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Particle size distribution in mini-emulsion polymerization

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Abstract

The particle size distribution polydispersities of a number of macro- and mini-emulsion latexes are reported. In cases where the macro-emulsion and mini-emulsions were produced under very nearly identical conditions, the mini-emulsion will have a polydispersity equal to, or only very slightly greater than, the equivalent macro-emulsion. ***To cite this article: K. Landfester et al., C. R. Chimie 6 (2003).***

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Résumé

Les polydispersités de distribution de taille des particules d'un certain nombre de latex de macro- et de mini-émulsion sont présentées. Dans les cas où les macro- et les mini-émulsions sont produites dans des conditions sensiblement identiques, la mini-émulsion aura une polydispersité égale, ou seulement très légèrement supérieure, à la macro-émulsion équivalente. ***Pour citer cet article : K. Landfester et al., C. R. Chimie 6 (2003).***

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1. Introduction

Emulsion and mini-emulsion polymerizations have many similarities, but particle nucleation and monomer transport are very different. Conventional emulsion (denoted herein as *macro-emulsion*) polymerization is started with a monomer emulsion comprised of relatively large (in the range of 5–10 microns) monomer droplets and significant free or micellar surfactant. Particle nucleation takes place early in the reaction via homogeneous (water phase) polymerization followed by precipitation, or via free radical entry into monomer-swollen micelles. Radicals can enter the monomer droplets, but this phenomenon is generally discounted because of the relatively small droplet surface area. Nucleation stops or slows significantly after

the surface area of the particles becomes sufficient to adsorb all of the surfactant from the micelles. The major locus of polymerization thereafter is in the nucleated particles. The monomer must move from the monomer droplets to the reaction sites in the particles by diffusion.

In mini-emulsion polymerization, an effective surfactant/costabilizer system is used to stabilize very small monomer droplets (50–500 nm). In order to break up monomer droplets to such size, high agitation is applied by sonication or homogenization [1]. The costabilizer (also known as a cosurfactant) is a highly monomer-soluble, highly water-insoluble material added to increase diffusional stability of the emulsion. Usually long-chain alkanes such as hexadecane or long-chain alcohols such as cetyl alcohol are employed as costabilizers [2,3]. Because these costabilizers cannot diffuse readily through the aqueous phase (due to their extremely low water solubility), removing monomer from a small monomer droplet will cause an increase in the concentration of the costabilizer, with a resultant increase in the free energy. Therefore, the use of a costabilizer will significantly retard, or even prevent Ostwald ripening (transfer of monomer from small droplets to large droplets to reduce the total surface energy of the system), and thus keep the small droplets stable during polymerization. For an ideal mini-emulsion polymerization, there is no mass transport involved. The large droplet surface area in mini-emulsions (because of small droplet size) results in most of the surfactant being adsorbed to the droplets with little free surfactant available to form micelles or stabilize aqueous phase polymerization. Therefore, the predominant nucleation mechanism in mini-emulsion polymerization is droplet nucleation.

There is a (perhaps unsupported) belief that, due to the fact that the original mini-emulsion droplets are formed by a shear process, the droplet size distribution will be broad, and so the resulting particle size distribution (PSD) will have a large polydispersity (as measured by the *polydispersity index*, defined as the mass average over the number average particle radius). This paper will discuss particle size polydispersity in mini-emulsions and attempt to dispel the idea that mini-emulsions necessarily have broader PSD than the equivalent macro-emulsions. Rather, we believe that the PSD of a mini-emulsion can be either broader or narrower than its macro-emulsion counterpart. In most cases, the mini-emulsion will have a polydispersity equal to, or only very slightly greater than, the equivalent macro-emulsion.

2. Literature data

2.1. Hexadecane as costabilizer

Fontenot and Schork [4] studied the mini-emulsion polymerization of methyl methacrylate using hexadecane as the costabilizer. A portion of their results is shown in Table 1. Polydispersities are listed for macro-emulsion, and mini-emulsions subjected to varying durations of sonication, at two levels of initiator. In this and all cases following, the macro-emulsions and mini-emulsions were made from the same recipe, but with the costabilizer left out in the macro-emulsion. The mini-emulsions and macro-emulsions were polymerized by the same procedure except that the sonication was eliminated for the macro-emulsions. It may be seen that at both initiator levels, the macro-emulsion is slightly more narrow that some of the mini-emulsions, but broader than others. An estimate of the standard deviation of the polydispersity measurement may be derived from linear regression of the data in Table 10 (below). This value is estimated to be ±0.01–0.02, and may be applied to all of the polydispersity data reported. With this standard deviation estimate, it may be seen that the differences in polydispersity between the macro- and mini-emulsions are not likely to be signifi-

