

# Seeded Emulsion Polymerization of Styrene: Incorporation of Acrylic Acid in Latex Products

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**ABSTRACT:** Seeded batch emulsion polymerization of styrene and acrylic acid was studied. The influence of pH and acrylic acid content on the polymerization rate and the amount of carboxylic acid groups incorporated in the final latex products was investigated. The distribution of the functional groups over the aqueous phase, the latex particle surface, and the interior of the latex particle was determined using aqueous conductometric titration and nonaqueous potentiometric titration at intermediate and complete overall conversions. Combined with kinetic results, the carboxylic acid group distribution history provided valuable information about the process of incorporation of acrylic acid in latex products. Two-step processes in which a shot of acrylic acid was performed in the last stage of the emulsion polymerization reaction were investigated as a strategy to increase the surface incorporation efficiency. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 875–885, 2000

**Key words:** seeded emulsion polymerization; styrene; acrylic acid; pH; acid distribution

## INTRODUCTION

The addition of small amounts of carboxylic monomers into emulsion polymerization recipes results in the production of carboxylated latexes, known for their advantageous industrial properties.<sup>1</sup> The features of carboxylated latexes are often related to the distribution of acid groups in the latex products. This distribution distinguishes between three main different loci: the aqueous phase, the particle interior, and the particle surface. Most of the advantageous properties of carboxylated latexes originate from the presence of acid groups on the outer surface of the

latex particles. However, the use of water-miscible carboxylic monomers in emulsion polymerization is somewhat contradictory to the heterogeneous aspect of a process leading to water-insoluble polymers. The challenge is to optimize the incorporation of the functional monomer into the polymer molecules since polymer molecules with incorporated carboxylic acid groups will ultimately reside in the outer shell of the latex particles.<sup>2,3</sup> In addition to the conventional parameters to be defined in emulsion polymerization, the nature of the water-soluble carboxylic monomer results in that the reaction and the outcome of the process are very sensitive to pH. Not only colloidal stability but also kinetics and phase equilibria are influenced by the pH of the reaction mixture. The pH strongly influences the polymerization behavior of carboxylic monomers in water<sup>4,5</sup> as

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well as their partitioning between the aqueous phase, the droplet phase, and the particle phase of an emulsion system. The affinity of the polar monomer for one phase or the other depends, indeed, very much on the degree of dissociation of the carboxylic groups.<sup>6</sup>

The influence of some reaction parameters on the course of the seeded emulsion polymerization of styrene in the presence of acrylic acid (AA) was reported in a separate article.<sup>7</sup> The influence of the pH, the temperature of the reaction mixture, and the size of the polystyrene seed latex particles on the kinetics of the polymerization as well as on the distribution of the acid groups in the final products was investigated. It was shown that the pH had only a slight influence on the rate of polymerization in the studied systems. However, the amount of acid groups in polymer molecules at the particle surface was almost completely governed by the pH. In agreement with several authors,<sup>8-10</sup> it was observed that at pH 7 the very hydrophilic carboxylic monomer in its dissociated form had the tendency to remain in the water phase. The hydrophilic nature together with additional electrostatic effects eventually preventing the effective entry of oligomeric radicals into the particles resulted in very poor incorporation of acid groups both on the surface as well as in the interior of the latex particles at pH 7. Indeed, generally less than 10% of the initial amount of AA was incorporated. However, at a pH value of 2.5, most of the initial AA was present in the final products as polymerized surface acid in the outer shell of the latex particles. For reactions carried out at pH 2.5, a significant amount of carboxylic groups was buried inside the latex particles as well.

The present work attempted to provide detailed mechanistic insight into the seeded emulsion copolymerization of styrene and AA. The parameters investigated include the pH of the reaction mixture and the molar ratio of the two monomers. Special attention was paid to the determination of the acid-group distribution during the course of the reaction. Attempts were made to determine the influence of a two-step process on the distribution of acid groups in the latex products. In the two-step process, the functional monomer was added at different conversions to the reaction mixture.

