

A Comparison between Miniemulsion and Conventional Emulsion Terpolymerization of Styrene, 2-Ethylhexyl Acrylate and Methacrylic Acid

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SYNOPSIS

The kinetics of the high solids content miniemulsion terpolymerization of styrene, 2-ethyl hexyl acrylate and the methacrylic acid and the final properties of the latexes produced by this method were compared with those resulting from the corresponding conventional emulsion polymerization process. The final latex properties considered were: latex viscosity both prior and after neutralization, mechanical stability, chemical stability, and freeze-thaw stability. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Miniemulsions are highly stable oil-in-water emulsions prepared using a mixed emulsifier system comprising an ionic surfactant and a water insoluble cosurfactant such as a fatty alcohol or a long chain alkane. The role of the cosurfactant, mainly in the case of long chain alkanes, is to prevent degradation of the miniemulsion due to molecular diffusion of the monomer.¹ Ugelstad, El-Aasser and Vanderhoff² in their pioneer study on the miniemulsion polymerization of styrene, showed that by dispersing the monomer into submicron and stable droplets, the surface area of these droplets was increased drastically and they can compete effectively for free radical capture. Therefore, it was postulated that monomer droplets were the main locus for particle nucleation in these polymerizations.

Since the initial work² was published, many investigators have studied the miniemulsion polymerization process.³⁻²² The kinetic and thermodynamic aspects of miniemulsion polymerization have been reviewed by Delgado and El-Aasser.²⁰ They concluded that the kinetic differences between conventional emulsion polymerization and miniemul-

sion polymerization are due to the particle formation mechanism and the influence of the cosurfactant on the concentration of the monomer in the different phases.

The particle nucleation mechanism proceeds through monomer droplet nucleation. Evidence supporting this mechanisms have been reported by Ugelstad et al.³ and Rodríguez¹³ who, for different systems, found that the number of final polymer particles increased when the number of monomer droplets increased. In addition, Tang et al.²¹ showed that, for the semicontinuous seeded emulsion polymerization of butyl acrylate, a small amount of new particles was formed in the system when monomer was added neat, whereas a significant secondary nucleation was observed when the monomer was added as a miniemulsion. The results also showed that monomer droplet nucleation takes place whenever miniemulsion droplets exist in the reactor. This unique mechanism for particle nucleation gives particles that are larger in size and with a particle size distribution broader than those produced by the conventional process.^{7,8,19}

The equilibrium concentrations of the monomers in the different phases depend on the distribution of the cosurfactant between the monomer droplets and polymer particles. Thus, an increase of the cosurfactant concentration in the monomer droplets reduces the equilibrium concentrations of the

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monomers in the polymer particles. This can explain the fact that the evolution of the copolymer composition for the miniemulsion copolymerization of vinyl acetate and butyl acrylate was different from that of the conventional emulsion process.⁹

Most of these studies were mainly fundamental investigations aiming at elucidating the mechanisms involved in the miniemulsion polymerization process. Therefore, they were carried out with latex formulated at low solids contents (< 35 wt %). However, almost all industrial recipes are high solids latexes (> 50 wt %). In addition, no comparison between the final properties of the latexes obtained by miniemulsion polymerization and those of the latexes produced through the conventional emulsion process has been reported. In the present work, the kinetics of the high solids (55 wt %) miniemulsion terpolymerization of styrene, 2-ethylhexyl acrylate and methacrylic acid and the final properties of the latexes produced by this method were compared with those resulting from the corresponding conventional emulsion terpolymerization. The final properties of the latex studied were: viscosity of the latex both prior and after neutralization, mechanical stability, chemical stability, and freeze-thaw stability.

EXPERIMENTAL

Technical grade monomers were used in this work. Styrene (S) contained 20 ppm of 4-tert butylcatechol as inhibitor. 2-Ethylhexyl acrylate (2 EHA) and methacrylic acid (MAA) contained p-methoxyphenol (40 and 200 ppm, respectively). The other materials were also used as received. Deionized water was used throughout the work.

