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Investigation of Stabilization and Kinetics in the Semi-Continuous Emulsion Copolymerization of Vinyl Acetate and Butyl Acrylate using Carboxylic Monomers

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Summary: This work investigates the influence of carboxylic monomers such as acrylic acid (AA) and methacrylic acid (MAA) on the reaction rate and the colloidal stability during semicontinuous vinyl acetate (VA) and butyl acrylate (BA) emulsion copolymerizations. A number of copolymerization runs was carried out under different reaction temperatures and concentrations of AA and MAA. Samples were collected for off-line analysis of particle size and conversion, allowing calculations of particle number values giving an indication of the particle stability. Additionally, partitioning analysis using conductometric and potentiometric titrations were performed in order to assess the distribution of carboxylic monomers among the main phases of the latex. Results showed that for both carboxylic monomers the increasing of the reaction temperature produces an increase in the coalescence rate and that the increasing of the concentration of these monomers leads to the increase in the amount of adsorbed COOH groups on the particle surface, which enhances latex stability. Nevertheless, when the concentration of methacrylic acid was increased a strong reduction of the polymerization rate was observed with a greater incorporation of acid groups buried in the particles.

Keywords: butyl acrylate; carboxylic; emulsion copolymerization; stability; vinyl acetate

Introduction

Small amounts of carboxylic monomers are usually employed in latex formulation in order to improve colloidal stability of the polymer particles. Carboxylic monomers improve several quality aspects of the latex as compatibility with pigments, adhesive characteristics, mechanical properties of the films and allow the incorporation of reactive groups on the particle surface.[1] They are also introduced in latex formulations to enhance colloidal stability due to the presence of carboxylic groups on the outer surface of the polymer particles.[2] In particular, the carboxylic groups originating from acrylic monomers such as Acrylic Acid (AA) and Methacrylic Acid (MAA) are generally distributed between the aqueous phase, the polymer particle surface and the particle core. Those species adsorbed over the surface of the polymer particles contribute to the latex stabilization by steric and electrostatic mechanisms.[3,4] Thus, the quantification of the partitioning of the carboxylic groups among the many phases is crucial to explain the stability characteristics for a given carboxylated latex, providing useful information that indeed explains the differences observed on

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the stability behavior of latexes prepared using monomers such as AA or MAA. Besides, partitioning data are also very important to design semicontinuous operations with proper monomer feed profiles viewing the control of copolymer composition. Several emulsion copolymerization reactions are carried out in industry in semicontinuous in order to avoid composition drift and reaction runaway as emulsion polymerizations are usually very exothermic. In semicontinuous reactions, monomer concentration at the reactor is, usually, much lower than at the beginning of a batch reaction. Therefore, monomer partitioning between aqueous and polymer phase could be strongly affected, especially for hydrophilic monomers as AA and MAA. There are several works[4–8] dealing with the role of carboxylic monomers in emulsion polymerization, nevertheless only a few of them studied the effect of these monomers in semicontinuous polymerization.[7,8]

Vinyl acetate (VA) and butyl acrylate (BA) copolymers are usually produced in semicontinuous reaction to avoid the composition drift due to the very different reactivity ratios of such monomers ($r_{VA/BA} = 0.037$ and $r_{BA/VA} = 6.35$).[9] The reactivity ratio ($r_{1/2} = kp_{11}/kp_{12}$) of these monomers with respect to the carboxylic monomers can also change depending on the type of monomer. In this sense, comparing the reactivity ratios concerning BA ($r_{AA/BA} = 0.58$, $r_{BA/AA} = 1.07$, $r_{MAA/BA} = 1.31$ and $r_{BA/MAA} = 0.35$)[10] and concerning VA ($r_{AA/VA} = 2.6$, $r_{VA/AA} = 0.04$, $r_{MAA/VA} = 20$ and $r_{VA/MAA} = 0.01$),[11,12] it is possible to observe a great difference between the reactivity ratios of VA with respect to AA and MAA. In the case of the BA, the difference between the two reactivity ratios is not so significant.