## KINETICS OF COPOLYMERIZATION

Monomer ratios have generally a considerable influence on both the aqueous-phase and the parti-

cle-phase polymerization during emulsion copolymerization processes. In the case of the emulsion copolymerization of styrene (S) and AA, a preliminary study<sup>7</sup> showed that for low fractions of free AA in the particle phase the average propagation rate constant  $\bar{k}_p$  in the particle phase could be best approximated by the propagation rate constant for the homopolymerization of S. However, due to the large amount of AA present in the water phase compared to S, this assumption is not valid any more for the determination of  $\bar{k}_{p, \text{aq}}$ , the average propagation rate constant in the aqueous phase. The aqueous-phase polymerization corresponds actually to a solution copolymerization. A simple model describing copolymerization kinetics is the so-called terminal model.<sup>11,12</sup> In this model, the addition rate of monomer units to a growing chain depends only on the nature of the terminal group and the nature of the reacting monomer. The average propagation rate constant  $\bar{k}_p$  and the relation between the monomer composition at the locus of polymerization ( $f$ ) and the momentary copolymer composition ( $F$ ) are, respectively, given by

$$\bar{k}_p = \frac{r_i f_i^2 + 2f_i f_j + r_j f_j^2}{\frac{r_i f_i}{k_{p_{ii}}} + \frac{r_j f_j}{k_{p_{jj}}}} \quad (1)$$

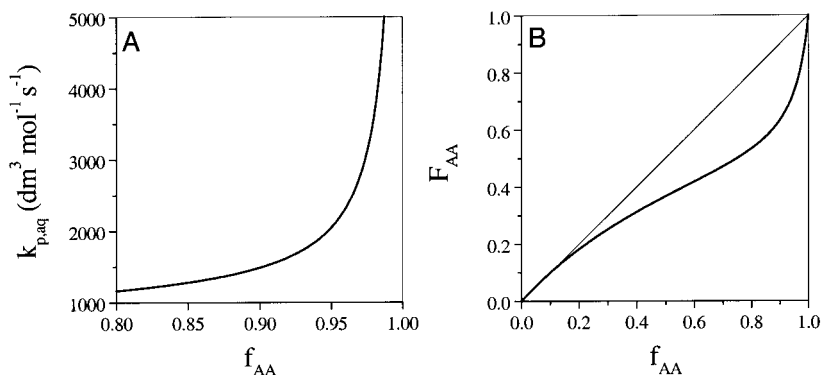
$$F_i = \frac{r_i f_i^2 + f_i f_j}{r_i f_i^2 + 2f_i f_j + r_j f_j^2} \quad (2)$$

where  $k_{p_{ii}}$  is the homopolymerization rate constant;  $r_i$ , the reactivity ratio; and  $f_i$ , the mol fraction of monomer  $i$  at the locus of polymerization.  $r_i$  is defined as

$$r_i = \frac{k_{p_{ii}}}{k_{p_{ij}}} \quad (3)$$

where  $k_{p_{ij}}$  is the rate coefficient for propagation of a terminal unit  $i$  with a monomer unit  $j$ .

For the copolymerization of S and AA in the aqueous phase,  $\bar{k}_{p, \text{aq}}$  depends on the reactivity ratios and the mol fraction of both monomers in this phase. Figure 1, which has been calculated with eqs. (1) and (2) and the parameters collected in Table I, shows the average propagation rate constant at 70°C and the mol fraction of AA momentary built into the copolymer formed in the aqueous phase as a function of the mol fraction of free AA in the aqueous phase.



**Figure 1** Copolymerization of S and AA in water: (A) calculated average propagation rate constant for the copolymerization of S and AA at 70°C in water as a function of the AA mol fraction in the monomer feed. Calculation with eq. (1) and the constants given in Table I; (B) calculated mol fraction of AA momentary built into the copolymer as a function of the mol fraction of free AA in the aqueous phase. Calculation with eq. (2) and the constants given in Table I.

