# Emulsion Copolymerization of Styrene and *n*-Butyl Acrylate in Presence of Acrylic and Methacrylic Acids: Effect of pH on Kinetics and Carboxyl Group Distribution

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**ABSTRACT:** The batch emulsion copolymerization of styrene with *n*-butyl acrylate in the presence of acrylic and methacrylic acids was investigated. Values of reaction rate and conversion observed at different pH values were examined. The effect of pH on the glass transition temperature of the polymers was also investigated and the results compared with model predictions. Its effect on the distribution of the carboxyl groups at different positions within the emulsion system (surface and core of particles, and in the aqueous phase) was also analyzed. Three methods were used to measure the number of carboxyl groups: conductimetry, organic phase potentiometry, and titration with a solution of sodium hydroxide in methanol. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 2343–2355, 1997

**Key words:** emulsion copolymerization; styrene; *n*-butyl acrylate; acrylic and methacrylic acids; kinetics; carboxyl groups

## INTRODUCTION

Carboxylic monomers are typically included in the formulation of emulsion polymerizations. These monomers improve the stability of dispersions used as bonding agents in paints and surface treatments for paper products, improve the adhesive characteristics of the latex, improve the mechanical properties of films formed from the polymer latex, and produce particles having reactive substrates on their surface.[1,2]

Given the industrial and scientific importance of functionalized lattices, numerous studies and patents are found in this area. Ceska,[1,3] Sakota,[4] and Vijayendran[5] studied the effect of carboxylic monomers on the distribution of functional monomers and on the mechanism of polymerization for both polystyrene and polystyrene-butadiene lattices. Shoaf and Poehlein[6] investigated the partitioning of acrylic and methacrylic acids (AA, MAA) between the organic (styrene, St) and aqueous phases using a thermodynamic approach to calculate the partition coefficients for both of these functional monomers. Zosel et al.,[7] Wang and Poehlein,[8,9] Kulikov et al.,[10,11] Egusa and Makuuchi,[12] Shoaf and Poehlein,[13,14] Matejicek[15] and van Doremaele et al.[16] all studied the kinetics of emulsion polymerization in the presence of functional monomers. These studies essentially concentrated on kinetic aspects of the polymerization with the objective of predicting the copolymer composition distribution, particle size and number, and rate of reaction.

The effect of pH, which leads to different levels of ionization, was studied by Guillaume et al.[17] and Hoy.[18] Emelie and colleagues[19,20] looked at the distribution of functional monomers in systems containing hydrophilic monomers (methyl methacrylate, MMA, *n*-butyl acrylate, BA). The impact of carboxylic monomers on particle morphology was discussed by Okubo et al.[21–23] and

Morgan[24] for the case of St-BA systems functionalized by MAA. Hildalgo[25] investigated core-shell polymers of St-BA that was also functionalized by this same acid. In general, it was found that the ionization of the carboxylic monomer plays an important role in the definition of the final morphology of the polymer particles.

Dobler[26] investigated the effect of carboxylic monomers on the mechanism and kinetics of particle coalescence of latex particles in the case of core-shell systems of St-BA emulsions functionalized by MAA. Hildago[25] and Dobler[26] also examined latex rheology and the mechanical properties of films formed from St-BA lattices functionalized by MAA.

In the current article we present a study of the emulsion copolymerization of St and BA in the presence of AA and MAA with the objective of investigating the distribution of the acid groups within the system (particle surface and interior, and in the aqueous phase) and the influence of pH on this property and on reaction kinetics.

## EXPERIMENTAL

### Materials

The St, BA, and MAA monomers were obtained from Jansen (France); the AA monomer was purchased from Aldrich (France). The monomers were distilled under a vacuum to remove any traces of inhibitor and were stored at 4°C prior to use.

The water soluble free radical initiator, potassium persulfate (KPS), was obtained from Jansen; the emulsifier, Hostapal BV (HBV), was obtained from Hoechst Gmbh (Germany). Both products were used as received. All polymerizations were carried out in deionized water.

### Polymerization

All polymerizations were carried out in batches. The molar ratio of the monomers was the same in all experiments: St/BA/AA or St/BA/MAA = 54/45/5. All polymerizations were carried out at 60°C for a minimum of 5 h. The different formulations and reaction conditions considered in this work are reported in Table I.

A schema of the automated reactor system is shown in Figure 1. The reactor is coupled with a controller that can be used to monitor and maintain both the temperature and pH in the reactor.

The 2-L glass reactor is equipped with an external temperature control jacket and a vapor condenser. The temperature of the water in the cooling jacket is controlled by a controlled temperature bath, and the condenser is cooled directly with tap water.

### Analysis of Conversion and Residual Monomer Content

The overall (mass) conversion of the reactions was evaluated using gravimetry. Samples were periodically withdrawn from the reactor, weighed, dried for several hours at 105°C, and reweighed.

Residual monomer composition was determined using gas phase chromatography (GPC). The operating conditions used in the GPC analyses are summarized in Table II.

### Purification of Polymers and SEC Analysis

The polymer was recovered from the emulsion by flocculation in slightly acidified methanol (0.02 g HCl/100 mL MOH). The precipitated polymer was filtered, washed with water, and then dried under a vacuum at 40°C for 30 min. The dried product was redissolved in THF, precipitated with methanol, and redried in the same manner for 24 h.

The purified copolymer was then dissolved in THF and the molecular weight was determined by SEC on a Waters 510 gel permeation chromatograph equipped with a 1.2-m long PSS gel mixed category B column. The eluant used was THF at a flow rate of 1.2 mL/min, and the sample volume was 20 $\mu$L in a 1% (w/w) solution. The apparatus was calibrated with polystyrene.

A Zimm plot analysis was used to calculate the weight average molecular weight using a Brookhaven BI8000 light scattering device. THF was again used as the solvent.

