Coagulation of Carboxylic Acid-Functionalized Latexes

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Summary: In the present work, the stability of particles produced by emulsion polymerization and stabilized by carboxylic acid groups was studied from turbidity measurements. To achieve this, a number of copolymerization runs was carried out under different reaction conditions, including the use of different carboxylic monomers. Partitioning analyses using conductimetric and potentiometric titrations were performed in order to assess the distribution of carboxylic monomers among the main phases of the produced latexes. Additionally, the stability and coalescence of particles were measured by turbidimetry in a diluted latex considering either the presence or not of the anionic surfactant sodium lauryl sulfate. Coalescence of particles was provoked in the latex samples at different temperatures by addition of an aliquot of a concentrated solution of electrolyte. The influence of surfactant, temperature and type of carboxylic acid group on the particle stability was investigated.

Keywords: carboxylated latex; copolymerization; emulsion; stability; turbidimetry

Introduction

Emulsion polymerization is a process of great industrial importance to produce latex for paints, toners, adhesives, coatings and other synthetic materials. For all these applications, the industrial process must provide polymeric latexes with the desired colloidal characteristics, with a particular attention on the latex stability. In this sense, carboxylic monomers have commonly been used in industrial latex recipes at small quantities to improve different quality parameters of the latex, including the compatibility with pigments, mechanical properties and the latex stability.[1–10] Carboxylation of latex polymer particles increases shear and freeze-thaw stability, brings desirable viscosity profiles vs. pH, has a positive effect on the polymer adhesion towards substrates like metals, clays, calcium carbonate or fibers, and provides the final product with sites on the particle surface for post-polymerization reactions.[2] Also, the final emulsion products are referred to as carboxylated latexes and carboxylated polymers.[3] These polymers are generally obtained by copolymerizing a monomer with low-water solubility like styrene or butyl acrylate with a water soluble carboxylic monomer such as acrylic, methacrylic, fumaric or itaconic acid, which may reach up to 10% by weight of the total amount of monomer.[1,3]

It has been recognized that the carboxylic groups originating from acrylic monomers are generally distributed in the latex products in different form: i) incorporated into copolymer chains buried in the polymer particles, ii) incorporated into the copolymer chains but located at or near the particle surface, iii) physically adsorbed onto the polymer particle surface acting as surfactant molecules, iv) incorporated into

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water-soluble copolymer chains dissolved in the aqueous phase and v) homopolymerized in the aqueous phase.[2–4] Furthermore, the final distribution of carboxylic groups in latex products is controlled by several factors, including the reactivity of the monomers, the hydrophilicity of the carboxylic acid monomer and its partitioning behavior, the pH of the reaction mixture and the process in which the functional monomer was supplied to the reaction mixture.[1,4] As a consequence, useful mechanistic information can be obtained from the determination of the carboxylic group distribution in the latex.

Different techniques have been used to characterize the distribution of carboxylic groups among the latex phases. Most of them rely on cleaning methods such as dialysis, ion-exchange resin treatment, serum (water phase) replacement or ultrafiltration/ultracentrifugation coupled with conductimetric titrations.[1–10] In particular, the evaluation of the surface of the carboxylated latex particles in terms of amount and type of chemically bound carboxylic acid groups is crucial to explain the stability characteristics for a given carboxylated latex. Basically, the characterization of the surface of the carboxylated latex particles include as a first step the removal of all the species simply adsorbed onto the surface. Then, the next steps are usually the protonation of the remaining anchored surface carboxylic acid groups and the quantification of those groups by means of titration. In this case, the titration procedure is based on the reactions between the functional groups and a titrant, considering carboxylic acid groups with a strong base or carboxylated groups with a strong acid. Those species adsorbed over the surface of the polymer particles contribute to the latex stabilization by steric and electrostatic mechanisms.[3–5] As a consequence, the surface properties of the carboxylated latex particle play an important role in determining the colloidal behavior of the latex and these are usually directly related to the preparative method employed. The objective of this work is to contribute to a better understanding of how carboxylated latexes particles are formed and stabilized during semicontinuous emulsion copolymerization reactions. To achieve this, a number of copolymerization runs was carried out under different reaction conditions, including the use of different carboxylic monomers (acrylic acid and methacrylic acid). Partitioning analyses using conductimetric and potentiometric titrations were performed in order to assess the distribution of carboxylic monomers among the main phases of the latex. Additionally, the stability and coalescence of particles were measured by turbidimetry in a diluted latex considering either the presence or not of the anionic surfactant sodium lauryl sulfate (SLS), at two distinct temperatures. These turbidimetric data enabled us to evaluate important stability parameters such as the stability ratio and the critical coalescence concentration, which are essential for modeling purposes.