$f_{AA}$  in the aqueous phase is given by the relation

$$f_{AA} = \frac{C_{AA,eq}}{C_{AA,eq} + C_{S,eq}} \quad (4)$$

where  $C_{AA,eq}$  and  $C_{S,eq}$  are the AA and S monomer concentration in the aqueous phase, respectively. At the beginning of the emulsion polymerization process,  $C_{S,eq}$  is given by  $C_{S,w}^{sat}$ , the solubility of S in water, and  $C_{AA,eq}$  can be calculated from the initial amount of AA monomer in the system and the volume of the different phases (see recipes in Table II) and from  $x_{AA}^{org}$ , the fraction of AA present in the organic phase (see Table I). The values collected in Table III correspond to the situation in the aqueous phase at the start of the polymerization.  $\bar{k}_{p,eq}$ ,  $f_{AA,0}$ , and  $F_{AA,0}$ , respectively, stand for the average propagation rate constant in the aqueous phase, the mol fraction of free AA in the aqueous phase, and the mol frac-

tion of AA momentary built into the aqueous phase copolymer when polymerization begins. Figure 1 and Table III show that for resulting  $f_{AA}$  values between 0.8 and 1,  $x_{AA}$  has a very strong influence on both the kinetics of the polymerization in the aqueous phase and the composition of the copolymer formed.

## EXPERIMENTAL

### Materials

The monomers styrene (Merck, Darmstadt, Germany) and acrylic acid (Fluka) were distilled under reduced pressure and stored at 5°C before use. The initiator used was sodium persulfate (Fluka, Buchs, Switzerland). The emulsifier sodium dodecyl sulfate (Merck) was used to prepare the seed latexes. The second-stage experiments were performed with an optimal amount of emulsifier to colloidally stabilize the growing particles while preventing secondary nucleation. The pH of the reaction mixtures was about 2.5 due to the presence of AA. For reactions performed at a pH of about 7, some sodium carbonate (Merck) was used. For the seeded emulsion polymerization of S in the absence of AA, some acetic acid (Merck) was used to obtain a pH value of 2.5. The ionic strength was adjusted with sodium chloride (Merck) and based on a constant overall concentration of sodium ions in the aqueous phase in all the experiments. All the chemicals were laboratory grade.

**Table I** Values for Various Parameters

Parameter	Value	Reference
$k_{pS}$ at 70°C (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	480	13
$k_{pAA}$ at 70°C (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	60,000	14
$r_{AA}$	0.1	15
$r_S$	0.9	
$C_{S,w}^{sat}$ (mol dm <sup>-3</sup> )	$4.3 \times 10^{-3}$	16
$x_{AA}^{org}$	0.12	6
$C_{MP}$ (mol dm <sup>-3</sup> )	5.5	17

**Table II Standard Recipe for Carboxylated Seeded Batch Emulsion Polymerization**

Seed	10 g of solid polymer
Styrene (S)	85 g
Acrylic acid (AA)	0/2/5/10 g
DI water	900 g
Sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ )	$10 \times 10^{-3} \text{ mol dm}^{-3}$
Sodium dodecyl sulfate (SDS)	$5.5 \times 10^{-3} \text{ mol dm}^{-3}$
Sodium carbonate ( $\text{Na}_2\text{CO}_3$ )	$0/50 \times 10^{-3} \text{ mol dm}^{-3}$
Sodium chloride (NaCl)	$100 \times 10^{-3}/0 \text{ mol dm}^{-3}$
$C_{M,0}^a$	0.91/0.940/ <b>0.985</b> /1.06 mol dm <sup>-3</sup>
Total AA ( $\mu\text{equiv g pol}^{-1}$ ) <sup>b</sup>	0/277/ <b>694</b> /1388

Concentrations given per unit volume aqueous phase.

<sup>a</sup> Initial overall monomer concentration.

<sup>b</sup> After complete conversion.