### Analysis of Carboxyl Group Concentrations

The combination of conductimetry and potentiometry used here to evaluate carboxyl group concentrations in a dispersion is a technique used by most researchers working on functionalized lattices. In the current work, three methods were used: conductimetry for evaluating the number of carboxyl groups on the surface of the latex particles, organic phase potentiometry, and titration with NaOH in a methanol solution to determine

**Table I   Polymerization Recipes and Operating Conditions**

|  | MAA 22 | MAA 4 | MAA 6 | AA 21 | AA 4 | AA 6 |
|---|---|---|---|---|---|---|
|  | pH 2.2 | pH 4 | pH 6 | pH 2.1 | pH 4 | pH 6 |
| St (g) | 150 | 150 | 150 | 150 | 150 | 150 |
| BA (g) | 138 | 138 | 138 | 138 | 138 | 138 |
| MAA (g) | 12 | 12 | 12 | — | — | — |
| AA (g) | — | — | — | 10 | 10 | 10 |
| HBV[a] (g) | 1.8 | 1.8 | 1.8 | 1.8 | 1.8 | 1.8 |
| KPS (g) | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 |
| Water (mL) | 1200 | 1200 | 1200 | 1200 | 1200 | 1200 |

[a] MAA, Systems functionalized with MAA; AA, systems functionalized with AA. pH controlled by continuous addition of NaOH to reactor.

the number of carboxyl groups in the particles themselves.

### Conductometric Analysis

Before analysis, the lattices were diluted to approximately 2% solids content (by mass) and exchanged using a mixture of cationic and anionic resins until a constant conductivity was obtained.[27] Measurements were made using a CDM 83 conductivity meter (Radiometer, Copenhagen) equipped with a CDC 304/nominal cell constant 1 cm$^{-1}$ platinum electrode (Radiometer). Titrant was added using an Electroburex type EBX3 (Tacussel) electronic burette. The strong acid (sulfate groups derived from the decomposition of the free radical initiator) was neutralized with 0.01$N$ NaOH, and then an excess of base was added to

the dispersion. The addition of this excess amount of base caused the particles to swell and thus facilitated the analysis of the number of carboxyl groups below their surfaces. It should also be noted that one cannot automatically assume that diffusion of the titration agent is instantaneous and the number of groups evaluated using this technique can thus vary (increase) as a function of time.[28,29] The excess NaOH levels were, in turn, neutralized with 0.01$N$ HCl. This was done immediately after the addition of the excess of NaOH in order to evaluate the number of groups on the particle surface and near its exterior.

### Potentiometric Analysis

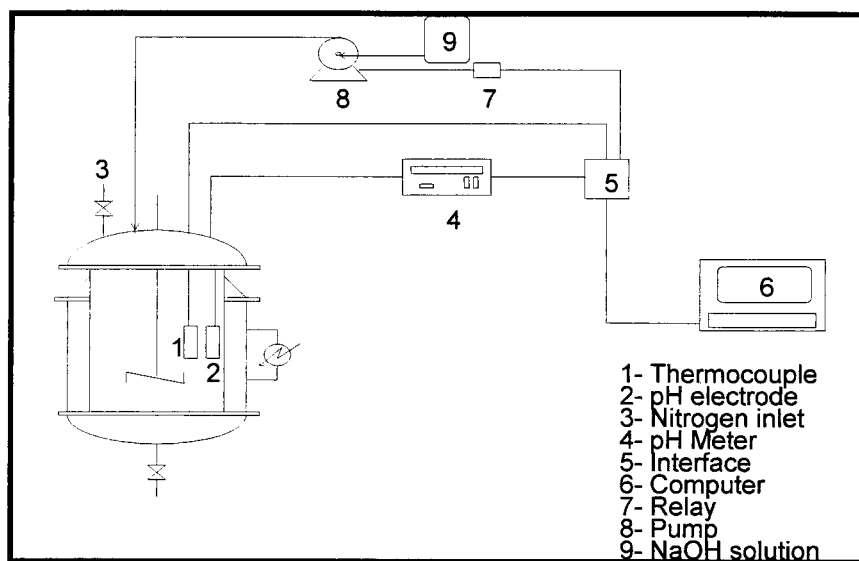The degree of incorporation of acid groups into the particles was evaluated by performing a po-



**Figure 1**   Automated reactor system for batch emulsion polymerization.

**Table II  Operating Conditions for GPC Experiments**

|  | Condition 1[a] | Condition 2[b] |
|---|---|---|
| Nitrogen pressure (carrier gas) | 3.6 bars | 3.6 bars |
| Hydrogen pressure | 1.4 bars | 1.4 bars |
| Air pressure | 2.2 bars | 2.2 bars |
| Injector temperature | 180°C | 180°C |
| Detector temperature | 180°C | 180°C |
| Oven temperature | 70°C | 70°C (3 min)−130°C (3 min) Heating rate, 70°C/min |
| Detector sensitivity | Range 8 | Range 8 |

tentiometric analysis in an organic medium. Both the simple titration and potentiometric analyses used during the course of this work were performed in two different organic media. A modified version of the method developed by Emelie[19] was used in the potentiometric analyses, which were performed on a TITRAPLUS TTP 320T (Tacussel) potentiometer equipped with a glass electrode in an XG 940 (Tacussel) organic solution. The reference electrode was a modified Calomel electrode, with the saturated KCl solution that is normally used being replaced by a saturated solution of KCl in methanol. This change significantly increased the signal during the potentiometric analysis, and thus allowed us to better identify the inflexion point.[30]

The titrant used was 0.1N tetrabutylammonium hydroxide in a mixture of benzene and methanol (9 : 1 parts by volume, respectively) that was added using the Electroburex EBX3 electronic burette.[30–33] The concentration of this solution was determined using a solution of benzoic acid in pyrridine.[30] Pyrridine was chosen as a solvent because Emilie[19] used it successfully. A blank was carried out for each series of measurements to determine the acidity of the solution.

The polymers were purified through repeated dissolution in THF and precipitation in methanol. The polymers were dried under a vacuum at 40°C for 24 h. The polymer thus obtained was dissolved in 100 mL of pyrridine to obtain solutions with three different concentrations.

The results of potentiometric tests were confirmed by dissolving polymer samples in 100 mL of DMF and precipitating them using a solution of NaOH in methanol.[26] A 0.3% solution of thymol blue in isopropyl alcohol was used as a color indicator in these analyses. The concentration of the NaOH/methanol solutions was determined using a solution of 0.1N HCl. As mentioned above,

blanks were used in each series of tests to determine the acidity of the solvent.

The fact that the results obtained using the three methods were almost identical proves that the techniques in question are quite reliable insofar as the evaluation of the carboxyl groups in and on the polymer particles is concerned, even at low acid concentrations.

## RESULTS AND DISCUSSION

### Distribution of Carboxyl Groups

The distribution of the carboxyl groups in a batch reactor is governed by the hydrophilic nature of the ionizing comonomers that, in turn, depends on the pH of the reaction medium. In the case of copolymerization in the presence of either AA or MAA, the pH would increase over the course of the reaction if it were left unchecked. However, the control system shown in Figure 1 allowed us to maintain constant levels of pH at all times.