Table 1

Polydispersity index as a function of initiator concentration and sonication time; hexadecane as costabilizer and MMA as monomer (from [4])

Sonication time	Polydispersity index
[I] = 0.005 mol l⁻¹_aq.	
Macro-emulsion	1.05
2 min	1.08
4 min	1.06
6 min	1.04
12 min	1.05
[I] = 0.01 mol l⁻¹_aq.	
Macro-emulsion	1.05
2 min	1.07
4 min	1.06
6 min	1.05
8 min	1.07
12 min	1.04

Table 2
Polydispersity index as a function of sonication time (hexadecane as costabilizer and styrene as monomer, from [5])

Sonication time	Diameter d_i (nm)	Polydispersity index
[I] = 0.3 mol L^{-1}_aq.		
Macro-emulsion		1.04
0.5 min	135	1.01
1 min	112	1.03
2 min	96	1.00
5 min	87	1.03
10 min	84	1.02
20 min	83	1.01

cant. Landfester et al. studied the mini-emulsion polymerization of styrene using hexadecane as the costabilizer [5]. In the case of subjecting styrene mini-emulsion varying during of sonication (see Table 2, [5]), very similar trends are seen as for the MMA mini-emulsions, the polydispersities can even be that small that a formation of colloidal crystals is possible. The particle size and the polydispersity of mini-emulsion droplets rapidly polymerized after sonication either do not depend on the amount of the hydrophobe, or are very weak functions of the amount of hydrophobe (see Table 3). It was found that doubling the amount of hydrophobe does not decrease the radius by a factor of 2 (as expected from a zero effective pressure) nor have any effect on the polydispersity, it is just that the effective pressure (pressure difference) have to be the same in every droplet, a mechanism, which in principle does not depend on the amount of hydrophobe.

It was found that the droplet size is initially a function of the amount of mechanical agitation [6]. The

Table 3
Hexadecane as costabilizer with styrene monomer (from [5])

Hexadecane level (gm)	Particle diameter d_i (nm)	Polydispersity index
Macro-emulsion	98	1.04
0.33	109	1.03
0.66	108	1.01
1.66	108	1.01
3.33	102	1.04
5	100	1.03
6.66	99	1.05
8.33	95	1.01

droplets also change rapidly in size throughout sonication in order to approach a pseudo-steady state, assuming a required minimum of energy for reaching this state is used [5]. Once this state is reached, it was found that the size of the droplet does not change any more. Higher sonication time causes a slight reduction in polydispersity.

After stopping sonication, a rather rapid and minor equilibration process has to occur where the effective chemical potential in each droplet (which can be expressed as an effective net pressure) is equilibrating. Since the droplet number after sonication is fixed, also the averaged size is not influenced by this process, but the droplet size distribution usually undergoes very fast change. It can be calculated that the Laplace pressure within the resulting nanodroplets and the osmotic pressure created by the hydrophobe are still far away from being equal: the Laplace pressure is still larger than the osmotic pressure. It was found that steady-state mini-emulsification results in a system 'with critical stability', i.e., the droplet size is the product of a rate equation of fission by ultrasound and fusion by collisions, and the minidroplets are as small as possible for the time scales involved. The equality of droplet pressures makes such systems insensitive against net mass exchange by diffusion processes (after the very fast equilibrium process at the beginning), but the net positive character of the pressure makes them sensitive to all changes of the droplet size. Experimental observation were made that steady-state homogenized mini-emulsions, which are critically stabilized, undergo droplet growth on the timescale of hundreds of hours, presumably by collisions or by hydrophobe exchange. The droplets seem to grow until a zero effective pressure is reached. As it can be seen from Table 4, during this growth, the polydispersity does not change significantly.

Table 4
Influence of a delay time between the ultrasonication and the polymerization (from [5])

Start of polymerization after sonication (h)	Particle diameter d_i (nm)	Polydispersity index
0	82	1.01
1	87	1.05
6	108	1.03
48	152	1.03
96	164	1.04

The conclusion to be drawn might be that there is indeed no significant difference in polydispersity between the mini-emulsion and the equivalent macro-emulsion.