Experimental Procedures and Techniques

Detailed experimental procedures, polymerization formulations, latex characterization and preparation techniques were described in a previous work of this group.[4] Industrial grade inhibited monomers, vinyl acetate (VA), butyl acrylate (BA), acrylic acid (AA) and methacrylic acid (MAA) were used throughout the reactions. Water was distilled. Sodium bicarbonate ($NaHCO_3$), potassium persulfate ($K_2S_2O_8$) and sodium lauryl sulfate (SLS) were used, respectively, as buffer, initiator and emulsifier. All materials were employed as received. Semicontinuous VA/BA emulsion copolymerizations were run at 40% solids content (mass of monomers with respect to total reaction mass), and the monomer mass ratio (VA:BA) was maintained at 80:20 w/w. Table 1 summarizes the main reaction conditions for all latex syntheses.

All the reactants were fed at the initial charge except for the monomers. Only 10%

Table 1.
Experimental conditions of the reactions.

Reactions	temperature	%MAA[a)]	%AA[a)]
MAA1%60	60 °C	1.0	–
MAA1%70	70 °C	1.0	–
MAA3%70	70 °C	3.0	–
AA1%60	60 °C	–	1.0
AA1%70	70 °C	–	1.0
AA3%70	70 °C	–	3.0

[a)] w/w % in relation to total VA and BA.

of the total amount of monomers was fed at the initial charge. The remaining 90% of monomers were begun to be fed after 20 minutes of reaction, being continuously fed during 90 minutes. With the purpose of avoiding differences on the latex stability due to the pH drift (normally found on this system), buffer concentration was set proportional to the carboxylic monomer concentration in order to keep the pH constant at a value of approximately 7. Copolymerization runs were carried out in a jacketed 1-litre glass reactor equipped with a reflux condenser, nitrogen gas inlet tube and a feed tube for monomers. Table 2 and 3 present the formulations employed in all reactions.

Overall conversions were determined gravimetrically. Quasi elastic light scattering (QELS) (Coulter N4 Plus) was used to determine the average particle size. Measurements were recorded at a 90° angle and an average of ten measurements was recorded. The number of polymer particles was calculated through conversion and average particle diameter data.

Table 2.
Formulation with 1% of carboxylic monomer (related to VA and BA).

Reactants	Initial Charge (g)	Feed (g)
VA	21.86	196.66
BA	5.47	49.16
Water	405.00	–
$NaHCO_3$	2.73	–
$K_2S_2O_8$	1.50	–
SLS	6.90	–
CM[a)]	0.27	2.46

[a)] CM – carboxylic monomer (AA or MAA).

Table 3.
Formulation with 3% of carboxylic monomer (related to VA and BA).

Reactants	Initial Charge (g)	Feed (g)
VA	21.44	192.96
BA	5.36	48.24
Water	405.00	–
$NaHCO_3$	8.04	–
$K_2S_2O_8$	1.50	–
SLS	6.90	–
CM[a)]	0.80	7.24

[a)] CM – carboxylic monomer (AA or MAA).