The distribution of carboxyl groups in systems produced at different levels of pH are shown in Figures 2 and 3. These results demonstrate that, because of their different hydrophilic characteristics, AA and MAA behave in different manners. This was already discussed in the literature.[19]

The results shown in Figure 2 demonstrate the hydrophobic nature of MAA under acidic conditions. At a pH of 2.2, almost all of the acid (88%) polymerizes inside the particles whereas the AA remains fairly evenly distributed between the aqueous phase (46%), the surface (23%), and interior (31%) of the particles. At a pH of 4 we are approaching the p$K_a$ of both AA and MAA at this temperature, and it can be seen that MAA shows almost the same behavior as in the case of a pH of 2.2. On the other hand, the concentration of AA
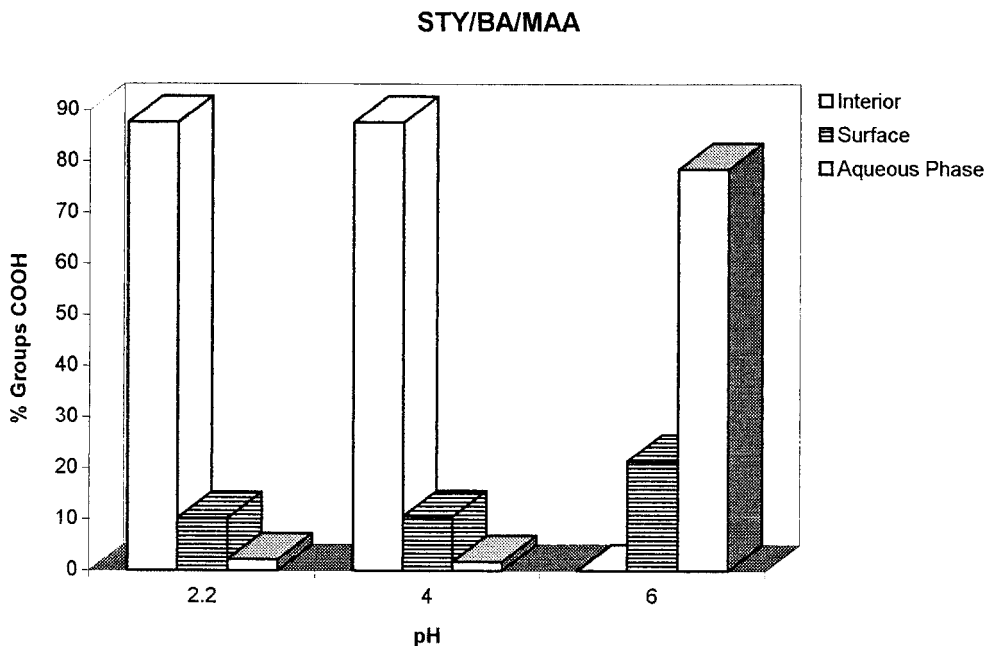
**STY/BA/MAA**



**Figure 2** Distribution of methacrylic acid groups (% mass of COOH groups) at different points in an emulsion system (interior and surface of particles, and in the aqueous phase) as a function of the pH of the reaction medium.

in the aqueous phase is significant under the same conditions of pH, with 77% of the acid being found dissolved in the aqueous phase. Finally, at a pH of

6 almost none of the MAA is found in the particles, with 21% being found on the surface of the particles and 79% in the aqueous phase. Figure 3
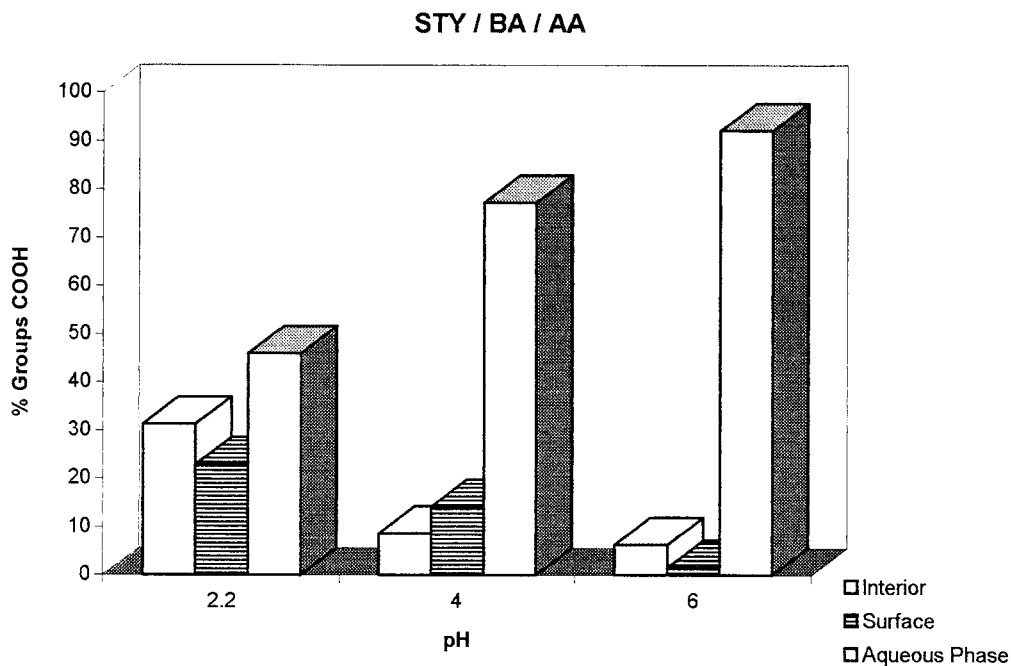
**STY / BA / AA**



**Figure 3** Distribution of acrylic acid groups (% mass of COOH groups) at different points in an emulsion system (interior and surface of particles, and in the aqueous phase) as a function of the pH of the reaction medium.

shows that under the same conditions, 92% of the AA is found in the aqueous phase and, unlike the MAA, only 1.6% is at the surface of the particles.

Emilie[19] studied the emulsion copolymerization of BA and MAA in the presence of AA and MAA with a natural evolution of pH (the pH varied from 3 to 5 over the course of the polymerization) and investigated the distribution of carboxyl groups as a function of the type of polymerization process used. In the case of a copolymerization in a closed (batch) reactor, AA and MAA exhibited very different behaviors, due, according to the author, to differences in their respective hydrophilic characteristics. AA was found in equal amounts in the aqueous phase and at the polymer–water interface whereas over two-thirds of the MAA was found in the interior of the particles. Emilie[19] concluded from this that the batch process led to a distribution governed by the hydrophilic nature of the ionizing comonomers. Because MAA is the more hydrophobic of the two, it polymerizes inside the particles whereas the more hydrophilic AA is found in both the aqueous phase and in the particles.