In a related effort, the role of AA on the kinetics and stabilization performance during semicontinuous VA/BA emulsion copolymerizations was reported by Araujo et al.[8] An experimental study was performed considering different variables including reaction temperature, AA concentration, solids contents and monomer feed compositions. It was shown that improved latex stability at higher temperatures may be achieved when increasing the AA concentration in the range from 0 to 1% AA (% in relation to the total mass of VA and BA). Even though important findings had been reported in that work, the particle surface characterization remained to be done as well as the effect of the type of carboxylic monomer.

The objective of the current work is to use partitioning analysis to understand VA/BA emulsion copolymerization stability from a more fundamental point view, looking at the amount of carboxylic groups of AA and MAA onto the particle surface. Semicontinuous vinyl acetate/butyl acrylate (80/20 w/w ratio) emulsion copolymerization runs with 40% of total solids content were conducted under different reaction temperatures and carboxylic monomer type and concentrations in a lab-scale reactor. Additionally, the partition coefficient of carboxylic species in the final latex was determined for each copolymerization run.

Experimental Procedures and Techniques

Industrial grade inhibited monomers, vinyl acetate, butyl acrylate, acrylic acid and methacrylic acid were used throughout the reactions. Water was distilled and sodium bicarbonate ($NaHCO_3$) was used as buffer. Potassium persulfate ($K_2S_2O_8$) was used as initiator. Sodium lauryl sulfate (SLS) was used as emulsifier. All materials were used 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% of the total amount of monomers was fed at the initial charge. The remaining 90% of monomers were begun to be fed after

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.

Table 3.
Recipe 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).

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 ystem), 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. Tables 2 and 3 present the recipes 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.

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. Therewith, 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 0.05 N followed by back titration using HCl 0.05 N. 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 0.1 N. The mixture was then titrated using a non-aqueous potentiometric method (solvent: tetrahydrofurane, titrant: NaOH 0.05 N); this gave the sum of the surface COOH groups and the buried COOH groups; therewith, the COOH groups located in the interior of the particles could be computed by the difference between the conductometric and potentiometric titrations cited before.

Table 2.
Recipe 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).

Results and Discussion

Effect of Carboxylic Monomers on the Reaction Kinetics and Latex Stability

A series of 6 experiments at different carboxylic monomer conditions was run to investigate the effect of changing temperature, carboxylic type and concentration on semicontinuous VA/BA copolymerizations. For low concentration of carboxylic monomers (1%) no effect on the conversion was observed when the type of carboxylic monomer (AA or MAA) was changed. All the reactions presented the same behavior for the conversion at the same temperature (Figure 1). Nevertheless, increasing the carboxylic monomer concentration to 3% a strong reduction in the polymerization rate was verified (Figure 2) for the reaction with MAA, whereas just a slight reduction was observed for the reaction with AA. This is the opposite behavior observed for MMA/BA copolymerization with AA and MAA[1] and can be explained by their respective reactivity ratios, as the VA radical reacts rapidly with MAA monomer, but the MAA radical reacts very slowly with VA monomer. Therefore, increasing the concentration of MAA the polymerization rate of VA was reduced. As VA represented almost 80% of the monomer fed the overall polymerization rate was strongly reduced.

As observed in a previous work,[8] particle concentration (Np) decreased with increasing reaction temperature for small amounts of AA (1%). According to the Figure 3, the same effect was observed for the reactions carried out in the presence of MAA. However, it is possible to observe that all reactions conducted with MAA presented lower Np when compared to the reactions with AA at the same temperature and concentration. It is also interesting to note that for MAA latexes, the particle stability is worse than in the AA case. For the MAA reactions the observed Np reduction at the end of reactions seems to be related to the coalescence of polymer particles, induced by reactor agitation whereas no such effect was observed for the reactions with AA (this point will be discussed in the next section).

