High-solids-content batch miniemulsion polymerization

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The feasibility of obtaining high-solids-content latexes through miniemulsion polymerization was investigated. It was found that, for the batch terpolymerization of styrene, 2-ethylhexyl acrylate and methacrylic acid, coagulum-free 60 wt% solids-content latexes can be obtained through the miniemulsion process, whereas the maximum coagulum-free solids-content latex attainable by means of conventional emulsion polymerization was 50 wt%. The effect of the type and amount of surfactant, amount of cosurfactant and sonication time on both the amount of coagulum and particle size was studied. In addition, the chemical, freeze–thaw and mechanical stabilities of the latexes were determined.

(Keywords: miniemulsion; terpolymerization; high solids content)

INTRODUCTION

Miniemulsions are produced by dispersing monomer in water by means of vigorous mechanical agitation or homogenization using a mixed emulsifier system including an ionic surfactant and a water-insoluble cosurfactant such as a fatty alcohol or a long-chain alkane. This process produces submicrometre monomer droplets having a large total surface area, and consequently the monomer droplets can compete effectively for free-radical capture. Therefore, upon addition of initiator, the monomer droplets are a significant locus for nucleation and its relative contribution to the overall nucleation process depends on the extent of the miniemulsification process. Ugelstad *et al.*[1–4] showed that the monomer droplets may become the main locus for particle nucleation if the monomer droplet size is reduced far enough. Chamberlain *et al.*[5] and Choi *et al.*[6] found that the particle formation stage for miniemulsion polymerization was much larger than for conventional emulsion polymerization. This was attributed to the low free-radical adsorption efficiency of the monomer droplets. In addition, these authors, as well as Tang *et al.*[7], found that not all monomer droplets become polymer particles. Therefore, monomer droplets must disappear by another mechanism different from nucleation such as monomer diffusion to growing particles or by collision with polymer particles[8,9].

Delgado and El-Aasser[10] reviewed the kinetic and thermodynamic aspects of miniemulsion copolymerization, concluding that, in addition to the particle formation mechanism, miniemulsion polymerization differs from conventional emulsion polymerization because of the influence of the cosurfactant on the partition of the monomers between the different phases. The presence of cosurfactant (hexadecane) in the monomer droplets reduces the free energy of mixing of the monomers in the monomer droplets. Therefore, the monomer is retained by the cosurfactant in the monomer droplets, lowering both the concentration of monomer in the polymer particles and the polymerization rate.

All these works were basic studies aimed at elucidating the mechanism involved in the miniemulsion polymerization process. Recently, Barnette and Schork[11,12] took advantage of the unique particle nucleation mechanisms of miniemulsion polymerization to eliminate the oscillations occurring in conventional emulsion polymerizations carried out in continuous stirred tank reactors (CSTR)[13]. Another interesting application of miniemulsion polymerization may be the production of high-solids-content latexes. The maximum solids content of a latex is limited by the viscosity of the reaction mixture. The viscosity of a latex decreases when the particle size and the broadness of the particle size distribution increase[14]. Owing to the different nucleation mechanism, the polymer particles produced in the miniemulsion process were larger in size and with a broader particle size distribution than those obtained in the conventional emulsion polymerization process[5,6,15]. An important consequence of this behaviour is that high-solids-content latexes of low viscosity may be produced by miniemulsion polymerization. In the present paper, the feasibility of obtaining high-solids-content latexes through miniemulsion polymerization is investigated for the batch miniemulsion terpolymerization of styrene (S), 2-ethylhexyl acrylate (2EHA) and methacrylic acid (MAA).