Polymerizations were carried out in a 1 L glass

unbaffled reactor equipped with a reflux condenser, stainless steel stirrer, sampling device, nitrogen inlet and a feed inlet tube. Both semicontinuous miniemulsion terpolymerizations and semicontinuous conventional emulsion terpolymerizations were carried out.

The semicontinuous miniemulsion terpolymerizations were carried out using the recipes given in Table I. The solids contents of these recipes were slightly above 55 wt %. Different emulsification processes were used for the initial charge and the feed. In order to prepare the miniemulsion initially charged into the reactor (10 wt % of the total recipe), the emulsifier was dissolved in water and a mixture of hexadecane (HD) and the three monomers was added to the aqueous solution. 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: 7; duty cycle: 60%; sonication time: 5 min.; temperature: 15°C. This miniemulsion was charged into the reactor, heated to 80°C under a nitrogen blanket, and then an aqueous solution of initiator was added. The miniemulsion was allowed to polymerize in batch for 15 min and then the feed was started. The feed was a miniemulsion that was formed by flowing a mixture of the monomers and hexadecane and an aqueous solution of emulsifier and initiator through the sonifier equipped with a continuous flow cell cooled with a water jacket. The conditions for the continuous sonication were as follows: output control: 7; duty cycle: 60%; residence time in the flow cell: 15 min; temperature: 15 ± 4°C. The flow rate of the mixture of monomers and hexadecane as well as that of the aqueous solution of initiator and emulsifier were adjusted to keep constant the composition of the miniemulsion feed. The

Table I Recipes Used in the Semicontinuous Miniemulsion Terpolymerizations

Run	Emulsifier : SLS		Emulsifier : Alipal CO-436
	MIN 1	MIN 2	MIN 3
Styrene (g)	158.8	158.8	159.6
2 Ethylhexyl acrylate (g)	281.0	281.0	282.4
Methacrylic acid (g)	29.19	29.19	29.33
K ₂ S ₂ O ₈ (g)	1.978	1.931	1.948
Emulsifier (g)	25.98	25.98	23.71
Hexadecane (g)	9.38	18.76	9.42
Water (g)	395.6	386.2	389.6

addition was completed in 5 h 30 min. Then, the reaction mixture was allowed to react in batch at the reaction temperature (80°C) for about 2 h.

Reactions using both sodium lauryl sulfate (SLS) and Alipal CO-436 (ammonium salt of sulfated nonylphenoxy poly (ethylenoxy) ethanol (4 ethylenoxide)) were carried out. Similar weight concentrations of these surfactants were employed (SLS: 5.54 wt %; Alipal: 5.03 wt %, based on monomers). In addition, two different HD concentrations (2 wt % and 4 wt % based on monomers) were used in the polymerizations carried out with SLS.

The semicontinuous conventional emulsion terpolymerizations were carried out using the recipes given in Table II. The solids content of these recipes was 55 wt %. All the ingredients of the initial charge (10 wt % of the total recipe), except the initiator that was dissolved in a small amount of water, were charged into the reactor stirred at 200 rpm and heated to 80°C. Then, the aqueous solution of the initiator was added. The emulsion was allowed to react for 15 min and then the feed was started. The feed was divided into two streams. The first was an emulsion containing the monomers, surfactant and a fraction of water. The second was an aqueous solution of the initiator. The flow rates of these streams were adjusted to finish the addition of both streams in 6 h. Polymerizations using both SLS and Alipal CO-436 were carried out. The concentrations of these surfactants in the recipe were the same as in the miniemulsion polymerizations.

Samples were withdrawn during the process and the polymerization was short-stopped with hydroquinone. The overall conversion was determined gravimetrically. The particle size was measured by dynamic light scattering. This value together with that of the overall conversion were used to estimate the number of polymer particles.

The viscosity of the final latex both prior and after neutralization with ammonia was measured

with a concentric cylinder viscosimeter (UK ELV-8) using spindle no. 4 at 30 rpm and 30°C. Mechanical stabilities were determined at room temperature by means of a high-speed (about 10,000 rpm) stirrer. The latex taken from the reactor at the end of the polymerization was subjected to high shear for 4 min. Then, the sample was filtered through a nylon cloth (63 mesh) and the retained solids washed with water. The dry weight of the coagulated material was determined as a measure of the mechanical stability. When no coagulated material was retained by the cloth, the particle size of the stirred latex was measured by DLS. An increase of the particle size suggests limited coagulation and hence the relative increase of the latex diameter was taken as a measure of the mechanical stability.