Carboxylic Monomers Partitioning

Partitioning results for the carboxylated latexes synthesized in the lab are summarized in Figure 4. 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. These results are in good agreement with the Np evolution during the synthesis, as shown in Figure 3, which indicated that

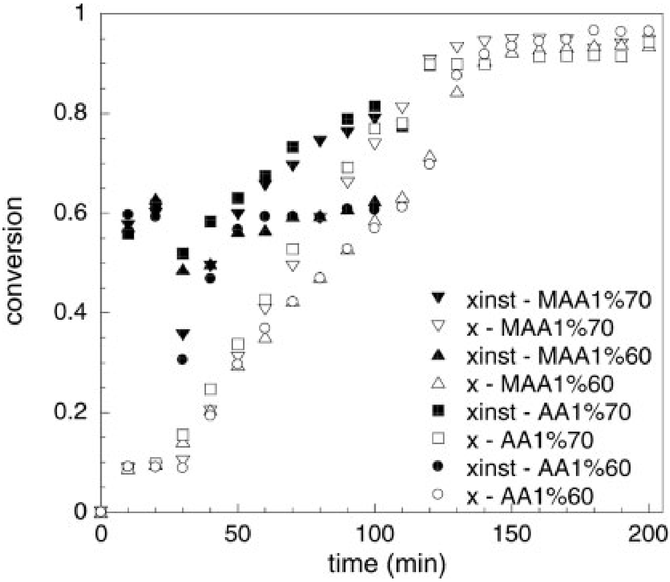

Figure 1.
Instantaneous (x_{inst}) and overall (x) conversion of the reactions with 1% of carboxylic monomers.

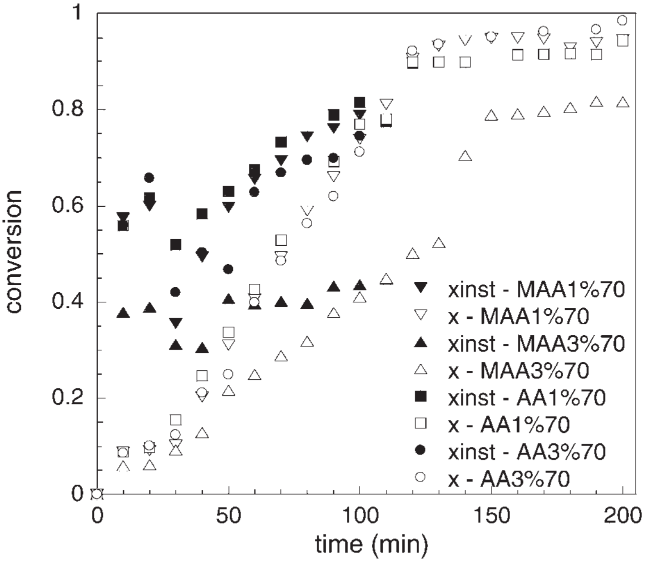

Figure 2.
Instantaneous (x_{inst}) and overall (x) conversion of the reactions at 70 °C.

coalescence rates diminish as higher carboxylic monomer concentrations are employed in the recipe.

Concerning 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 can be linked to the fact that AA is more hydrophilic than MAA.[13] With reference to MAA partitioning, results show a strong incorporation of acid groups buried inside the particles.

Colloidal stability is well recognized to be also influenced by temperature.[14] In

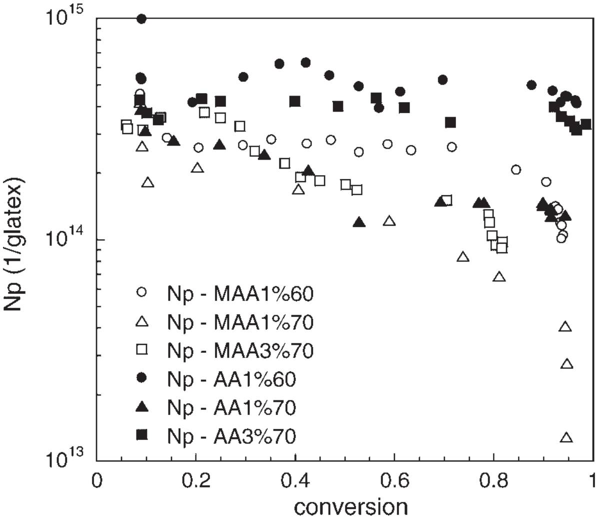

Figure 3.
Particle concentration (Np) versus overall conversion.

