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Butyl Acrylate and Vinyl Acetate Semicontinuous Emulsion Copolymerizations: Study of Stabilization Performance

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Summary: The use of small amounts of carboxylic monomers in industrial recipes with high solids content enhances colloidal stability due to the presence of carboxylic groups on the outer surface of the polymer particles. Understanding the relationship between several different but interdependent phenomena, including particle nucleation, kinetics, particle aggregation, monomer type, solids content, the role of the carboxylic monomer and the influence of reaction temperature may improve the control over particle size and latex stability. In this work, the kinetics and stabilization performance of semicontinuous vinyl acetate (VA) and butyl acrylate (BA) emulsion copolymerization reactions are studied under different reaction temperatures, acrylic acid (AA) concentrations, solids contents and monomer feed compositions. Results show that choosing optimal AA concentrations and reaction temperatures are key factors in order to enhance the stabilization performance in semicontinuous VA/BA emulsion copolymerization.

Keywords: acrylic acid; butyl acrylate; colloidal stability; emulsion polymerization; vinyl acetate

Introduction

Several semicontinuous emulsion polymerization reactions are carried out in industry at non-isothermal conditions and high solids content. The use of small amounts of carboxylic monomers in industrial recipes with high solids content enhances colloidal stability due to the presence of carboxylic groups on the outer surface of the polymer particles, providing both steric and electrostatic stabilization of the colloid.[1] Understanding the relationship between several different but interdependent phenomena, including particle nucleation, kinetics, particle

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aggregation, monomer type, solids content, the role of the carboxylic monomer and the influence of reaction temperature may improve the control over particle size[2] and latex stability.

The vinyl acetate / butyl acrylate emulsion copolymer is very important in paint and paper coatings industry[3,4] and presents some very challenging peculiarities due to the very different solubilities of these monomers in the aqueous phase and also due to the very different reactivity ratios ($r_{VA/BA} = 0.037$ and $r_{BA/VA} = 6.35$).[5-8]

In this work, the kinetics and stabilization performance of semicontinuous vinyl acetate and butyl acrylate emulsion copolymerization reactions are studied under different reaction temperatures, acrylic acid concentrations, solids contents and monomer feed compositions.

Experimental

Industrial grade inhibited monomers, vinyl acetate (VA), butyl acrylate (BA) and acrylic acid (AA), were used throughout the reactions. Water was distilled and deionized. Sodium carbonate (Na_2CO_3), potassium persulfate ($Na_2S_2O_8$) and Sodium Lauryl Sulfate (SLS) were used, respectively, as buffer, initiator and emulsifier. All materials were used as received.

The experimental setup comprises a 600 ml jacketed glass reactor connected to a condenser to avoid monomer losses due to evaporation during the reaction. The startup procedure in all reactions comprised filling the reactor with the initial charge and heating until the reaction temperature is reached. The reactants were fed in two different streams: 1) an initiator solution and 2) the organic phase. In order to remove traces of dissolved oxygen, both feed tanks and the reactor were continuously purged with nitrogen. Tables 1, 2 and 3 present the experimental conditions of each reaction. Monomer conversion was measured by gravimetry, particle diameter was measured by photon correlation spectroscopy (Malvern - Zetasizer 3000 apparatus) and particle number was calculated as described in Araujo et al.[9]

Results

Effect of reaction temperature and acrylic acid concentration on latex stability

Semicontinuous VA and BA (80/20 weight ratio) emulsion copolymerization reactions with high solids content (55%) are studied under different reaction temperatures and AA concentrations (see Table 1). Feed streams 1 and 2 were continuously fed during 120 minutes in all reactions. All reactions were performed at a pH of about 7 as the stability of carboxylic-acid stabilized lattices is expected to be pH dependent.[10]

Table 1. Formulation of reactions with 55% solids content and 80/20 VA/BA weight ratio.

	VA (g)	BA (g)	AA (wt %)[a]	Water (g)	SLS (g)	$Na_2S_2O_8$ (g)	Na_2CO_3 (g)
Initial charge	—	—	—	190.10	9.442	—	1.336
Feed stream 1	217.00	54.25	0 / 0.46 / 0.92	—	—	—	—
Feed stream 2	—	—	—	39.90	—	1.312	—

[a] weight % in relation to total VA and BA weight.