EXPERIMENTAL

Technical-grade monomers were used in this work. Styrene contained 20 ppm 4-t-butylcatechol as inhibitor. 2EHA and MAA contained *p*-methoxyphenol (40 and 200 ppm, respectively). Hexadecane (HD, Aldrich), potassium persulphate (KPS, Merck), sodium bicarbonate (Merck), sodium lauryl sulphate (SLS, Merck), and A103 (disodium salt of polyoxyethylenenated nonyl

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Table 1 Recipes used in the first series of experiments

Run	Monomers (g)	Water (g)	A103 (wt%)[a]	HD (wt%)[a]	$K_2S_2O_8$ (wt%)[b]	$NaHCO_3$ (wt%)[b]	Solids content (wt%)
A1	32.42	65	1	4	1	1	35
A2	31.16	65	1	4	2	2	35
A3	42.44	55	1	4	1	1	45
A4	41.37	55	1	4	2	2	45
A5	47.53	50	1	4	1	1	50
A6	46.56	50	1	4	2	2	50
A7	52.69	45	1	4	1	1	55
A8	51.81	45	1	4	2	2	55
A9	57.95	40	1	4	1	1	60
A10	57.17	40	1	4	2	2	60
A11	63.37	35	1	4	1	1	65
A12	62.68	35	1	4	2	2	65
A13	69.01	30	1	4	1	1	70
A14	68.41	30	1	4	2	2	70
A15	75.02	25	1	4	1	1	75
A16	74.52	25	1	4	2	2	75

[a] Based on monomers
[b] Based on water

phenol half ester of sulphosuccinic acid, Cyanamid) were used as received. The water was distilled as deionized (DDI).

The miniemulsions were made by first preparing two solutions, emulsifier and sodium bicarbonate in water and hexadecane in a mixture of the three monomers. These were mixed and the system was subjected to sonication (Branson Sonifier 450) under agitation provided by a magnetic bar stirrer. The conditions for the sonication were as follows: output control, 8; duty cycle, 80–90%. In order to avoid an increase of temperature, the mixture ($\simeq 100\,cm^3$) was immersed in an ice and water bath during the sonication. Then 80 cm^3 of the miniemulsions were transferred to 130 cm^3 glass bottles fitted with screw caps containing sealing gaskets. The atmosphere was flushed with nitrogen by inserting two hypodermic needles through the gasket, one for the nitrogen inlet and the other providing an outlet. A potassium persulphate solution was then injected through the gasket and the bottles were tumbled end-over-end at 38 rpm in a water bath held at 75°C. Polymerizations were carried out to high conversion. Then, the latexes were cooled, filtered through a nylon cloth (63 mesh), the retained solids washed with water and the dry weight of the coagulated material determined. The overall conversion was determined gravimetrically. The particle size was measured by dynamic light scattering. In order to measure the particle size, the samples were diluted to a 10^{-4} solids content, leaving enough time to allow the remaining monomer to diffuse out the polymer particles. Therefore, the particle size measured was that of the unswollen latex particles. This value together with the overall conversion was used to estimate the number of polymer particles.

All the experiments were carried out at 75°C keeping the monomer molar ratio constant (S/2EHA/MAA = 45/45/10). Four series of experiments were carried out. The recipes for the first series of polymerizations are given in *Table 1*. All the experiments in this series were carried out using 4 wt% of HD and 1 wt% of emulsifier A103 (both based on monomers). In these reactions the solids content was varied from 35 to 75 wt%. For each solids content two concentrations of initiator (1 and 2 wt%, based on water) were used. The 35 wt% miniemulsions were prepared using a sonication duty cycle of 80% for 2 min. The rest were sonicated for 5 min. In addition, a duty cycle of 90% was used for solids contents equal to or greater than 60 wt%.

For the sake of comparison, a series of conventional emulsion polymerizations were carried out using equivalent conditions to those of the miniemulsion polymerizations of the first series of experiments, but without both hexadecane and sonication process. The recipes for this series of conventional emulsion polymerizations are presented in *Table 2*.

In the third series of polymerizations, the type (SLS vs. A103) and the amount of emulsifier and the amount of cosurfactant were varied in miniemulsion polymerizations of 60 and 65 wt% solids contents. The polymerization recipes used in this series are given in *Table 3*. In runs C1 and C5 no cosurfactant was used but the mixture of monomers with the aqueous solution of emulsifier was subjected to sonication.