The partition coefficients of carboxylic species were determined for each final latex. The latex samples were cleaned previously using mixtures of both cationic and anionic ion exchange resins. Thus, both small oligomers dissolved in the aqueous phase and physically adsorbed carboxylated ones are removed during this cleaning stage. The rate of ion exchange was monitored by periodic measurements of the latex conductivity. The ion exchange procedure was judged to be completed when the latex conductivity was constant and lower than 0.04 mS/cm. An aliquot of the cleaned latex was purged using N_2 for at least 30 minutes and then titrated conductimetrically by forward titration using NaOH 0.05N followed by back titration using HCl 0.05N. The weak acid portion of the titration curve was attributed to the carboxylic groups (COOH) located at the particle surface. Another aliquot of the cleaned latex was acidified by adding an excess of HCl 0.1N. The mixture was then titrated using a non-aqueous potentiometric method (solvent: tetrahydrofurane, titrant: NaOH 0.05N); this gave the sum of the surface COOH groups and the buried COOH groups; therefore, the COOH groups located in the aqueous phase could be computed by the difference between the conductimetric and potentiometric titrations cited before.

The stability and coagulation of particles were measured by turbidimetry in a diluted latex with and without addition of SLS, according to the procedures described elsewhere.[11] In short, the stability of carboxylated polymers was assessed using turbidity measurements, where kinetics of coagulation was followed by measuring the slope of turbidity curves versus time. Coagulation of particles was provoked in the latex samples by addition of an aliquot of a concentrated solution of electrolyte. Measurements were performed at a constant temperature of 25 °C or 50 °C. The stability ratio (W) in a homocoagulation processes is defined as the ratio of the rate of rapid to slow coagulation processes – equation,[1] where τ is the turbidity and C_E the electrolyte concentration.

$$W = \frac{(d\tau/dt)_{0,C_E > C.C.C.}}{(d\tau/dt)_{0,C_E}} \tag{1}$$

For electrolyte concentrations higher than the critical coagulation concentration (C.C.C.), the electrostatic repulsive forces are completely cancelled and rapid coagulation occurs due to the Brownian motion of polymer particles; below this point, coagulation is slower. The use of equation (1) is based on the assumption that turbidity is a linear dependent function of time. This may be true for the initial moments of the coagulation process.[11] The turbidity measurements were conducted in a Visible-UV spectrophotometer Hitachi U-1800, which is able to perform kinetic measurements of the intensity of scattered light after an electrolyte shot.

For latexes stabilized with ionic surfactants or/and charged groups on the surface of the particles, the stabilization mechanism is based on the creation of electrostatic repulsive forces between polymer particles.[10,11] These surface groups can arise from, i) the initiator used; ii) adsorbed or grafted surface active agents; iii) adsorbed or grafted polymeric species. The ionic species physically or chemically adsorb onto particle surface forming a charged layer near the surface. The surface charges are in equilibrium with counter-ions in both the inner and diffuse regions of the electrical double layer. The inner part is called the Stern region where counter-ions are strongly adsorbed onto ions located on particle surface. The diffuse part is called the Gouy-Chapman region where counter-ions are freely distributed because of the lower attractive force between surface ions and counter-ions. Based on this representation, Deryaguin and Landau[12] and Verwey and Overbeek[13] established the DLVO theory applied to electrically charged surfaces submerged in a diluted solution of salts. According to this theory, the total potential energy of interaction (V) can be determined as the sum of the attraction energy (V_A) and the repulsion energy (V_R):

$$V = V_A + V_R \tag{2}$$

Attractive forces between polymer particles are produced from the interaction between temporary dipole on one molecule and the induced one on a neighboring.[14] This energy is proportional to the semi-empirical Hamaker constant (A) which depends on the polymer properties, the molecular polarizability and the properties of the liquid phase where particles are dispersed.[15] The experimental data of stability obtained by turbidity analyses may serve as input for a mathematical model based on DLVO theory to estimate the Hamaker constant. The model in question can be used for the theoretical description of the coagulation between particles in the reacting systems with confidence. The coagulation rate between two polymer particles can be calculated as a function of the radius (r) of each polymer particle as described by the following equation:

$$B_{ij} = B_{ji} = \frac{2k_BT}{3\eta W_{ij}} \frac{(r_i + r_j)^2}{r_i r_j} \tag{3}$$

where k_B is the Boltzmann constant, T is the medium temperature, η is the latex viscosity and W_{ij} is the Fuch's stability ratio, which can be derived theoretically and compared to the experimental values obtained by using equation (1). Finally, this model can be incorporated into a population balance model (PBE) in order to describe the coagulation between particles for systems with or without reaction.[11]