The partitioning of carboxylic monomers between the aqueous and particulate phases depends on the pH of the reaction environment.[6,34] A previous study showed that the partitioning of MAA between the water and a mixture of St and BA decreased considerably as the pH was increased.[34] The negative charge on the dissociated (anionic) form of MAA renders it more polar than the nondissociated form, and thus increases its relative attraction for other polar molecules such as water and decreases its attraction for nonpolar species such as St or BA. Increasing the pH leads to higher concentrations of the dissociated form of the acid, and the quantity of MAA found in the organic phase decreases correspondingly. We verified that at a pH greater than 6, all of the MAA can be found in the aqueous phase at both 25 and 70°C.

### Reaction Kinetics

Conversion–time curves of the copolymerization of St and BA are shown in Figure 4. These curves will be used as a reference for what follows. This experiment was carried out under the same conditions given in Table I, but in the absence of a carboxylic acid. The only exception to this was that unlike the other experiments where the molar ratio St/BA was equal to 1.3 at the beginning of the reaction, here it was equal to 1.
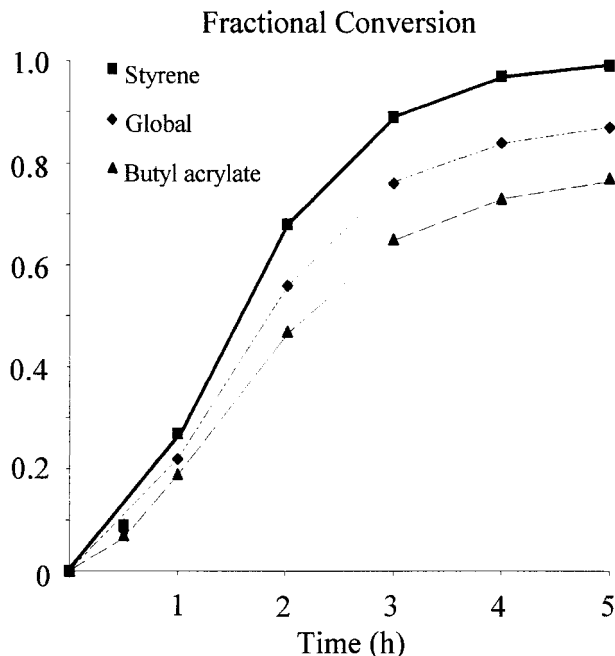


**Figure 4** Copolymerization of styrene and butyl acrylate; experimental results for a reaction without carboxylic acids. Molar ratio Sty/BA = 1. The pH evolved naturally over the course of the reaction. Other conditions are given in Table I.

The kinetics of the copolymerization in the presence of MAA at different pH values are shown in Figures 5–7. The effect of the pH on the rate of consumption of MAA can be clearly seen from these graphs. Given that the individual rate curves for MAA are similar at pH 2.2 and 4, it is probably safe to say that at a pH lower than the $pK_a$ ($pK_a$ of MAA = 4.36),[6] the rate of consumption of MAA is independent of the pH. On the other hand, at a pH of 6 the kinetics of the consumption of MAA is significantly slower than at lower pHs.

In a similar vein, Kabanov et al.[35] observed that the propagation rate constants of MAA and AA are both dependent on the pH. Here, the rate of polymerization decreased strongly with pH increasing to values of 6–7. Beyond this limit, the rate increased again to a maximum at pH values of 11–12. The observed rate increase from pH 7 to 12 might be due to cationic bonding of the carboxylate radicals with sodium cations (produced by the base NaOH used to neutralize the system), the result of which would be to decrease the electrostatic repulsion of the anionic monomers.[36]

The modification of the ionic nature of these molecules also has a direct influence on values of the reactivity ratios, $r_{ij}$, of the monomers.[37,38]
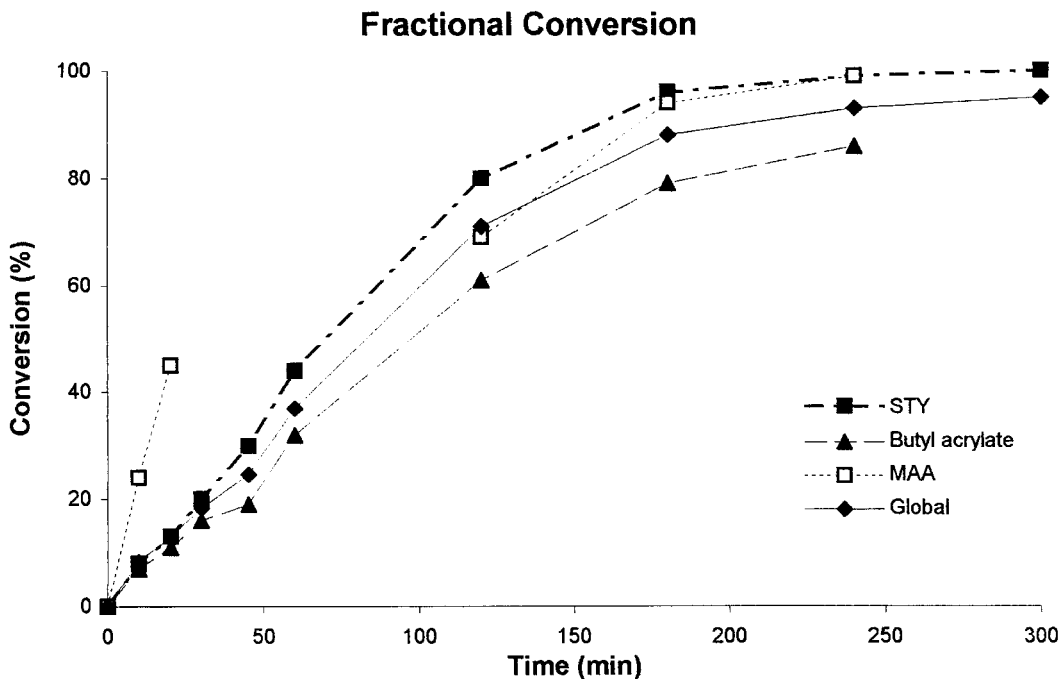
## Fractional Conversion