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 poststabilization was mixed with 10 cc of salt solution. The salt solutions used were NaCl (0.1M and 1M); CaCl₂ (0.1M and 1M); and Al₂(SO₄)₃ (0.1M and 0.5M). The mixing between the latex and the salt solution was carried out slowly under agitation (titration-like) and kept at room temperature for 24 h. Then the salt tolerance of the latex was determined by measuring either the amount of coagulum formed or the increase in particle diameter.

Latexes can freeze during storage, 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.

Table II Recipes Used in the Semicontinuous Conventional Emulsion Terpolymerizations

Run	Emulsifier : SLS	Emulsifier : Alipal CO-436
	EM1	EM2
Styrene (g)	176.5	177.4
2 Ethylhexyl acrylate (g)	312.2	313.7
Methacrylic acid (g)	32.43	32.56
K ₂ S ₂ O ₈ (g)	2.250	2.217
Emulsifier (g)	28.87	26.34
Water (g)	450.0	443.4

RESULTS AND DISCUSSION

Kinetics

Figure 1 presents the time evolution of the fractional conversion for the experiments carried out using sodium lauryl sulfate as emulsifier. The fractional conversion is defined as the weight fraction of the monomers already fed into the reactor that has been converted into terpolymer. For all the reactions, the first point corresponds to the end of the batch preperiod. It can be seen that the polymerization rate is higher in the case of conventional emulsion than for the two miniemulsion processes. In addition, the amount of cosurfactant in the recipe showed no effect on the polymerization rate. Figure 2 presents the evolution of the total number of polymer particles for the reactions carried out with SLS. As in the case of the fractional conversion evolution, the first point of each curve corresponds to the end of the batch preperiod. It can be seen that the three reactions showed a continuous particle nucleation during the process, being the number of polymer particles formed in the conventional emulsion process larger than those in the miniemulsion polymerizations. In addition, for the miniemulsion processes, the number of polymer particles slightly increased with the amount of HD in the recipe. Figure 2 shows that the differences in polymerization rate between the miniemulsion process and the conventional emulsion polymerization were mainly due to the different number of polymer particles generated in these systems. This is in agreement with previously reported results^{7,8,19} that, for different mono-

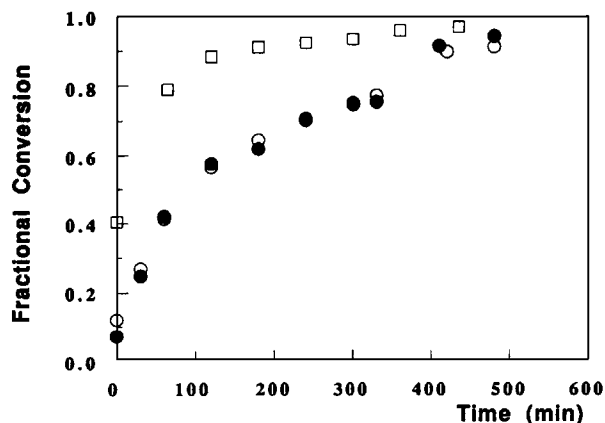


Figure 1 Time evolution of the fractional conversion for the polymerizations using SLS 5.54 wt %. Legend: (○) miniemulsion terpolymerization, 2 wt % HD; (●) miniemulsion terpolymerization, 4 wt % HD; (□) conventional emulsion terpolymerization.