Results and Discussion

Partitioning of Carboxylic Groups

The distribution of the carboxylic acid groups among the latex phases was presented before in a recent work from this group,[4] and is briefly described in the current paper. Table 4 summarizes partitioning results for the carboxylated latex synthesized in the lab. The observed increase in the amount of adsorbed COOH groups on the particle surface with increasing carboxylic monomer concentration might favor the colloidal stability of those latexes. As shown by Araujo et al.,[4] coalescence rates during the polymer synthesis diminish as higher carboxylic monomer concentrations are employed in the formulation. Regarding the use of low carboxylic monomer concentrations (1%), AA monomer provided enhanced latex stability and greater amount of adsorbed COOH groups on the particle surface, when compared to MAA results. This greater AA adsorption capacity was supposed to be linked to the fact that AA is more hydrophilic than MAA.[16] Concerning MAA partitioning, Table 4 results show a strong incorporation of acid groups buried in the particles.

On the other hand, the influence of the temperature over the colloidal stability is well understood.[17] Besides increasing the water solubility of monomers and the polymerization rates, the use of higher temperatures may enhance the Brownian motion of the polymer particles in the latex. As a result of that, coalescence is more likely to occur.

Measurement of Stability Ratio

The stabilization of the carboxylated latexes can arise from either steric mechanism (due to the presence of protonated COOH groups on the surface) or electrostatic mechanism (due to the presence of non-protonated COOH groups and of chemically adsorbed sulfate end groups). The stabilization provided by carboxylic end groups was studied for diluted cleaned latex systems at distinct temperatures and considering the addition of SLS. The degree of stability offered to polymer particles by these species was determined using turbidity measurements. All runs were performed using cleaned carboxylated latexes as polymer particles seed and NaCl as electrolyte. For SLS stabilized latexes, the samples were prepared by adding a known amount of a surfactant solution to the cleaned seed latex that was left to reach equilibrium for at least 30 minutes. At this point, particles were stabilized by both surfactant and carboxylic groups. Then, the strength of stability measured has the contribution of the two stabilization species. Table 5 summarizes the surface properties of the carboxylated latexes studied here, including average particle size of latex samples, the surface density of carboxylic groups determined through partitioning tests and the calculated surface density of SLS for those samples involving the addition of surfactant solution (proportional to the SLS coverage). Note that the data of surface density of COOH groups confirm the results observed before about the ability of AA monomer in providing greater amounts of acid groups over the

Table 4.
Partition of carboxylic groups: adsorbed particle surface and buried species

Latex	$\left(\frac{\text{mol}}{\text{ml polymer}}\right)_{\text{surface}}$	$\left(\frac{\text{mol}}{\text{ml polymer}}\right)_{\text{buried}}$
AA1%60	65.3	91.3
AA1%70	103.6	50.5
AA3%70	135.0	148.5
MAA1%60	31.9	100.7
MAA1%70	29.7	118.9
MAA3%70	161.4	195.9

Table 5.
Surface properties of the carboxylated latexes: average particle size and surface density of carboxylic groups and surfactant species.

Latex	Dp	$[\text{–COOH}]_{\text{surface}}$	$[\text{SLS}]_{\text{surface}}$
	nm	mol/cm^2	mol/cm^2
MAA1%60	144	6.6×10^{-11}	3.2×10^{-7}
MAA1%70	202	8.6×10^{-11}	4.5×10^{-7}
AA1%70	133	1.9×10^{-10}	2.9×10^{-7}
AA3%70	115	2.2×10^{-10}	2.5×10^{-7}