**Figure 5**   Emulsion copolymerization of St and BA in the presence of MAA at pH 2.2 (exp. MAA2 in Table I).

Ceska[1,3] and Sakota and Okaya[2,4] studied the variation of the rate of polymerization of St in the presence of carboxylic acids as a function of the degree of neutralization of the reaction environ-ment. They observed that the rate of reaction was strongly dependent on this parameter, as well as on the amount of acid introduced and the hydrophobic nature of these same acids.
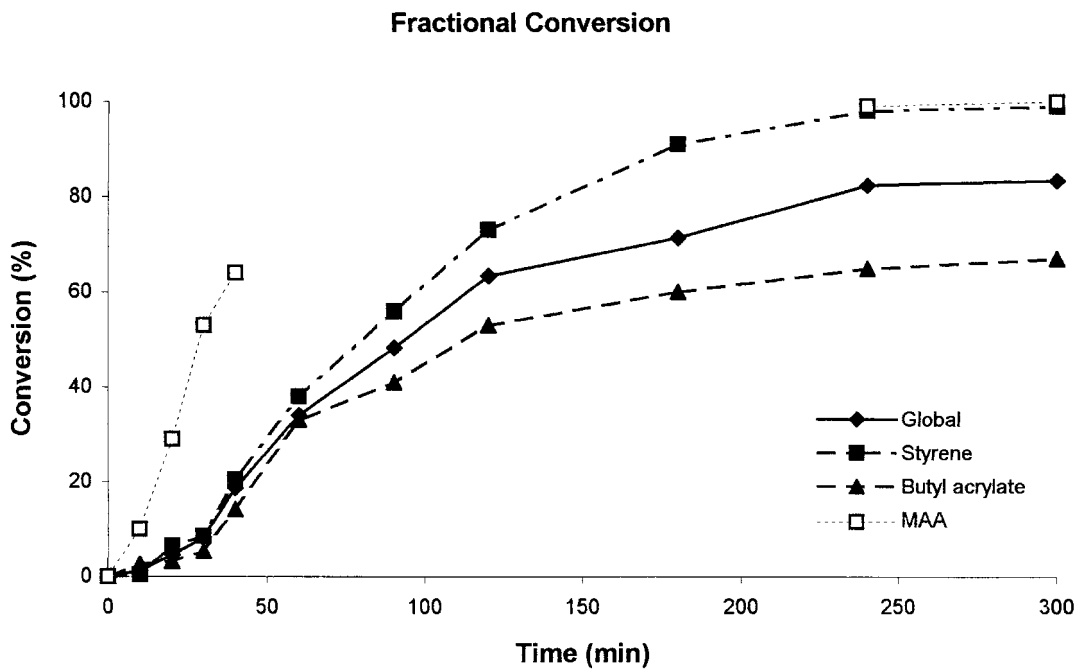
## Fractional Conversion



**Figure 6**   Emulsion copolymerization of St and BA in the presence of MAA at pH 4 (exp. MAA4 in Table I).
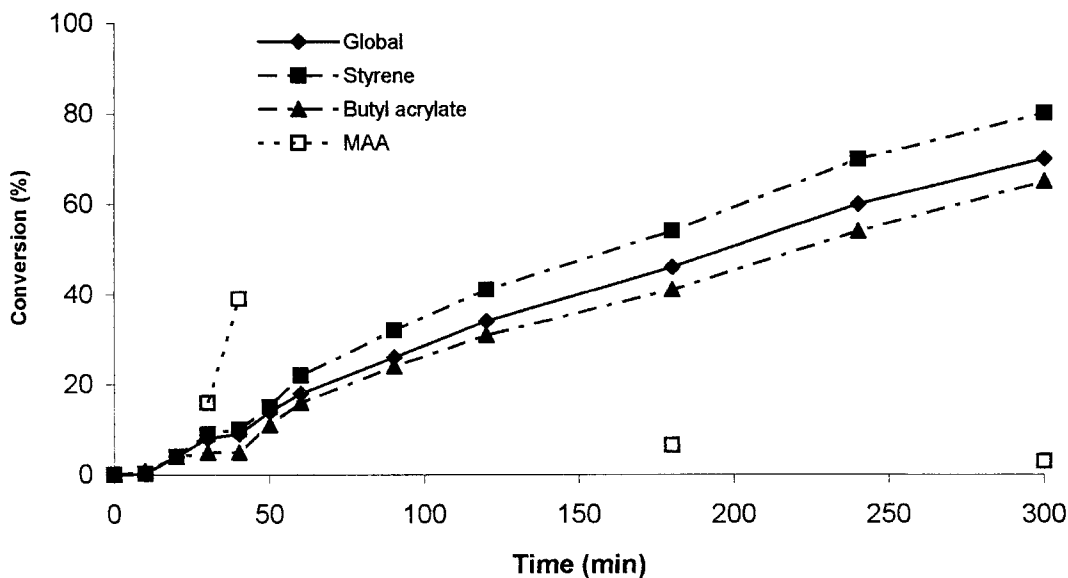
**Fractional Conversion**



**Figure 7**  Emulsion copolymerization of St and BA in the presence of MAA at pH 6 (exp. MAA6 in Table I).

An analysis of the residual carboxylic content of the latexes becomes rather difficult at low carboxylic acid concentrations, especially when one is working under alkaline conditions. In this case it is necessary to add hydrochloric acid to the solutions to be analyzed in order to eliminate the carboxylic acid salts that are formed when the neutralizer (here NaOH) is added to the system, which makes it further impossible to use GPC to measure the concentrations. Also, due to the poor reproducibility of GPC experiments with MAA, only a few experimental points were available (see Fig. 6).

The overall rates of conversion for the St/BA/MAA and St/BA/AA systems are summarized in Figures 8 and 9 at different pHs and as a function of time.[39] In both cases the pH had a measurable effect, with the rate of conversion increasing as the pH decreased. This overall tendency was the same for MAA and AA, with the conversion attaining higher values more rapidly at lower pH. It can also be seen that the increase in the conversion rate as the pH goes from 4 to 2.2 was larger for AA (Fig. 9) than it was for the same increase in the presence of MAA.