Thoroughly cleaned mixed-bed resins of Dowex 50W  $\times$  4 and Dowex 1  $\times$  4 (Fluka) were used to remove the excess electrolytes from the latex products. Hydrochloric acid and sodium hydroxide (titrisol®, Merck) were used in the titration work.

#### Latex Preparation and Sampling Methods

A jacketed cylindrical stainless-steel reactor, volume 5 dm<sup>3</sup>, equipped with a 12-bladed turbine impeller placed at  $\frac{1}{3}$  of the liquid level from the bottom was used to prepare a polystyrene seed latex. The seed latex had a number-average particle diameter of 100 nm determined by transmission electron microscopy. After reaction, the excess of emulsifier was removed from the seed latexes using a procedure described hereafter. This cleaning step was essential to reduce the total amount of surfactant. Secondary nucleation could be avoided during the seeded polymerization.

The seeded experiments were carried out in a jacketed cylindrical stainless steel/glass reactor, volume 1.2 dm<sup>3</sup>, equipped with a 6-bladed turbine impeller placed at  $\frac{1}{3}$  of the liquid level from the bottom, a nitrogen inlet, and a sampling valve. Table II gives an overview of the recipes.

All the ingredients except the initiator were supplied to the reactor. Before the addition of the initiator, the reactor headspace was flushed with nitrogen and the reaction mixture was equilibrated for about 30 min at reaction conditions expressed in terms of temperature and stirring speed. AA was supplied to the reactor before the equilibration period or at different overall conversions of the polymerization process. All the seeded polymerizations were performed at a temperature of 70°C.

During all the experiments, the conversion was measured gravimetrically by withdrawing 5 mL of the reaction mixture. For the determination of

**Table III Values of Various Parameters in the Aqueous Phase**

Parameter	Total AA in Recipe (g)			
	0	2	5	10
$x_{AA}^a$	0	0.03	0.08	0.15
$C_{AA,aq} + C_{S,aq} \text{ (mol dm}^{-3}\text{)}^b$	$4.3 \times 10^{-3}$	$32 \times 10^{-3}$	$72 \times 10^{-3}$	$140 \times 10^{-3}$
$f_{AA,0}^c$	0	0.85	0.94	0.965
$F_{AA,0}^d$	0	0.57	0.70	0.80
$k_{p,aq} \text{ (dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\text{)}^e$	500	1280	1870	2500

<sup>a</sup> AA/S molar ratio in the recipe (see Table II).

<sup>b</sup> Concentration of S and AA in the aqueous phase (see Tables I and II).

<sup>c</sup> Calculated with eq. (3).

<sup>d</sup> Calculated with eq. (2) and values given in Table I.

<sup>e</sup> Calculated with eq. (1) and values given in Table I.

the AA incorporation, 50 mL of the reaction mixture was withdrawn at regular time intervals. The cleaning steps and the characterization procedures for the AA distribution in the latex products were always performed rapidly after sampling.

### Particle-size Analysis

The latex products were characterized in terms of particle size and particle-size distribution. Transmission electron microscopy (TEM) was preferentially used to obtain accurate values of the particle-size distribution and to check for secondary nucleation. The distribution and average size were determined from the electronmicrographs by counting at least 500 particles.

### Cleaning and Characterization of Carboxylated Latexes

The latexes were cleaned according to a procedure described in a separate article.<sup>7</sup> It consisted of dialysis followed by ion exchange on a mixed bed of equivalent amounts of anionic and cationic ion-exchange resins. The amount of carboxylic acid groups present on the outer surface and inside the latex particles was determined using a combination of aqueous conductometric titration and non-aqueous potentiometric titration. The total amount of surface acid groups was computed from the results of the so-called back conductometric titration of a known amount of latex with a solution of HCl in water. The amount of acid groups present in the latex particles (surface and core) was determined by the potentiometric titration with a solution of NaOH in water of a known amount of latex diluted with THF. The procedures are described into detail in a separate article as well.<sup>7</sup>

The amount of carboxylic groups detected by the different titration methods was compared to the total amount of AA supplied to the system (see Table II). So, the actual incorporation yield was obtained.