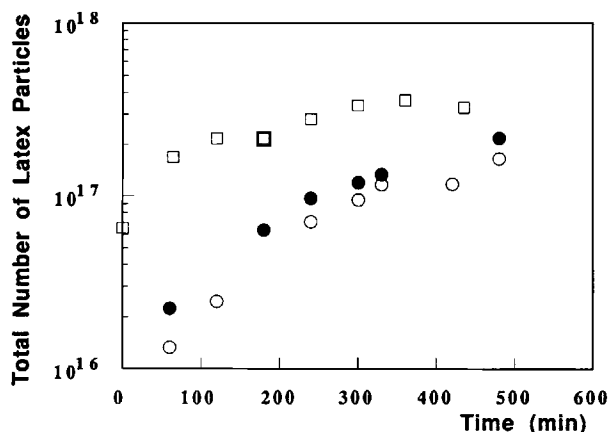


Figure 2 Evolution of the total number of latex particles in the reactor for the experiments using SLS (5.54 wt %). Legend: (○) miniemulsion, 2 wt % HD; (●) miniemulsion, 4 wt % HD; (□) conventional emulsion.

mers, showed that the particles produced in the miniemulsion polymerization were larger in size and the particle size distribution, PSD, was broader than those produced in the conventional process. In addition, the presence of HD may further reduce the miniemulsion polymerization rate because the cosurfactant affects the concentration of the monomers in the polymer particles in such a way that an increase of the HD concentration in the monomer droplets reduces the concentration of the monomers in the polymer particles.¹⁵ This can explain that the polymerization rate of the two miniemulsion experiments was the same even though the number of polymer particles obtained using 4 wt % HD was greater than that produced using 2 wt % HD.

The time evolution of the fractional conversion and the total number of polymer particles for the reactions carried out using Alipal CO-436 are presented in Figures 3 and 4, respectively. The kinetic behavior is similar to that obtained using SLS, namely the polymerization rate and the number of polymer particles obtained in the miniemulsion process were lower than those of the conventional emulsion system. In addition, comparison between the results obtained using Alipal CO-436 and those obtained with SLS showed that, for the miniemulsion process, the number of polymer particles formed with Alipal CO-436 was greater than that obtained given SLS whereas the opposite was found for the conventional process.

Latex Rheology

Figure 5 shows the influence of the polymerization process (miniemulsion vs. conventional emulsion)

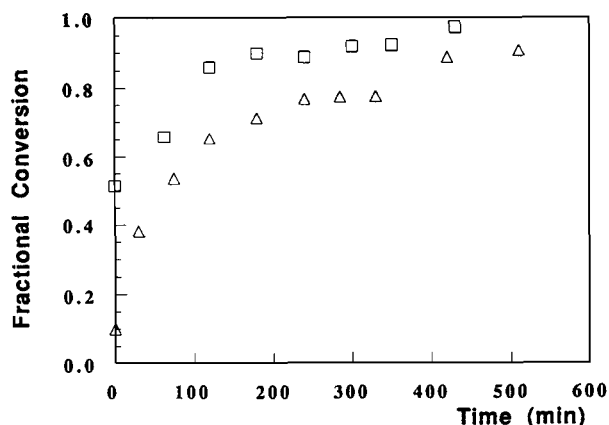


Figure 3 Time evolution of the fractional conversion for the polymerizations carried out using Alipal CO-436 (5.03 wt %). Legend: (Δ) miniemulsion terpolymerization, 2 wt % HD; (\square) conventional emulsion terpolymerization.

on the latex viscosity for the two emulsifiers used. In this figure, the latex viscosities measured prior and after neutralization with ammonia were included. Polymerizations proceeded under acidic conditions because no buffer was used. Table III presents the variation of the pH during polymerization. It can be seen that the systems become slightly more acidic during polymerization. The viscosity of the acidic latex is important because it is the viscosity of the latex in the reactor that is critical for reactor performance. Thus, the maximum solids content of the latex that can be produced is limited by the viscosity of the reaction mixture. On the other hand, latexes are stored and used in a neutralized form, therefore the latex viscosity after neutraliza-