2.2. Dodecyl mercaptan as costabilizer

Mouron et al. [7] and Wang et al. [8] have used dodecyl mercaptan (DDM) as the costabilizer in styrene and MMA mini-emulsion polymerizations, respectively. Some of the results are shown in Tables 5 and 6. For styrene (Table 5), the macro-emulsion is compared with mini-emulsions containing varying levels of DDM (costabilizer). In this case the macro-emulsion has a broader particle size distribution than all but one of the mini-emulsions. For MMA (Table 6), mini-emulsions and the equivalent macro-emulsions are compared at varying initiator concentration. In this case the macro-emulsions all have narrower particle size distributions, although the difference is hardly significant.

2.3. Polymethyl methacrylate as costabilizer

Reimers and Schork [9] have used polymethyl methacrylate as the costabilizer for methyl methacrylate mini-emulsion polymerization. A portion of the results is shown in Table 7. In this case, the mini-emulsion has a more narrow particle size distribution than the equivalent macro-emulsion.

Table 5
Dodecyl mercaptan as costabilizer with styrene monomer (from [7])

DDM level (gm)	Polydispersity index
Macro-emulsion	1.02
1	1.01
2	1.01
3	1.02
4	1.04

Table 6
Dodecyl mercaptan as costabilizer with methyl methacrylate monomer (from [8])

Initiator (mol l^{-1}_aq.)	Macro-emulsion PDI	Mini-emulsion PDI
0.005	1.02	1.02
0.01	1.01	1.02
0.02	1.01	1.02

Table 7
Polymethyl methacrylate as costabilizer with methyl methacrylate monomer (from [9])

	Polydispersity index
Macro-emulsion	1.02
Mini-emulsion	1.01

2.4. Influence of the amount of the surfactant

Colloidal stability is usually controlled by the type and amount of the employed surfactant. In mini-emulsions, the fusion-fission rate equilibrium during sonication and therefore the size of the droplets directly after primary equilibration depends on the amount of surfactant. Colloidal stability is usually controlled by the type and amount of the employed surfactant. For styrene mini-emulsions using sodium dodecylsulfate (SDS) as surfactant, droplet sizes between 180 nm down to 32 nm can be obtained. The polydispersity slightly increases with decreasing size, but is still quite low (see Table 8). Similar molecular amounts of the simple cationic surfactant, cetyltrimethylammonium bromide (CTAB), compared to the anionic surfactant, SDS, result in similar particle sizes showing that the particle size is essentially controlled by a limit of the surfactant coverage of the latex particles [10,11]. Again, the polydispersity increases with decreasing size (see Table 9), but is only slightly higher than in the SDS mini-emulsions.

Table 8
Polydispersity index as a function of SDS concentration (from [5])

SDS concentration (% compared to monomer)	Particle diameter d_i (nm)	Polydispersity index
0.3	180	1.03
0.5	134	1.07
1.0	108	1.02
1.5	94	1.02
2.1	89	1.08
3.5	82	1.08
4.9	82	1.03
6.8	65	1.03
10.3	55	1.05
17.0	46	1.06
25.2	42	1.07

Table 9
Polydispersity index as a function of CTAB concentration (from [11])

CTAB concentration (% compared to monomer)	Particle diameter d_i (nm)	Polydispersity index
0.4	347	1.01
0.7	159	1.05
1.2	125	1.05
2.4	102	1.04
3.6	86	1.01
10.0	59	1.09
16.7	59	1.13

3. Effect of process variables on particles size polydispersity

In order to investigate the effect of process variables on final polydispersity, a half-factorial design of miniemulsion polymerizations were carried out at 30% solids. The monomer was methyl methacrylate, the initiator was potassium persulfate, the surfactant was sodium lauryl sulfate, and the costabilizer was hexadecane. Monomer droplet size reduction was provided by a Fisher 300W Sonic Dismembrator working at a relative output of 60%. Batch size was approximately 0.35 l. Monomer as purified by distillation, and the reactions were carried out under a nitrogen blanket at 50 °C. A factorial design of experiments was carried out by selecting a high and low value to each of the process variables initiator concentration, surfactant concentration, hexadecane concentration and sonication time. In addition, a center point for the design was run. Particle size analysis was carried out with a ProteinSolutions DynaPro Dynamic Light Scattering Instrument. The experiments are summarized in Table 10.