If we compare the rate curves obtained in the presence of each of the carboxylic acids with that obtained for the copolymerization without either acid, we can see that the rate was higher in the presence of either AA or MAA at a constant pH of 2. At a pH of 4 (Fig. 6), the overall rate of polymerization was again higher in the St/BA/MAA than in the St/BA system. On the other hand (Fig. 9), the overall rate in the presence of AA at this same pH (exp. AA4) was lower than that of the reference system. These results can be explained, or at least interpreted, by examining the different particle sizes found for each experiment. The variation of the (average) particle size as a function of time for each copolymerization is given for St/BA/MAA in Figure 10 and for St/BA/AA in Figure 11.

The general shape of the curves in Figure 10 is similar, at pH 2.2 and 4, and for the St/BA reference system, the average particle size seems to evolve quantitatively in much the same way. However, at pH 6 the particles were approximately 50% bigger in diameter.

However, as shown in Figure 11, the results for the case of AA terpolymerizations was different. At a pH of 2.1 the general shape of the curves for MAA and for AA were similar, but the particles obtained at the end of the St/BA/AA reaction were 14 nm smaller than the particles obtained at the same pH with MAA. Santos and colleagues[39] recently demonstrated that the rate of decomposition of KPS does not change in this zone of pH. Therefore, it would appear that another factor
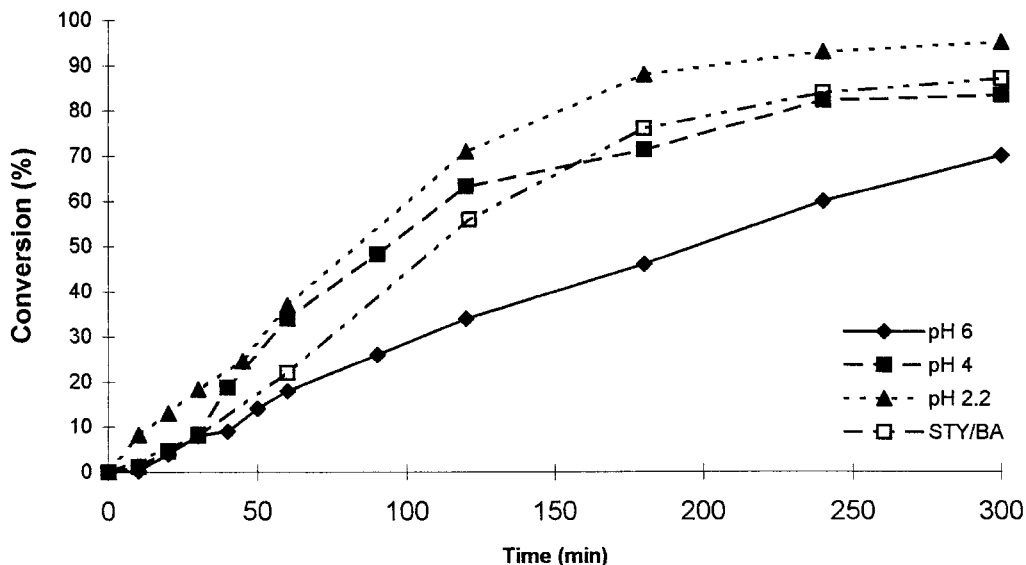
## Overall Conversion STY/BA/MAA



**Figure 8**  Overall conversions as a function of time at different pHs for the copolymerization of St and BA in the presence of MAA.

plays a role in the kinetics of these reactions. The different particle sizes could in fact have an influence on the average number of radicals per particle, which plays a direct role in the polymerization kinetics and the overall rate of reaction. Shoaf

and Poehlein[14] studied the emulsion copolymerization of St with MAA at different values of pH and found that the rate of polymerization of MAA depended on the pH and the rate of polymerization of the acid decreased as the pH increased.
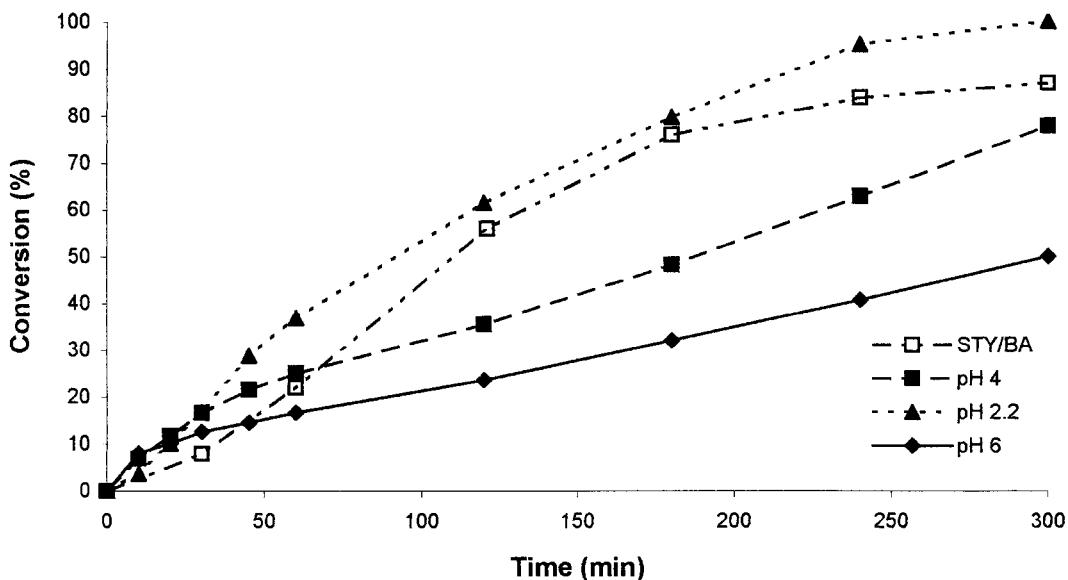
## Overall Conversion STY/BA/AA