Figures 1 and 2 show that reactions performed with different amounts of AA (0.46 and 0.92 wt % in relation to total VA and BA weight) at 60°C were virtually equal, presenting the same behavior for global conversion (X) and particle size (Dp) (Figure 1) and for instantaneous conversion (X_{inst}), particle number (Np) and average number of radicals per polymer particle (ñ) (Figure 2). Nevertheless, the reaction performed without AA (not shown in Figures 1 and 2) lead to coagulation just after the end of the monomer feeding period when a high polymer plus monomer content was reached in the reactor. Higher reaction temperatures lead to a different behavior for different AA amounts with higher stability for higher amounts of AA. Stability, observed by the increase of particle diameter due to the aggregation of particles (decrease of the number of particles), decreased with increasing reaction temperature for small amounts of AA (0.46%) and the aggregation of polymer particles, induced by reactor agitation, increased strongly after reaching 55% of polymer plus monomer content.

Low AA concentrations seem to have no influence on polymerization kinetics as the evolution of the global conversion (Figure 1) and of the instantaneous conversion (Figure 2a) of all reactions at the same temperature were the same with 0.46% or 0.92% of AA. It is also interesting to observe that, apparently, at low concentrations (<1% of AA), AA has no significant effect on particle nucleation as at the beginning of the reactions carried out at the same temperatures the average particle diameters were the same for the same conversions (Figure 1) indicating, therewith, that the number of polymer particles were also the same (Figure 2b). Only when the solids content increased in the reactor, at 70°C and 80°C, the particle diameter and, consequently, the number of polymer particles presented a different behavior for different amounts of AA.

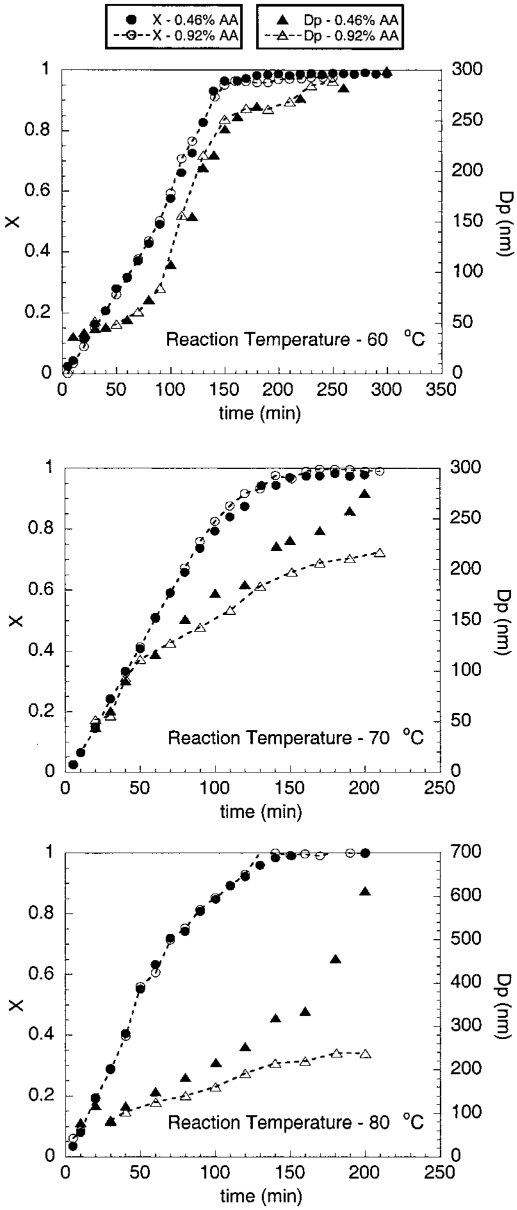

Figure 1. Evolution of global conversion (X) and average particle diameter (Dp) at different reaction temperatures (60°C, 70°C and 80°C) and different amounts of acrylic acid (0.46 wt. % and 0.92 wt. % in relation to total vinyl acetate and butyl acrylate).

Yuan et al.[11] also observed an increase in particle aggregation with increasing reaction temperature during the styrene-butadiene batch emulsion polymerization stabilized with poly(acrylic acid), PAA, chains formed in the aqueous phase. It was suggested that this effect of aggregation may arise from the dehydration of the PAA chains in the aqueous phase with heating.[12] Therefore, the decrease in stability observed in Figure 1, especially of latex produced with a lower AA concentration (0.46%), with higher reaction temperatures can, possibly, be attributed to the breakage of the hydrogen bonds of the stabilizing PAA chains.