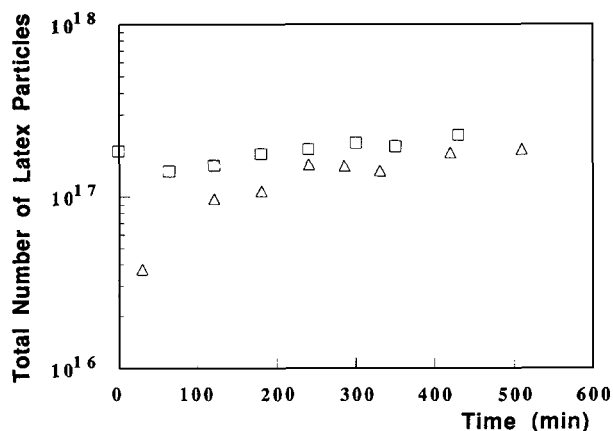


Figure 4 Effect of the polymerization process on the total number of polymer particles for the reactions using Alipal CO-436 (5.03 wt %). Legend: (Δ) miniemulsion terpolymerization, 2 wt % HD; (\square) conventional emulsion terpolymerization.

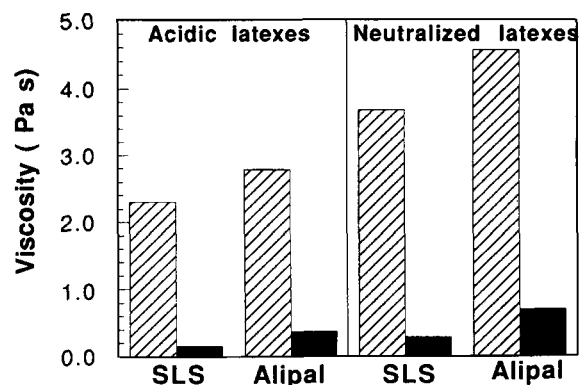


Figure 5 Effect of the polymerization process, (\blacksquare) miniemulsion vs. (\hatched) conventional emulsion, on the latex viscosity. Miniemulsions contained a 2 wt % of hexadecane.

tion is important for latex applications. Figure 5 shows that the latexes obtained by means of miniemulsion terpolymerization presented a viscosity much lower than that of the latexes produced by conventional emulsion polymerization. This behavior can be explained taking into account that, due to the different nucleation mechanisms, the polymer particles produced in the miniemulsion process were larger in size and with a broader PSD than those obtained in the conventional emulsion polymerization process, and the larger the particle size and the broader the particle size distribution the lower the latex viscosity.²³ An important consequence of this behavior is that miniemulsion polymerization may be an interesting method to prepare extra high solids content latexes (> 65 wt %) with manageable viscosity.

A significant increase of the emulsion viscosity was observed when the latexes were neutralized with ammonia to pH = 7. Acid-containing emulsion polymers swell upon addition of a base such as ammonia²⁴ and this results in an increase of the volume fraction of the polymer particles in the latex and hence in an increase of the viscosity.

Table III Evolution of the pH During the Polymerizations

Run	Initial pH	Final pH
EM 1	2.9	2.3
MIN 1	2.9	2.2
MIN 2	2.9	2.3
EM 2	2.8	1.9
MIN 3	2.9	1.9

Table IV Results of the Mechanical Stability Tests

Run	Coagulum (wt %)	Particle Diameter (nm)	
		Before Test	After Test
EM 1	0	141	171
MIN 1	0	174	170
MIN 2	0	159	166
EM 2	0	158	162
MIN 3	0	164	194

Comparison between the viscosities of the latexes obtained with SLS and those produced using Alipal CO-436 showed that the viscosities of the former latexes were lower than those of the latexes produced with Alipal CO-436. In addition, these differences cannot be attributed to the differences in size because for instance the latex obtained from run EM2 (conventional emulsion using Alipal CO-436) presented both viscosity and particle size larger than those of the run EM1 (conventional emulsion using SLS). These results suggest that the increase in viscosity observed for the Alipal CO-436 latexes was due to an increase of the effective volume fraction of the polymer particles which resulted from the hydration of the ethoxy groups of the Alipal CO-436.

Mechanical Stability

No coagulum was observed for any of the latexes after the mechanical stability test. In addition, Table

IV presents the effect of the high shear on the particle size. This table shows that, in general, the particle size increased after the application of the high shear suggesting a limited coagulation.