In the fourth series of polymerizations the sonication time was varied in miniemulsion polymerizations containing 30 and 60 wt% solids contents. The recipes of these polymerizations are presented in *Table 4*. The miniemulsions formed after the sonication process were allowed to rest for 15 min. Some phase separation was observed in the case of the 30 wt% miniemulsions sonicated for both 5 and 10 min (miniemulsions D2 and D3). These miniemulsions were stirred for 10 min at 1100 rpm using a stirrer. After this treatment no phase separation was observed in the case of miniemulsion D2 but miniemulsion D3 still showed some phase separation after some rest.

Table 2 Recipes used in the second series of experiments

Run	Monomers (g)	Water (g)	A103 (wt%)[a]	$K_2S_2O_8$ (wt%)[b]	$NaHCO_3$ (wt%)[b]	Solids content (wt%)
B1	33.71	65	1	1	1	35
B2	32.41	65	1	2	2	35
B3	44.16	55	1	1	1	45
B4	43.05	55	1	2	2	45
B5	49.47	50	1	1	1	50
B6	48.46	50	1	2	2	50
B7	54.85	45	1	1	1	55
B8	53.94	45	1	2	2	55
B9	60.35	40	1	1	1	60
B10	59.54	40	1	2	2	60
B11	66.02	35	1	1	1	65
B12	65.30	35	1	2	2	65
B13	71.94	30	1	1	1	70
B14	71.32	30	1	2	2	70
B15	78.28	25	1	1	1	75
B16	77.75	25	1	2	2	75

[a] Based on monomers
[b] Based on water

Table 3 Recipes for the miniemulsion polymerizations included in the third series of experiments

Run	Monomers (g)	Water (g)	A103 (wt%)[a]	HD (wt%)[a]	$K_2S_2O_8$ (wt%)[b]	$NaHCO_3$ (wt%)[b]	HD/A103	Solids content (wt%)
C1	66.98	45	1	0	2	2	0/1	60
C2	66.31	45	1	1	2	2	1/1	60
C3	65.64	45	1	2	2	2	2/1	60
A10	64.32	45	1	4	2	2	4/1	60
C4	63.12	45	1	6	2	2	6/1	60
C5	68.31	45	2	0	2	2	0/2	60
C6	67.61	45	2	1	2	2	1/2	60
C7	66.92	45	2	2	2	2	2/2	60
C8	65.58	45	2	4	2	2	4/2	60
C9	64.30	45	2	6	2	2	6/2	60
C10	72.11	45	2	6	2	2	6/2	65
Run	Monomers (g)	Water (g)	SLS (wt%)[a]	HD (wt%)[a]	$K_2S_2O_8$ (wt%)[b]	$NaHCO_3$ (wt%)[b]	HD/SLS	Solids content (wt%)
C11	53.58	40	1	8	2	2	8/1	60
C12	61.75	35	1	2	2	2	2/1	65
C13	60.00	35	1	5	2	2	5/1	65
C14	58.35	35	1	8	2	2	8/1	65
C15	57.82	35	2	8	2	2	8/2	65
C16	59.44	35	2	5	2	2	5/2	65

[a] Based on monomers
[b] Based on water

Latex paints may employ ions as part of the pigment system or may be applied over new masonry where soluble calcium salts are present. Therefore, stability towards these ions is important. In order to measure the chemical stability of the latexes, a 10 g sample of the latex without any post-stabilization was mixed with 10 cm^3 of salt solution. The salt solutions were NaCl (Panreac) (0.1 and 1 M), $CaCl_2$ (Panreac) (0.1 and 1 M), and $Al_2(SO_4)_3$ (Probus) (0.1 M). The mixing between the latex and the salt solution was carried out slowly under agitation (titration-like) and then kept at room temperature for 24 h. The salt tolerance of the latex was