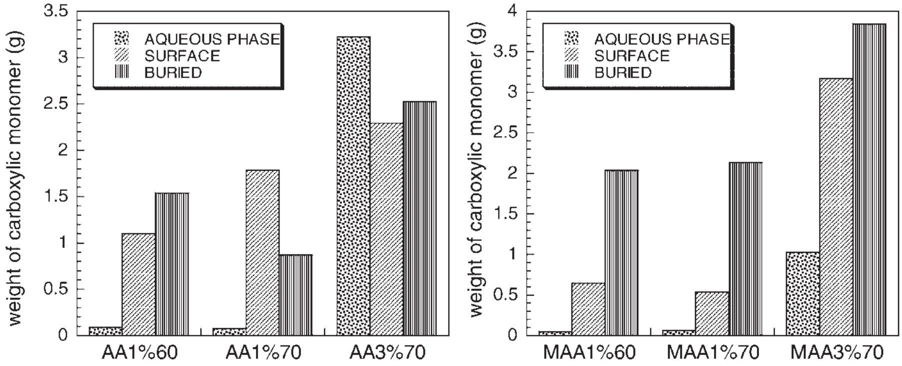

Figure 4.
The distribution of carboxylic groups from AA and MAA monomers in different locations of the carboxylated P(VA/BA) copolymer latexes: aqueous phase, adsorbed on particle surface and buried inside the particles.

fact, increasing the temperature results in the increase of the water solubility of monomers and the polymerization rates. Besides, the Brownian motion of the polymer particles in the latex is generally enhanced when higher temperatures are employed. As a result of that, coalescence is more likely to occur. Recall that in Figure 3, experimental data show an Np reduction when temperature was varied from 60 °C to 70 °C for both AA and MAA monomers. Therefore, increased coalescence rates are observed when the polymerization reactions were performed with increased temperature. In the particular case of AA, the coalescence of particles was observed only at 70 °C (and at 1% monomer content). On the other hand, MAA reactions presented particle coalescence in all conditions, but the highest coalescence rates were observed at 70 °C.

It should be emphasized that for these MAA experiments involving coalescence, the resulting amounts of adsorbed COOH groups on the particle surface are very similar for both syntheses (1% of MAA) carried out at 60 °C and 70 °C. However, in the case of AA, a more hydrophilic monomer, the greater amount of adsorbed COOH groups on the particle surface found at the run at 70 °C could be attributed to the higher initiator decomposition and polymerization constants that increase the polymerization rate at the aqueous phase. Therefore, a higher amount of PAA is formed at the aqueous phase and adsorbed on particle surface.

As a final remark, temperature effects on COOH group distribution could not be inferred unequivocally by partitioning data. In fact, if the temperature played a role on the COOH groups distribution, this effect would be masked by the coalescence phenomenon, which is also enhanced by the temperature.

Conclusions

Results showed that the effect of carboxylic monomers and reaction temperature on the latex stability is very well-defined. The latex stability decreased in the reactions with a lower carboxylic monomer concentration (1%) and higher reaction temperature (70 °C). Increasing the concentration of the carboxylic monomers from 1 to 3% leads to the decrease of the polymerization rate. This effect was much more pronounced in the MAA reactions as the reactivity ratios of VA and MAA are significantly different. Besides that, experimental partitioning quantifications indicated that AA monomer provided enhanced latex stability and greater amount of adsorbed COOH groups on the particle surface, when compared to MAA results. As a conclusion, low concentrations of AA monomer (1%) are enough to maintain the Np constant during the reaction systems studied here. Concerning MAA partitioning, results show a strong incorporation of acid groups buried in the particles.

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