**Figure 9**  Overall conversions as a function of time at different pHs for the copolymerization of St and BA in the presence of AA.
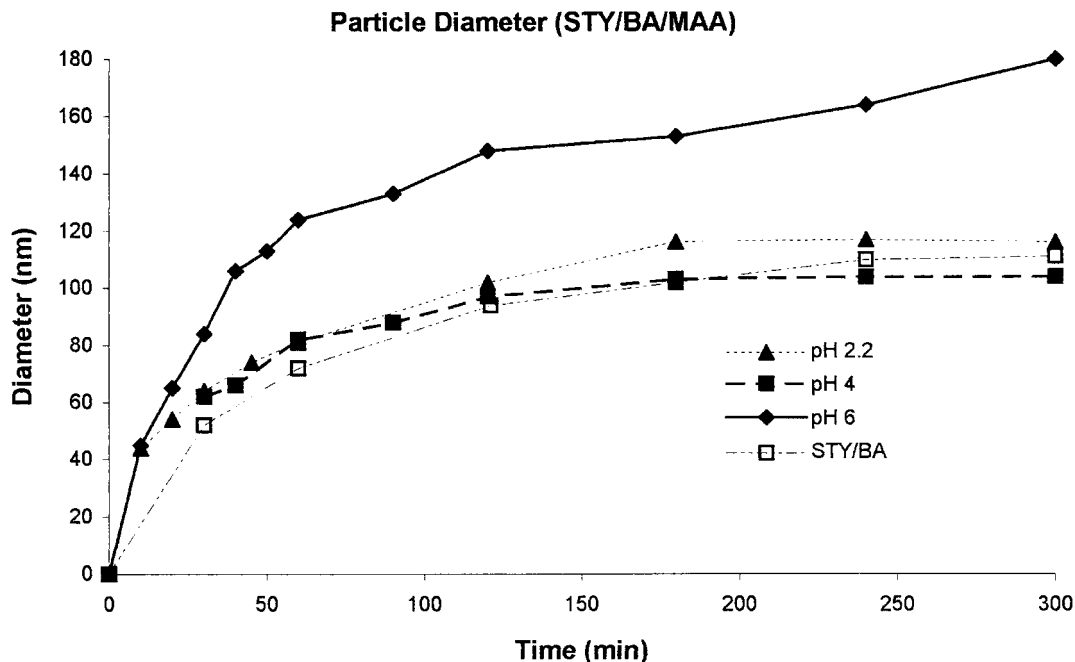
**Particle Diameter (STY/BA/MAA)**



**Figure 10** Variation of the particle diameter as a function of time for the copolymerizations of St/BA/MAA at different pHs. St/BA is included for comparison.

The authors explained these results in part through the low reactivity of the ionized form of the acid.

They also observed that the rate of polymerization of St is lower at fixed pH (controlled through the addition of NaOH) than in systems where the pH is allowed to evolve naturally.[39] According to Shoaf and Poehlein,[14] increasing the pH contributes to a decrease in the concentration of the comonomer acid in the organic phase (in this case

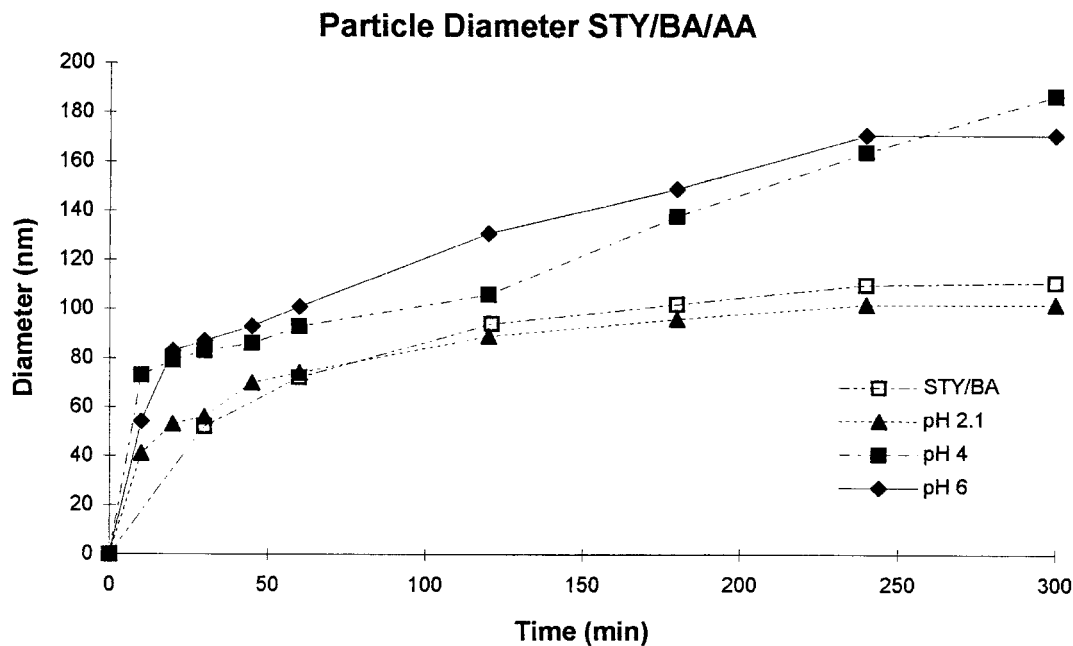**Particle Diameter STY/BA/AA**



**Figure 11** Variation of the particle size as a function of time for the copolymerization of St/BA/AA at different pHs. St/BA is included for comparison.

St). The comonomer should thus preferentially polymerize in the aqueous phase. The oligoradicals that form in the water phase will thus be enriched in the ionized form of the acid and will therefore have a difficult time entering the particles. In this case the entry rate for this type of oligoradical would be quite low if the acid were partially neutralized, and this low entry rate would be reflected by a decrease in the overall rate of polymerization of St inside the particles.

In a study of the seeded emulsion polymerization of St with MAA and AA at 85°C, Shoaf and Poehlein[14] demonstrated that the rate of polymerization of MAA is higher than that of AA. They claimed that a difference in the way that each of the acids was partitioned in the system was the reason for these observations. Because the MAA was more hydrophobic than the AA, it was found in relatively higher concentrations in the organic phase. They also verified that the rate curve for the consumption of MAA follows the same general form as that of St (i.e., the rates of polymerization of MAA and St remain roughly proportional). However, it was found that, for the same ratio of St/carboxylic acid, the rate of conversion of AA was very slow at the beginning of the reaction and did not become significant until a good portion of the St had been consumed. A reaction mechanism for the St/AA pair was proposed wherein most of the reaction took place in the particles at the beginning of the polymerization while the system was still rich in St. Once most of this monomer had been consumed, the principle site of polymerization shifted to the aqueous phase. According to Shoaf and Poehlein,[13,14] this change of site can be explained by either an increase in the hydrophilic nature of the (relatively) AA-enriched oligoradicals that were formed once most of the styrene had been consumed, or by a barrier potential-related problem caused by the presence of PAA* oligoradicals that might be absorbed onto the surface of the particles.

Natsuhara[40] also studied the copolymerization of St and BA in the presence of MAA and AA for different molar ratios of St/BA and at different acid concentrations. He demonstrated that the presence of AA in these systems did not significantly change the reaction kinetics with respect to those observed in systems without a carboxylic acid. Furthermore, he found that the presence of MAA seemed to decrease the instantaneous rates of polymerization of both St and BA. According to Natsuhara,[40] the dominant reaction mechanism depends on the type of acid added to the system.