The data were analyzed by linear regression using the following model:

$$D = D_{cp} + a\,I' + b\,S' + c\,H' + d\,t' \qquad (1)$$

Here D is the polydispersity; a, b, c and d are regression constants; and I', S', H' and t' take on values of -1, 0 or 1 representing the low, center and high values of initiator concentration, surfactant concentration, hexadecane constriction and sonication time, respectively. Regression of the data to the form of Equation (1) results in:

$$D = 0.05 + (0.0175)\,I' + (0.0)\,S' \qquad (2)$$
$$+ (0.0)\,H' + (0.0025)\,t'$$

with a correlation index (R^2) of 0.95. Since the input variables have all been scaled to the range -1 to $+1$, the coefficients can be compared directly, to indicate the relative importance of input changes of the specified range on the polydispersity. It may be seen that neither surfactant concentration nor hexadecane concentration (over the ranges investigated) has an effect on polydispersity. These effects would seem to indicate that, above some lower threshold of stability the monomer droplets are stable, against both coalescence and Ostwald ripening. The largest effect on polydispersity is that of initiator concentration, where high initiator concentration causes high polydispersity. The standard error of the coefficient a may be calculated as 0.006. A t-test may be performed to determine if the value of a (0.0175) is statistically different from zero, indicating a significant effect of initiator concentration on polydispersity. At a 95% confidence level, the value of a is 0.0175 ± 0.0167. Since the confidence interval does not overlap zero, there is a significant effect of initiator concentration on

Table 10
Factorial design of experiments for particle size polydispersity

Exp. #	Initiator (mol l^{-1}_aq.)	Surfactant (mol l^{-1}_aq)	Hexadecane (g/100 g_monomer)	Sonication time (min)	Polydispersity index	Particle radius (nm)
1	0.025	0.030	4.63	6	1.05	139.7
2	0.040	0.050	7.40	10	1.07	46.3
3	0.040	0.050	1.85	2	1.05	40.7
4	0.040	0.010	7.40	2	1.05	148.4
5	0.040	0.010	1.85	10	1.06	143.1
6	0.010	0.050	7.40	2	1.02	44.7
7	0.010	0.050	1.85	10	1.02	50.6
8	0.010	0.010	7.40	10	1.02	56.6
9	0.010	0.010	1.85	2	1.03	68.4

polydispersity at the 95% confidence level. If the initiator concentration is too low, then droplet nucleation would occur over a longer period of time, and polydispersity would increase. The probable cause for this effect is homogenous nucleation brought on by high (water soluble) initiator concentration. A smaller effect is that of sonication time. A *t*-test as above indicates that this effect is insignificant at the 95% confidence level.

4. Conclusions

Based on the data above, we believe that it is possible, via mini-emulsion polymerization, to make a polymer latex with a particle size distribution that approaches that made by macro-emulsion polymerizations. In some cases, the mini-emulsion product may be even narrower than the macro-emulsion. There are two significant mechanisms leading to this narrowness. First, the monomer droplet size distribution is determined by the thermodynamics of swelling, and not solely by the droplet size distribution induced by the sonicator or homogenizer. For this to be true, the process should include a *ripening time* between sonication and polymerization. During this ripening time, the droplets will come to swelling equilibrium. Studies show that the ripening time is of the order seconds to minutes, and is naturally included in the preparation of batch polymerizations. Second, the narrowness of the particle size distributions predicated on the ability to nucleate nearly all of the droplets over a short period of time. If droplet nucleation takes place over a longer period of time, some particles will have polymerized for a longer time, and some droplets will loose monomer by mass transfer to growing particles before the droplets begin to polymerize. Using hexadecane or polymer as a costabilizer will facilitate one hundred percent droplet nucleation, while the use of cetyl alcohol does not. Miller et al. [12] have shown that a small amount of polymer dissolved in the monomer droplets enhances droplet nucleation. Also, the initiator flux must be high enough to nucleate all of the droplets within a short time interval.

In summary, the mini-emulsion route to polymer latexes should not be dismissed solely of the requirement of narrow particle size distribution, particularly when the unique properties of the mini-emulsion process may be of particular advantage.

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