Observing the evolution of particle number in relation to monomer conversion in Figure 2c, it is possible to note that the number of particles formed at the beginning of the reactions decreased with the increase of reaction temperature. One would expect the opposite, as higher temperature would lead to more free radicals and thus more particles. The same behavior was observed by Yuan et al.[11] who suggested that the newly formed particles at higher temperatures are not as stable as those formed at lower temperatures, needing to increase in size and surface charge density through aggregation until a new equilibrium state is reached. At 60°C, a strong aggregation was observed after the end of monomer feeding and may, possibly, be explained by the higher surface area of particles making the surface charge density not enough to avoid aggregation at this high conversion.

Figure 2c shows that in all reactions the average number of radicals per polymer particle (ñ) increased along the reactions being below 0.5 up to approximately 60% conversion. The low values of ñ are attributed mainly to the significant transfer to monomer reactions of VA and to the solubility of VA radicals in water. The increase of ñ along the reactions accompanied the decrease o particle number. The evolutions of ñ were similar in experiments with 0.46 and 0.92 wt. % of AA, showing that, due to the low concentration, AA had no major effect on radical desorption. Only in the reactions carried out at 80 °C ñ was slightly higher when a lower AA concentration was used since in this reaction even at low conversions Np was slightly lower.

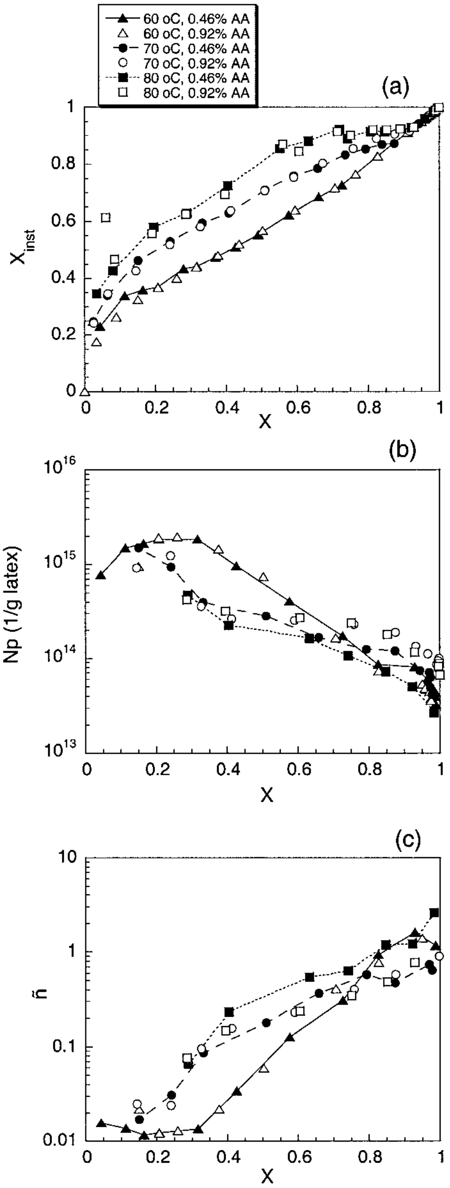

Figure 2. Evolution of instantaneous conversion (X_{inst}), particle number (Np) and average number of radicals per polymer particle (ñ) at different reaction temperatures (60°C, 70°C and 80°C) and different amounts of acrylic acid (0.46 wt. % and 0.92 wt. % in relation to total VA and BA).

Effect of solids content on latex stability

In order to study the effect of different solids contents on latex stability, a semicontinuous vinyl acetate (VA) and butyl acrylate (BA) (80/20 weight ratio) emulsion copolymerization reaction with a lower final solids content (40%) was carried out at 60°C (see Table 2). The results were compared with those of the reaction with 55% of final solids content performed at the same temperature (Table 1). In this new reaction feed streams 1 and 2 were continuously fed during 95 minutes to keep the same feed rate in both reactions.

Table 2. Formulation of reaction with 40% solids content and 80/20 VA/BA weight ratio.