Table 4 Recipes used in the fourth series of polymerizations

Run	Monomers (g)	Water (g)	SLS (wt%)[a]	HD (wt%)[a]	$K_2S_2O_8$ (wt%)[b]	$NaHCO_3$ (wt%)[b]	Sonication (min)	Solids content (wt%)
D1	27.75	75	1	4	2	2	2	30
D2	27.75	75	1	4	2	2	5	30
D3	27.75	75	1	4	2	2	10	30
D4	62.57	45	1	4	2	2	2	60
D5	62.57	45	1	4	2	2	5	60
D6	62.57	45	1	4	2	2	10	60

[a] Based on monomers
[b] Based on water

Table 5 Results obtained in the first series of experiments

Run	Polymer particle diameter (nm)	Coagulum (wt%)	Overall conversion	Solids content based on conversion (wt%)
A1	240	0	0.96	34
A2	243	0	0.93	33
A3	254	0	0.97	44
A4	230	0	0.95	43
A5	253	0	0.97	49
A6	214	0	0.96	48
A7	242	0	0.97	54
A8	210	0	0.97	54
A9	241	0	0.97	58
A10	229	0	0.94	56
A11	220	10.4	1	65
A12	218	4.1	0.97	63
A13	256	57.8	1	70
A14	233	10.9	0.99	69
A15	256	8.4	0.92	69
A16	287	14.1	0.94	71

determined by measuring the amount of coagulum formed. When no coagulated material was retained by the cloth, the particle size was measured and the relative increase of the particle size was taken as a measure of the chemical stability.

Latexes can suffer freeze during storage, and therefore the resistance to freeze-thaw cycles is very important for commercialization. In order to measure the freeze-thaw stability, the latexes were subjected to cycles where the sample was frozen at −18°C for 12 h and then allowed to thaw at room temperature for 12 h. Both the amount of coagulum formed and the increase of the particle size were taken as a measure of the freeze-thaw stability.

Mechanical stabilities were determined at room temperature by means of a high-speed (about 10 000 rpm) stirrer. The latexes were subjected to high shear for 5 min, then either the amount of coagulum formed or the relative increase of the particle size was taken as a measure of the mechanical stability.

RESULTS AND DISCUSSION

Table 5 presents the results obtained in the first series of experiments. The latexes obtained up to a 60 wt% solids content were liquids whose viscosity increased with the solids content, whereas the products obtained above 60 wt% solids content were gel-like solids. Nevertheless, these gels redispersed upon addition of some water, allowing one to separate the coagulum from the latex. The particle size given in *Table 5* for these latexes were those of the filtered latexes. *Table 5* shows that no coagulum was found up to a 60 wt% solids content. However, significant amounts of coagulum were observed for solids contents over 60 wt%. It can be seen that, in agreement with previously reported results[6,15], particle size decreased when initiator concentration increased. On the other hand, the amount of coagulum seems to decrease when initiator concentration increased.

Figure 1 presents a comparison between the coagulum formed in the conventional emulsion polymerizations and that corresponding to the miniemulsion polymerizations. It can be seen that the amount of coagulum formed in the conventional emulsion polymerization process was larger than that found for the miniemulsion process. Thus, a coagulum-free 60 wt% solids-content latex can be obtained through the miniemulsion process whereas the maximum coagulum-free solids-content latex attain-