Chemical Stability

Table V presents the results obtained from the chemical stability test. The salt tolerance of the latex without any poststabilization was determined by measuring the amount of coagulum formed. The salt solutions used were NaCl (0.1M and 1M), CaCl₂ (0.1M and 1M), and Al₂(SO₄)₃ (0.1M and 0.5M). When coagulum was not observed, the latex particle diameter was measured and the relative increase of the particle size was used as a measure of the chemical stability. Therefore, Table V includes both coagulum percentage (for the cases where coagulum was observed) and polymer particle diameter (when coagulum was not found).

Table V shows that the latex produced through conventional emulsion polymerization using SLS was stable upon addition of a 0.1M solution of NaCl but a significant increase of the particle size was observed when a 1M NaCl solution was used. This increase in size suggests limited coagulation. In addition, this latex coagulated completely when the ionic strength of the salt solution was further increased and when CaCl₂ and Al₂(SO₄)₃ were used. This behavior was due to the fact that SLS is an anionic emulsifier that promotes electrostatic stabilization of the latex particles, and hence the decrease of the double-layer thickness due to the in-

Table V Results Obtained in the Chemical Stability Tests

Process	Emulsifier	Before Test	Particle Size (nm)					
			After Test					
			NaCl		CaCl ₂		Al ₂ (SO ₄) ₃	
			0.1M	1M	0.1M	1M	0.1M	1M
Emulsion	SLS	141	157	213	(100%)	(100%)	(100%)	(100%)
Miniemulsion								
2 wt % HD	SLS	173	172	185	(6%)	(23%)	(100%)	(100%)
Miniemulsion								
4 wt % HD	SLS	159	149	162	(3.5%)	(25%)	(100%)	(100%)
Emulsion	Alipal CO 436	158	163	152	153	173	(100%)	(100%)
Miniemulsion								
2 wt % HD	Alipal CO 436	164	176	165	172	173	(100%)	(100%)

(%) Coagulum percentage.

crease in anionic strength of the aqueous phase resulted in a decrease in the stability of the latex particles.

The latex prepared by means of miniemulsion polymerization showed a better chemical stability as compared to those from the conventional emulsion process. These latexes remained unaffected upon addition of NaCl and were partially coagulated by the CaCl_2 solutions. In this case, the amount of coagulum increased with the concentration of the CaCl_2 solution. In addition, the chemical stability of the miniemulsion latexes seems to increase with the HD content. On the other hand, these latexes suffered complete coagulation when mixed with the $\text{Al}_2(\text{SO}_4)_3$ solutions.

The increase of the stability of the miniemulsion latexes can be due to both the larger particle size and the different distribution of the methacrylic acid in the miniemulsion polymer particles as compared with those obtained by means of conventional emulsion polymerization. The surface area of the latex particles decreases when the particle size increases and hence, for a given amount of emulsifier, the coverage of the surface increases. Therefore, the chemical stability of the latex increases. On the other hand, the latex stability is promoted by the presence of carboxyl groups on the particle surface. The distribution of the carboxyl groups between the surface and the core of the polymer particle depends on both the hydrophobicity of the monomer forming the core and the method of latex preparation. Thus, El-Aasser et al.²⁴ found that batch polymerization gave higher concentration of carboxyl groups at or near the particle surface, whereas the semicontinuous polymerization carried out under starved conditions gave a more uniform distribution throughout the particle. In addition, the concentration of carboxyl groups at the particle surface increased when the hydrophobicity of the monomer forming the core increased. In the miniemulsion experiments, the hydrophobicity of the particle core was greater than the one in the conventional emulsion process because of the presence of hexadecane. Moreover, comparison between the kinetics of the miniemulsion processes and those of the conventional emulsion polymerizations (Figs. 1 and 3) shows that the conventional emulsion polymerizations were carried out under conditions close to the starved conditions, whereas the miniemulsion polymerizations, due to their low polymerization rate, were rather far from the starved conditions, namely, they had some batch-like character. Therefore, it is expected that the concentration of carboxyl groups at or near the

particle surface was greater for miniemulsion latexes than for those produced by means of the conventional emulsion process, and this may further stabilize the miniemulsion latexes.