In the case of copolymerization in the presence of MAA, this author proposed that the oligoradicals formed in the aqueous phase either combined rapidly with the latex particles or precipitated rapidly to form new emulsion particles. Furthermore, regardless of how the oligoradicals leave the water phase, the reaction would continue as a terpolymerization in the organic phase. On the other hand, in the St/BA/AA system, once formed, the oligoradicals continue to polymerize in the aqueous phase much longer than they would in the St/BA/MAA system. In this event, the oligoradicals would add significantly more carboxylic acid than they would in the presence of MAA, and the copolymerization of St with BA would take place in the presence of a much lower concentration of the comonomeric acid.

Furthermore, Emilie[19] showed that the functionalization of MMA-BA copolymers by either MAA or AA also depends on the co-acid in the system. Here it was demonstrated that the initial rate of homopolymerization of MMA and BA in the presence of a functional monomer was more rapid than the homopolymerization without the carboxylic acids, and the most significant increase in the observed rate was noted when BA was polymerized in the presence of MAA. This tendency was reversed when MMA was copolymerized. According to Emilie,[19] this observation was most likely due to the fact that MAA has a greater affinity for the least soluble monomer and that AA has a greater affinity for the more hydrophilic monomer. In the case of a terpolymerization, Emilie also showed that the MAA caused an increase in the initial overall rate of reaction whereas AA had little effect.[19] Also, the final conversion obtained in a given time was higher with MAA than AA. It would be noted that all of Emilie's[19] experiments were carried out in a batch reactor with a natural evolution of pH (which increased over the course of the polymerization from near 3 at the beginning to approximately 5 at the end).

Experimental measurements of the weight average molecular weights determined using the Zimm plot method, and of the glass transition temperatures ($T_g$) using a DTA analysis are given for all of the experiments in Table III. It was not possible to report the average molecular weights using the SEC method because the pressure in the column was too high due to the very high molecular weights of the polymers produced. These copolymers, rich in BA, interacted with the columns and, in certain cases, even caused them to become plugged. Nevertheless, the results of the

**Table III   Experimental Measurements of Average Molecular Weights ($M_w$) and Glass Transition Temperatures ($T_g$) Function of pH**

| | MAA | | | AA | | |
| --- | --- | --- | --- | --- | --- | --- |
| | pH 2.2 | pH 4 | pH 6 | pH 2.1 | pH 4 | pH 6 |
| $M_w{}^a$ | $2.02 \times 10^6$ | $1.51 \times 10^6$ | $1.27 \times 10^6$ | $1.85 \times 10^6$ | Insoluble | Insoluble |
| $T_g$ (°C)$^a$ | 29 | 28 | 27 | 26 | 24 | 23 |

Zimm plot analysis showed that the variation of the reaction pH had a measurable impact on the molecular weights of the polymers produced. In the case of copolymerization in the presence of MAA, the molecular weight decreased as pH increased. In the AA system the copolymers obtained at pH 4 and 6 were insoluble in the solvent used for the Zimm plots; therefore, we cannot draw any conclusions about the evolution of the molecular weight distribution. However, it can be seen that the molecular weights obtained at a pH of 2.2 for both acids were approximately the same.

The experimental results of the measurement of the $T_g$ of the copolymers are also presented in Table III. The copolymers produced in the presence of MAA had a higher $T_g$ than those formed in the presence of AA, and in both systems the $T_g$ decreased as the pH increased. If we accept the value estimated using the approach discussed by Guillot,[41] the $T_g$ of the St/BA system without any carboxylic acids is 24°C. It can then be concluded that the use of MAA at any pH leads to the formation of copolymers having a higher glass transition than the reference system. However, except at a pH of 2.1 where the $T_g$ of the copolymer formed in the presence of AA was only slightly greater than that of the reference system, the use of AA led to the formation of copolymers having a $T_g$ equal to, or slightly lower than that of St/BA alone. This last observation was most likely due to the very low rate of incorporation of AA at pH of 4 and 6. However, it is important to point out that these conclusions were based on a slight tendency observed in the results of the evaluation of the $T_g$. More work needs to be done on the evaluation of $T_g$ before we can say that such narrow margins are statistically significant.

## CONCLUSION

The acidic monomers used in this study, MAA and AA, are distributed differently throughout the three phases of the emulsion system (particle interior, particle surface, aqueous phase). The more hydrophobic of the two carboxylic acids (MAA) is found at higher concentrations inside the latex particles than is AA, especially at acidic pH. In general, the AA is more equally distributed throughout the system than the MAA is at the same pH.

The presence of these ionizing comonomers also has an impact on the overall kinetics of the polymerization. The exact change depends on the type of acid used and the pH of the reaction environment. It appears that the reaction mechanism is not the same for both acids and is also a function of the pH. The lower rates of polymerization observed for MAA are quite possibly due to a problem of radical desorption, which leads to a reduction in the average number of radicals per particle (with respect to the St/BA system). The fact that the rates are lower at low pH also lends support to this idea because it is at these levels of pH that the acid concentration is highest inside the latex particles.

The final properties of the copolymers also depend on the type of acid and on the pH of the reaction environment. For example, increasing the pH decreases the average molecular weight of the copolymers formed in the presence of MAA. This is also coherent with the idea of radical desorption, because at more acidic pHs the desorption of radicals from the polymer particles would lead to the formation of longer macromolecules at constant monomer concentrations.

Also, the impact of pH on the partitioning of the acidic comonomers throughout the system has an impact on the glass transition temperatures. The effect is less pronounced when AA is the carboxylic acid added to the system (i.e., the $T_g$ of the final polymer differs from that of the reference system by a smaller margin than in the case of MAA) because AA is more evenly distributed and is found at relatively higher concentrations in the aqueous phase than MAA. Because the MAA is

found at relatively high concentrations inside the particles, it has a greater influence on the final glass transition temperature of the copolymer.

Finally, it must be pointed out that the results presented above were obtained in a batch reactor. Extending this to a semibatch process with different feed policies would certainly allow us to alter the distribution of functional groups in the polymer particles. Proper selection of addition rates and times, as well as reaction conditions including the pH, would give us control over how and when the carboxyl groups are incorporated into the polymer. This will be the subject of a publication from this laboratory in the very near future.

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