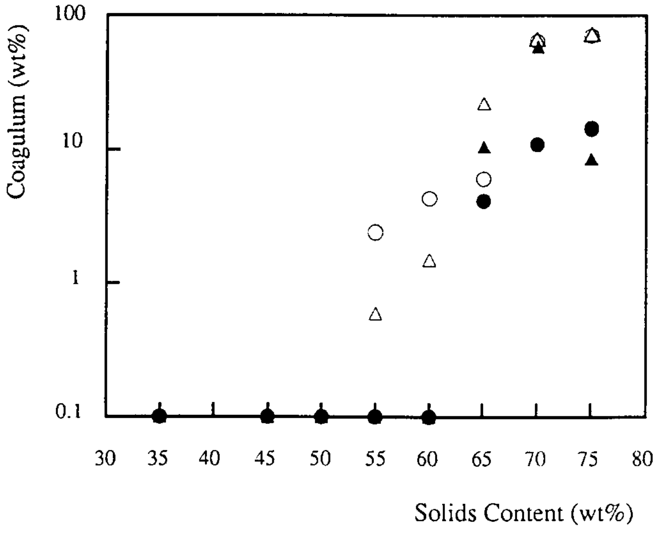

Figure 1 Coagulum formed in the miniemulsion polymerization process as compared with that produced in the conventional emulsion polymerization. Miniemulsion polymerization: (▲) 1 wt% KPS; (●) 2 wt% KPS. Conventional emulsion polymerization: (△) 1 wt% KPS; (○) 2 wt% KPS

Table 6 Effect of the type and amount of emulsifier, and the amount of cosurfactant on the amount of coagulum

(a) A103

Run	Coagulum (wt%)	Conversion	Solids content based on conversion (wt%)
C1	18	1	60
C2	≃0	1	60
C3	0	1	60
A10	0	0.94	56
C4	0	1	60
C5	0	0.96	59
C6	0	1	60
C7	0	1	60
C8	0	1	60
C9	0	1	60
C10	5	1	65

(b) SLS

Run	Coagulum (wt%)	Conversion	Solids content based on conversion (wt%)
C11	0	0.94	57
C12	1	0.91	60
C13	≃0	1	65
C14	≃0	0.96	63
C15	0	1	65
C16	0	0.93	61

able by means of conventional emulsion polymerization was 50 wt%.

Table 6 presents the effect of the type (A103 vs. SLS) and amount of emulsifier, and the amount of cosurfactant on the amount of coagulum. Considering first the experiments carried out using A103, it can be seen that a significant amount of coagulum was formed in run C1 where no hexadecane was included in the recipe. Nevertheless, the formation of coagulum was avoided in run C5 by doubling the amount of emulsifier. On the other hand, coagulum-free 60 wt% solids-content latexes can be obtained with 1 wt% A103 using cosurfactant. However, 5% of coagulum was obtained when the solids content was increased to 65 wt%. *Table 6* shows that coagulum-free 65 wt% solids-content latexes can be obtained using SLS as emulsifier. However, the product obtained was gel-like and redispersed upon addition of some water.

Figure 2 presents the effect of the amounts of A103 and cosurfactant on the polymer particle diameter. It can be seen that the particle size decreased when either the amount of emulsifier or the amount of cosurfactant increased. The effect of the emulsifier is similar to that occurring in conventional emulsion polymerization: the greater the amount of emulsifier the greater the total surface area of the polymer particles that can be stabilized, and therefore the smaller the particle size. The effect of the hexadecane content is related with the effect of the cosurfactant on the monomer droplet size. According to Delgado *et al.*[16], when the amount of HD increased the droplet size decreased and hence the initial emulsion contained more droplets. Therefore, the number of droplets that can be nucleated increased, giving more polymer particles, namely, smaller polymer particles. The small polymer particle size obtained for experiment C5 (HD = 0, A103 = 2 wt%) suggests that a significant part of the nucleation occurred through a conventional nucleation mechanism such as homogeneous nucleation. This is in agreement with the results reported by Durbin *et al.*[17], who found that, when the monomers were premulsified in the presence of an anionic surfactant but no cosurfactant by means of homogenation or ultrasonication, droplet nucleation competed with the conventional mechanisms of nucleation.

Table 7 presents the effect of the sonication time on the latex particle size of miniemulsions formed using SLS and containing 30 and 60 wt% solids content. It can be seen that the sonication time has no effect on the particle size. On the other hand, no coagulum was observed in these polymerizations.