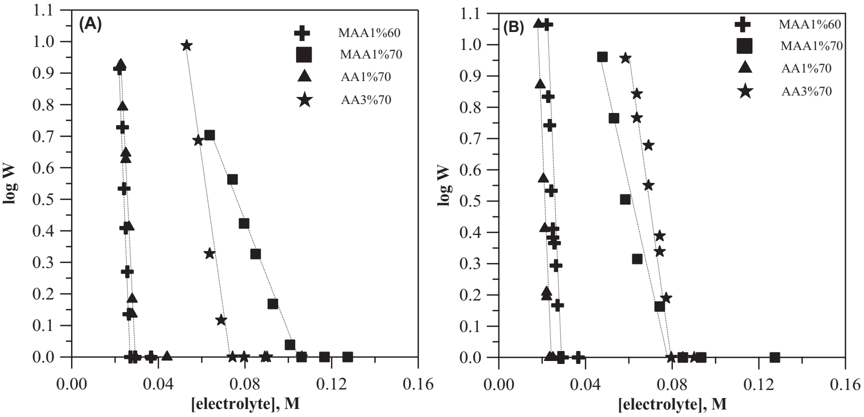

Figure 1.
Stability ratio versus electrolyte concentration for carboxylated latexes without SLS: (A) 25°C and (B) 50 °C.

polymer particle surface. On the other hand, the surface density of SLS species is clearly linked to the polymer particle size as the total area of polymer particles decreases with increasing particle radius for the same polymer content.

Figure 1 shows the experimentally measured stability ratio versus electrolyte concentration curves for carboxylated latexes (MAA and AA), without addition of SLS, at 25 °C and 50 °C. In addition to calculating the stability ratio, one can also determine the C.C.C. of each latex sample. This concentration was obtained from the intercept with the abscissa of the logW-C plots, and the results are given in Table 6. The stabilization of polymer particles for each carboxylated system can be compared through the obtained values of C.C.C.

From Figure 1, note that similar stability behavior were observed for latexes MAA1%60 and AA1%70 for both temperatures. These latexes also provided the lowest values of C.C.C. during the test. On the other hand, tests with high values of C.C.C. were observed for MAA1%70 and AA3%70, indicating improved stability. It is interesting to observe that even though the MAA monomer provided lower amount of adsorbed COOH groups on the particle surface (Table 5), high C.C.C values were obtained for this carboxylic monomer, which reflects the high stabilization power of MAA species by steric effects.

Figure 2 and 3 show the stability behavior for the different carboxylated latexes in the presence of SLS and at distinct temperatures. The addition of small amount of surfactant to the latex produces an increase of C.C.C. due to the improvement of polymer particles stability, mainly when the tests are conducted at 25 °C. In the presence of SLS, the stability is essentially due to electrostatic effects.

Table 6.
Values of C.C.C determined by turbidity measurements for seed carboxylated latex with and without SLS stabilization, at distinct temperatures.

Latex	C.C.C., M	C.C.C., M	C.C.C., M	C.C.C., M
	Without SLS	Without SLS	[SLS] = 3.4 × 10^{-4} M	[SLS] = 3.4 × 10^{-4} M
	T = 25°C	T = 50°C	T = 25°C	T = 50°C
MAA1%60	0.027	0.028	0.467	0.153
MAA1%70	0.106	0.085	1.123	0.255
AA1%70	0.029	0.023	0.084	0.059
AA3%70	0.074	0.078	0.255	0.157

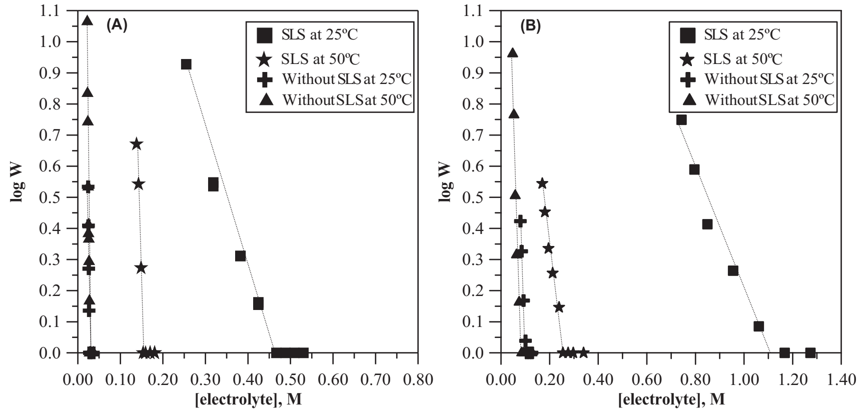

Figure 2.