## RESULTS

### Overall Polymerization Rate

The parameters being varied in the seeded emulsion copolymerization of S and AA were the pH of the reaction mixture and  $x_{AA}$ , the overall molar ratio of AA and S in the final latex (see Table III).

Each experiment was checked for secondary nucleation with TEM. The particle growth in seeded systems must indeed occur in the absence of any particle formation to avoid systematic errors in the determination of the rate of polymerization per latex particle. The results obtained by TEM showed, in most cases, that the final particle-size diameter and the polydispersity were in good agreement with the initial seed latex particle-size distribution.

For an emulsion copolymerization, the overall polymerization rate per unit volume of the aqueous phase,  $R_p$ , can be expressed by

$$R_p = \frac{\bar{k}_p \bar{n} N_p C_{Mp}}{N_{av}} \quad (5)$$

where  $\bar{k}_p$  is the average propagation rate constant at the locus of polymerization which is the particle phase;  $\bar{n}$ , the average number of radicals per particle;  $C_{Mp}$ , the monomer concentration in the particles;  $N_p$ , the number of latex particles per unit volume of the aqueous phase; and  $N_{av}$ , Avogadro's number.

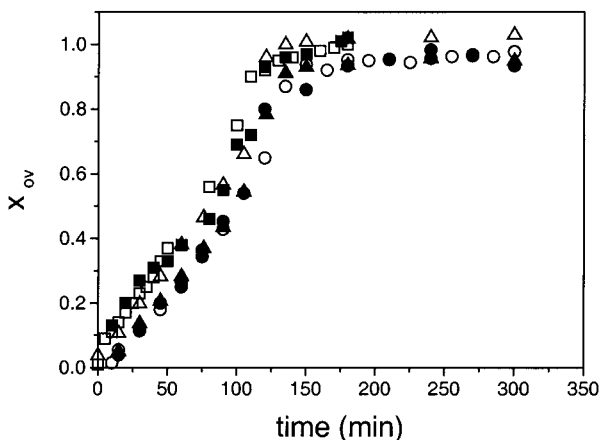
$R_p$  can be calculated from the conversion-time history in a batch process by the relation

$$R_p = C_{M,0} \frac{dX_{ov}}{dt} \quad (6)$$

where  $C_{M,0}$  is the initial total monomer concentration (see Table II), and  $X_{ov}$ , the overall conversion. Although the aqueous phase plays a crucial role in the polymerization process, the main locus of polymerization is the particle phase. The contribution of the aqueous phase polymerization to  $R_p$  has, therefore, been assumed negligible.

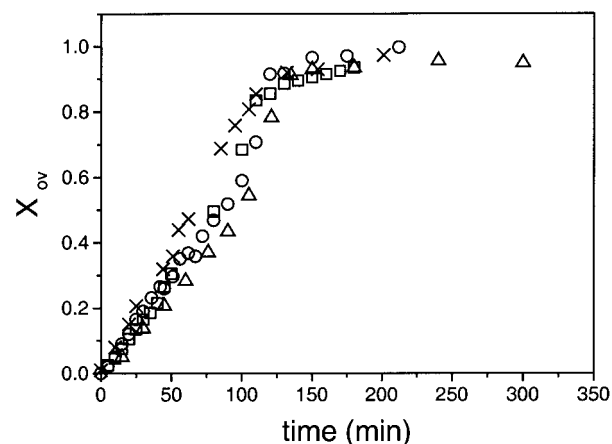
In the present study,  $N_p$  was constant throughout the polymerization and  $R_p$  was calculated with eq. (6) from the conversion-time histories in the conversion region between 0 and 0.4 (see Fig. 2 for a typical example). In the time interval corresponding to this conversion region, unreacted monomer is still present in the reaction mixture as a separate phase and variations in  $C_{Mp}$  are assumed to be negligible (see Table I).