	VA (g)	BA (g)	AA (wt %)[a]	Water (g)	SLS (g)	$Na_2S_2O_8$ (g)	Na_2CO_3 (g)
Initial charge	—	—	—	308.00	9.442	—	1.060
Feed stream 1	172.00	43.00	0.46	—	—	—	—
Feed stream 2	—	—	—	32.00	—	1.048	—

[a] weight % in relation to total VA and BA weight.

As expected, both reactions presented almost the same behavior in relation to global conversion (see Figure 3). On the other hand, the final particle diameters of both reactions were completely different and the differences of polymer concentrations due to the different solids contents are not enough to explain this behavior. To understand this behavior it is necessary to observe the evolution of particle number in relation to the polymer plus monomer content that reaches its maximum value after the end of monomer feeding. As it is possible to observe in Figure 4, the number of polymer particles was almost constant in both reactions until a 40% polymer plus monomer content was reached. After reaching 40% of polymer plus monomer content in both reactions, particles became less stable and significant aggregation began. This behavior is probably due to the increase of the rate of collisions between particles, and therefore the increase of the aggregation rate, as the total volume of the polymer phase increases in the reaction medium. The aggregation was more intense in the reaction with the higher solids content.

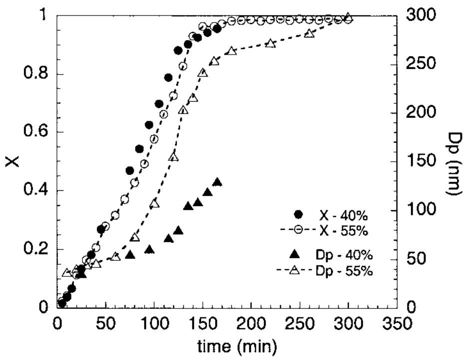

Figure 3. Evolution of global conversion (X) and average particle diameter (Dp) along the reactions (80/20 VA/BA ratio; 60°C; 0.46% AA) with different final solids contents (40% and 55%).

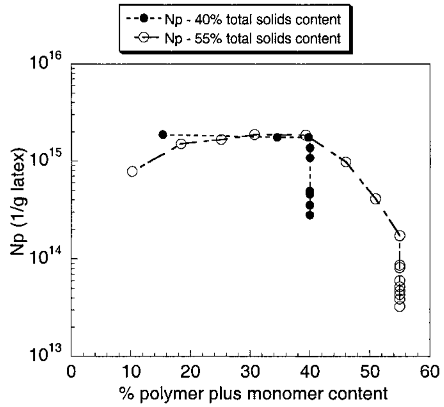

Figure 4. Evolution of particle number (Np) in relation to the increase of polymer plus monomer content (%) along the reactions (80/20 VA/BA ratio; 60°C; 0.46% AA) with different final solids contents (40% and 55%).

Effect of monomer feed stream composition on latex stability

Vinyl acetate and butyl acrylate have very different reactivity ratios[5,6], for this reason, in many VA and BA copolymerization reactions gradients are observed in polymer composition and monomer concentrations along the reaction.[5,7,8] To study the effect of monomer feed composition (relation between VA and BA) on latex stability, a semicontinuous vinyl acetate and butyl acrylate (50/50 weight ratio) emulsion copolymerization reaction with high solids content (55%) was carried out at 60°C (see Table 3). The results were compared with those of the reaction with 55% of total solids content carried out at the same temperature but with a different VA/BA weight ratio (80/20) in the monomer feed stream (Table 1). Feed streams 1 and 2 were continuously fed during 120 minutes.

Table 3. Formulation of reaction with 55% solids content and 50/50 VA/BA weight ratio.

	VA (g)	BA (g)	AA (wt %)[a]	Water (g)	SLS (g)	$Na_2S_2O_8$ (g)	Na_2CO_3 (g)
Initial charge	—	—	—	190.10	9.442	—	1.336
Feed stream 1	135.63	135.63	0.46	—	—	—	—
Feed stream 2	—	—	—	39.90	—	1.312	—

[a] weight % in relation to total VA and BA weight.