In order to check this point, the distribution of the carboxyl groups in the particles were determined following the method developed by El-Aasser et al.²⁴ The carboxyl groups of the latex were arbitrarily divided into five loci: (1) the particle surface; (2) the first subsurface layer; (3) the second subsurface layer below the first subsurface layer; (4) the unneutralized core; and (5) the serum. The surface carboxyl groups were defined as all groups neutralized within 15 seconds after the addition of the base (sodium hydroxide). The first and second subsurface layers were taken as the carboxyl groups neutralized in the first 10 minutes of the experiment and from 10 minutes to 24 h, respectively. Any carboxyl group unneutralized after 24 hours were taken as unneutralized core. Figure 6 presents the distribution of the carboxyl groups in particles produced by miniemulsion polymerization (run MIN 2) and conventional emulsion polymerization (run EM 1). It can be seen that the miniemulsion latexes have a higher concentration of carboxyl groups at or near the particle surface than the latexes obtained by the conventional emulsion process. This may contribute to the better stability of the miniemulsion latexes as compared with the conventional ones.

Table V also shows that the chemical stability of the latex produced using Alipal CO-436 was better than those obtained with SLS. This can be explained taking into account the steric stabilization provided by the hydration of the ethoxy groups of the Alipal

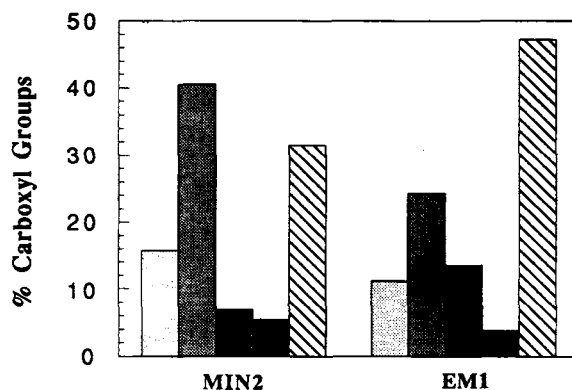


Figure 6 Distribution of the carboxyl groups for miniemulsion latexes and conventional emulsion latexes. (□) serum, (▨) surface, (■) first subsurface layer, (■) second subsurface layer, (▩) unneutralized core.

CO-436. In addition, it can be seen that for the Alipal CO-436 the steric stabilization concealed the effect of the polymerization process.

Freeze-Thaw Stability

All the latex coagulated completely after one freeze-thaw cycle. This was expected taking into account the process occurring during the freeze-thaw test. When freezing occurs ice crystals separate from the unfrozen latex reducing the volume of the continuous phase and increasing the ionic concentration of this phase. Therefore, the stability of the latex is reduced and the latex, which is subjected to high pressure, coagulates. The coagulation during the freezing process is more intense as the minimum film forming temperature of the latex decreases. Nevertheless, this effect can be counteracted by increasing the amount of carboxylate groups copolymerized.²⁵ Also nonionic surfactants with long ethoxy chain can reduce coagulation during the freeze-thaw process.²⁶ The system used in this work was mainly electrostatically stabilized although some steric stabilization may result from the Alipal CO-436 short ethoxy chains. In addition, the latex had a low minimum film forming temperature and were used without further stabilization.

CONCLUSIONS

In the foregoing, a comparison between miniemulsion and conventional emulsion terpolymerization of styrene, 2-ethylhexyl acrylate and methacrylic acid has been carried out. Both the kinetics and the final properties of the latexes were considered. It was found that the polymerization rate was higher in the case of conventional emulsion polymerization than for the miniemulsion process. This difference was mainly due to the larger number of polymer particles generated in the conventional process as compared with the miniemulsion polymerization. On the other hand, the latexes obtained by means of miniemulsion terpolymerization presented a viscosity much lower than that of the latexes produced by conventional emulsion polymerization. In addition, the viscosity of the latex produced with SLS was lower than that the latexes obtained with Alipal CO-436. All of the latexes showed a good mechanical stability but a poor freeze-thaw behavior. The better salt tolerance of the miniemulsion latexes, as compared with the conventional latexes, may be due to both the larger particle size and the higher concen-

tration of methacrylic acid at or near the particle surface of the miniemulsion latexes.

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