The average number of growing chains per particle  $\bar{n}$  was estimated using eqs. (5) and (6). As already discussed in a separate article,<sup>7</sup>  $\bar{k}_p$  in the particle phase was approximated by the propagation rate constant for the homopolymerization of S (see Table I).



**Figure 2** Overall conversion as a function of time for the seeded batch emulsion polymerization of S and AA at 70°C at (solid symbols) pH 2.5 and (open symbols) pH 7. Reactions carried out at different AA/S molar ratios: (■) no AA; (▲) AA/S = 0.08/0.92; (●) AA/S = 0.08/0.92 with continuous sampling.

The results collected in Table IV show that all the polymerizations proceeded in the transition region between Smith–Ewart case 2 and case 3 kinetics with  $\bar{n} \geq 0.5$ .<sup>18</sup> The increase in the polymerization rate observed for conversions higher



**Figure 3** Overall conversion as a function of time for the seeded batch emulsion polymerization of S and AA at 70°C at pH 2.5. Reactions carried out at different AA/S molar ratios: (□) no AA; (○) AA/S = 0.03/0.97; (△) AA/S = 0.08/0.92; (x) AA/S = 0.15/0.85.

than 0.6 (see Figs. 2 and 3) can be attributed to a gel effect.

For  $x_{AA} = 0$  and  $x_{AA} = 0.08$ , the pH of the reaction mixture had no influence on the polymerization rate and, therefore, on  $\bar{n}$  (see Table IV and Fig. 2). This behavior can be attributed to the rate

**Table IV** Results from All Runs

Experiment	pH	$x_{AA}$	$N_p$ (dm <sup>-3</sup> )	$R_p/N_p$ (10 <sup>-21</sup> mol s <sup>-1</sup> )	$\bar{n}$	Surface AA <sup>a</sup>	Buried AA <sup>a</sup>
AA Introduced at 0 min							
PS-0L	2.5	0	$2.1 \times 10^{16}$	3.90	0.9	—	—
PS-0H	7.0	0	$2.1 \times 10^{16}$	4.70	1.1	—	—
PSAA-2L	2.5	0.03	$2.1 \times 10^{16}$	4.30	1.0	65	27
PSAA-5L	2.5	0.08	$2.3 \times 10^{16}$	3.50	0.8	37	25
PSAA-5H	7.0	0.08	$2.3 \times 10^{16}$	4.40	1.0	6	6
PSAA-5Lbis <sup>b</sup>	2.5	0.08	$2.3 \times 10^{16}$	3.90	0.9	40	—
PSAA-5Hbis <sup>b</sup>	7.0	0.08	$2.3 \times 10^{16}$	3.90	0.9	5	—
PSAA-10L	2.5	0.15	$R_p = 1.28 \times 10^{-4}$ mol dm <sup>-3</sup> s <sup>-1</sup> ,			70	30
Secondary nucleation							
AA Introduced After 80 min							
S80-PSAA-L	2.5	0.08	$2.1 \times 10^{16}$	4.30	1.0	45	10
S80-PSAA-H	7.0	0.08	$2.1 \times 10^{16}$	4.50	1.0	10	8
AA Introduced After 100 min							
S120-PSAA-L	2.5	0.08	$2.1 \times 10^{16}$	4.10	0.9	50	5
S120-PSAA-H	7.0	0.08	$2.1 \times 10^{16}$	4.70	1.1	10	1

<sup>a</sup> Expressed in percent of the initial amount of acid groups.