Figure 5 compares the behavior of particle number (Np) and global conversion (X) along those two reactions carried out at 60°C, with 55% of total solids content and 0.46% of AA. The reactions presented different VA/BA weight ratios in the monomer feed streams (50/50 and 80/20 VA/BA weight ratios). The reaction with a higher BA content (50/50) was faster at the beginning of the reaction than the reaction with lower BA content (80/20), but after the end of monomer feeding period, monomer conversion slowed down in the reaction with higher BA content and the reaction almost stopped. This effect was due to the very different reactivity ratios of VA and BA, as the more reactive monomer in this copolymerization (BA) acts as a retardant of the propagation of the other monomer (VA), i.e., when higher BA concentration was used, after the end of monomer feeding period there are more BA type radicals that have remarkably lower reactivity with the remaining VA monomer. The higher the BA concentration the more significant is this effect.[8] On the other hand, when higher VA concentration (80/20) was used, copolymerization takes place during the feeding period with a higher amount of VA type radicals (in comparison with the 50/50 case), and after the end of this period, when almost no free BA monomer was left, the polymerization rate is dominated by the fast VA homopolymerization ($k_{p,VA}$ = 2.35×10^6 cm^3 mol^{-1} s^{-1} ; $k_{p,BA}$ = 1.51×10^5 cm^3 mol^{-1} s^{-1}).[6] It seems that in this copolymerization, monomer feed composition does not presented any significant effect on particle nucleation as both reactions presented almost the same evolution of particle number at the beginning of the reactions.

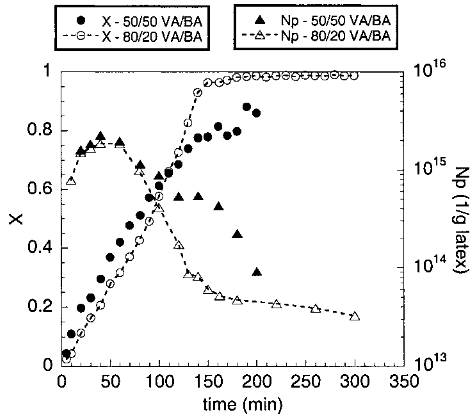

Figure 5. Evolution of particle number (Np) and global conversion (X) along the reactions (55% of total solids content; 60°C; 0.46% AA) with different monomer ratios (50/50 and 80/20).

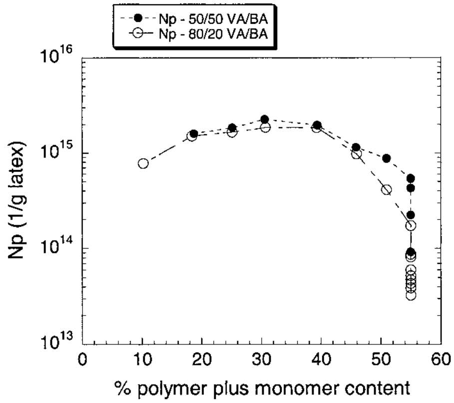

Figure 6. Evolution of particle number (Np) in relation to the increase of polymer plus monomer content (%) along the reactions (60°C; 0.46% AA) with different VA/BA ratios (50/50 and 80/20).

It is possible to observe in Figure 6 that both reactions presented the same behavior concerning particle stability until reaching 45% polymer plus monomer content. Only after this point the reaction with the 50/50 VA/BA weight ratio presented a slightly higher particle stability when compared to 80/20 VA/BA weight ratio.

Conclusions

Results show that AA, at low concentrations, seems to have no influence on VA/BA copolymerization kinetics or any significant effect on particle nucleation. On the other hand, the effect of AA on particle stabilization is very pronounced. Not only did the reaction performed without AA coagulate completely right after the end of the monomer feeding period when a high solids content was reached in the reactor (55%), but it was also observed that higher AA concentrations resulted in lower aggregation rates during the reactions and, therefore, in smaller average particle diameters. The increase of the average particle diameter, due to particle aggregation, was observed in all reactions and was more intense after reaching 40% polymer plus monomer content. It was also observed that the aggregation rate increases with reaction temperature, this effect of reaction temperature was more significant in reactions carried out with lower AA concentrations. This effect can possibly be attributed to the breakage of the hydrogen bonds of the stabilizing poly(acrylic acid) chains as reported by Yuan et al.[11]. Finally, choosing optimal AA concentrations and reaction temperatures are key factors in order to enhance the stabilization performance and may also be useful tools for controlling polymer particle size in semicontinuous VA/BA emulsion copolymerization.

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