miniemulsions has not been measured. A representation of the

distribution in terms of analytical functions has been discussed. Two analytical forms, normal and lognormal, have been mentioned. It has been shown that for narrow distributions, there is not much of a difference between the two, whereas for broad distributions, the differences between the two at the small end become significant. Previous experiments, in which the rearrangement of the droplet size distribution was studied with time for a particular cosurfactant that was more nonideal and in which the retardation of this behavior was examined with an increase in its amount, have been analyzed in detail according to the molecular diffusion phenomenon. This analysis has led to the conclusions that the initial droplet distribution should contain a significant fraction of small particles, and this is true for a broad distribution. Furthermore, this distribution will be bimodal. Experimental proof in favor of our conclusion regarding bimodal distribution has been cited. Finally, the practical significance of our work has been discussed. That is, this can provide a process route for producing emulsion polymers with very high solid contents.

## NOMENCLATURE

### Symbols

$d$	diameter
$m$	ratio of the equivalent number of molecular segments
$MW$	molecular weight
$P$	probability density distribution function
$R$	universal gas constant
$T$	temperature
$V$	molar volume

### Greek characters

$\alpha$	$4\gamma V_m/RT$
$\gamma$	interfacial tension
$\mu$	chemical potential

$\rho$	density
$\sigma$	standard deviation
$\phi$	volume fraction
$\chi$	interaction parameter

### Subscripts

$c$	cosurfactant
$i$	$i$ th class of distribution
$m$	monomer
$w$	water

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