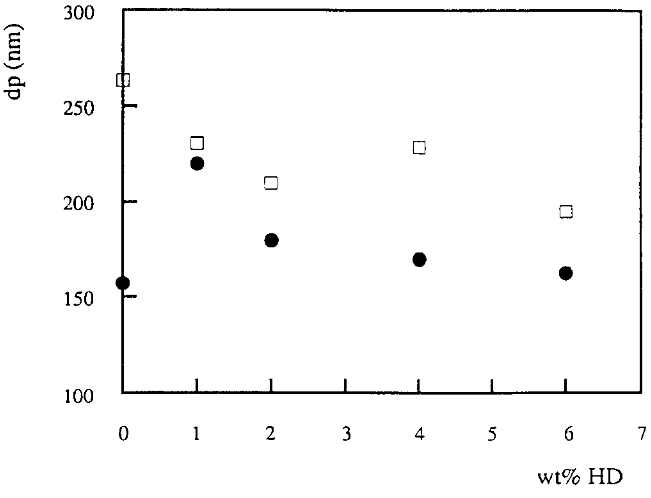

Figure 2 Effect of the amount of A103 and cosurfactant on the polymer particle diameter: (□) A103 = 1 wt%; (●) A103 = 2 wt%

Table 7 Effect of the sonication time on the latex particle size of miniemulsions formed using SLS

Run	D1	D2	D3	D4	D5	D6
Particle diameter (nm)	207	235	233	172	174	189

Table 8 Effect of high shear on the particle size

Run	A1	A3	A5	A7	A9
Solids content	35	45	50	55	60
d_p before test (nm)	240	254	253	242	242
d_p after test (nm)	228	217	219	237	243

Chemical stability

All miniemulsion latexes were stable upon addition of 0.1 and 1 M solutions of both NaCl and $CaCl_2$. In addition, while the addition of the solutions of NaCl did not affect the particle size, a significant increase of the particle size was observed when 1 M $CaCl_2$ solution was added. This suggests a limited coagulation. On the other hand, all miniemulsion latexes were coagulated by the 0.1 M solution of $Al_2(SO_4)_3$.

Freeze–thaw stability

Miniemulsion latexes stabilized with A103 and having several solids contents (35, 45, 50, 55 and 60 wt%) were subjected to freeze–thaw cycles. It was found that latexes with solids contents equal to or greater than 50 wt% completely coagulated after the first cycle. The latex containing a 45 wt% solids content partially coagulated in the first cycle. On the other hand, the 35 wt% solids-content latex was stable to five cycles. The slight increase of the particle size of this latex after five cycles (from 240 nm to 278 nm) indicates that some coagulation occurred during the test.

The miniemulsion latexes stabilized with SLS were less stable to freeze–thaw cycles than those formed using A103. Thus, the latex D2 (SLS, 30 wt% solids content) showed 11 wt% of coagulum after the first cycle. The difference between the two emulsifiers may be due to the 32 ethoxy groups of the A103 because long ethoxy chains can reduce coagulation during the freeze–thaw process[18].

Mechanical stability

No coagulum was observed for all the miniemulsion latexes after mechanical stability test. In addition, *Table 8* presents the effect of high shear on the particle size. It can be seen that for low solids contents particle size slightly decreased after the mechanical test, suggesting some reversible flocculation.

CONCLUSIONS

The feasibility of obtaining high-solids-content latexes through miniemulsion polymerization was investigated. It was found that, for the batch terpolymerization of styrene, 2-ethylhexyl acrylate and methacrylic acid, coagulum-free 60 wt% solids-content latexes can be obtained through the miniemulsion polymerization process, whereas the maximum solids content attainable by means of the conventional emulsion polymerization was 50 wt%. This difference was attributed to the monomer droplet nucleation mechanism occurring in miniemulsion polymerization. This mechanism gives polymer particles that are larger in size and with a broader particle size distribution than those obtained in the conventional emulsion polymerization process. Therefore, the viscosity of the miniemulsion latexes is lower than that of the conventional latexes and hence higher solids-contents latexes can be produced by the former method. It was found that some coagulum was formed when the amounts of surfactant and cosurfactant were reduced below some critical values. All latexes were mechanically stable. In addition, they showed a good tolerance to NaCl and $CaCl_2$ solutions but they are coagulated by 0.1 M $Al_2(SO_4)_3$ solution. On the other hand, all latexes except the 35 wt% latex showed a poor freeze–thaw stability.

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