Stability ratio versus electrolyte concentration for latexes with and without SLS addition: (A) MAA1%60 and (B) MAA1%70.

It is important to note at Figure 2 and 3 that the temperature markedly influences the stability behaviour of the latex samples studied here only when SLS is present. In the absence of SLS the effect of the temperature is negligible.

Also, it can be observed from Table 6 that the sample with the greatest stability (highest C.C.C. value) here occurred for the MAA1%70 sample in the presence of SLS at 25 °C. This result can be explained by the highest density of SLS species adsorbed over the surface and by the high Dp value obtained for this latex (which means lower Np), as reported in Table 5. According to the Table 6, the second more stable latex here was the MAA1%60, which corresponds to the second density of SLS species adsorbed over the surface. Finally, the latexes prepared using AA monomer, which involved lower densities of SLS species over the surface, provided low degree of stability during coalescence experiments. Again, this indicates that even though the AA monomer is able to yield greater amount of carboxylic groups over the particle surface, these species possess poorer ability to sustain the colloidal stability of the polymer latex during changes of the ionic strength.

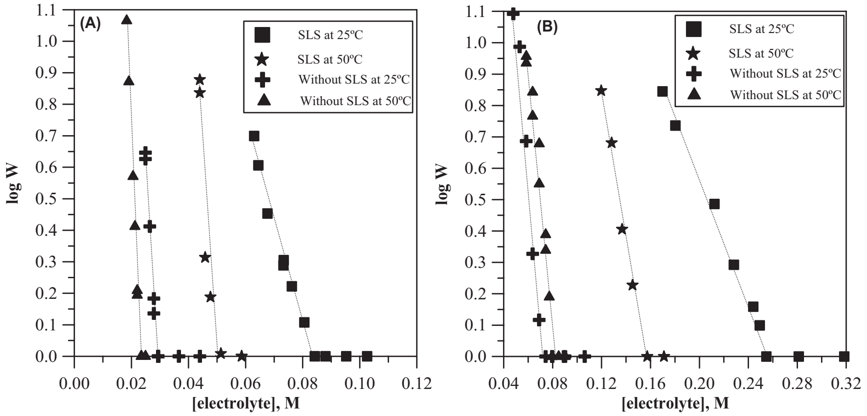

Figure 3.

Stability ratio versus electrolyte concentration for latexes with and without SLS addition: (A) AA1%70 and (B) AA3%70.

Conclusions

The evaluation of the surface properties of the carboxylated latex particles in terms of amount and type of chemically bound carboxylic acid groups is crucial to explain the stability characteristics for a given carboxylated latex. In the current paper, the stabilization of carboxylated polymer particles was investigated from an experimental point of view for different stabilization systems, including AA and MAA species at distinct temperatures. First of all, AA monomer yielded greater amount of adsorbed COOH groups on the particle surface when compared to MAA results obtained during partitioning analysis. Turbidity measurements were used to determine the stability imparted by each stabilizing species and, to identify the relative influence of SLS in the stabilization of particles when distinct mechanisms act at the same time. The highest stability values were found for MAA systems containing SLS, and the lowest values were observed for polymer particles without surfactant addition, in which the stability was assured by carboxylic end groups coming from AA monomer on the surface of the particles. These results reveal that the MAA monomer may produce a further steric effect on the stabilization of the particles, when compared to the AA case. Finally, the colloidal stability of the different carboxylated latexes was evaluated at 25 °C and 50 °C, showing a sharp reduction of the stabilization performance when a higher temperature was employed only when SLS was present. In the absence of SLS the effect of the temperature was negligible. These experimental stability data may be used as input to an electrostatic stability model in order to estimate Hamaker constants for each stabilization system. Further studies will be conducted in order to incorporate this electrostatic stability model into a population balance to describe the evolution of the particle size distribution during the addition of electrolytes for a non-reacting system.

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