<sup>b</sup> With sampling for the determination of AA incorporation at different conversions.

of radical entry, which seems to be independent of pH as already reported in a previous study.<sup>7</sup>

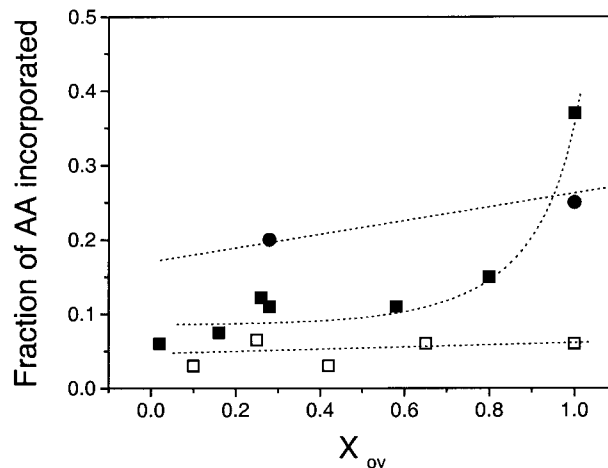
The results collected in Figure 3 and Table IV show that the rate of polymerization at pH 2.5 is not significantly dependent on the AA content for  $0 \leq x_{AA} \leq 0.08$ . However, an increase in the polymerization rate was observed for  $x_{AA} = 0.15$ . The particle-size analysis of the final latex with TEM showed a bimodal distribution. Secondary nucleation could not be avoided. In these conditions, no conclusion could be drawn concerning the kinetics of particle growth and the process of AA incorporation.

### Incorporation of Acid Groups

Table IV gives the amount of surface and buried acid groups in all the latex products after complete conversion. For  $x_{AA} = 0.15$ , all the acid was incorporated in the latex products as surface and buried acid groups. Because of the occurrence of secondary nucleation during the corresponding experiment, more AA was eventually buried in the second generation of latex particles since the precursor particles of the newly formed population originate from AA-rich oligomers. Moreover, some of the buried acid groups were likely to migrate to the surface of the particles, stretch out into the aqueous phase, and contribute to the amount of surface acid and the colloidal stability of the particles. Additionally, the latex particles offered a considerably larger total surface area for entry than when secondary nucleation was avoided. This eventually resulted in an increased amount of surface acid groups as well. For both  $x_{AA} = 0.03$  and  $x_{AA} = 0.08$ , no secondary nucleation occurred and about 25% of the initial AA was buried inside the particles (see Table IV).

The absolute amount of surface acid groups increased with  $x_{AA}$ . The absolute amount of acid groups present in the serum at the end of the polymerization also increased with  $x_{AA}$ . Although there is only one experiment with  $x_{AA} = 0.03$ , the results collected in Table IV point out a more efficient incorporation of AA at lower  $x_{AA}$ .

To obtain more insight into the mechanism of incorporation of AA in latex particles, the distribution of acid groups between the interior and the surface of the particles was determined throughout the whole emulsion polymerization process. Figure 4 shows the fraction of the initial amount of AA present as surface acid as a function of the overall conversion for polymerizations performed with  $x_{AA} = 0.08$  at pH values of 2.5 and 7. As

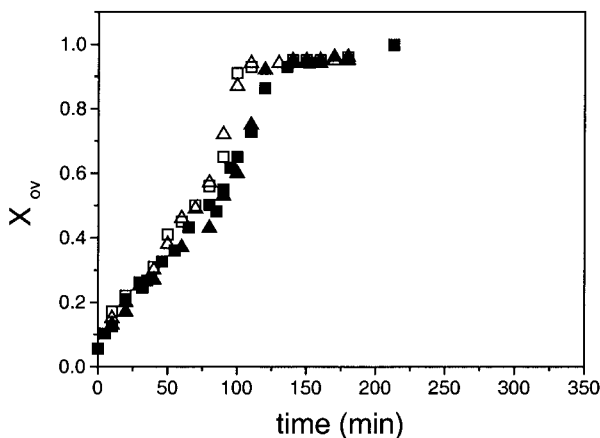


**Figure 4** Incorporation of AA as a function of the overall conversion for the seeded batch emulsion polymerization of S and AA at 70°C. Reactions carried out at an AA/S molar ratio of 0.08/0.92: (■) pH 2.5, surface acid; (●) pH 2.5, buried acid; (□) pH 7 surface acid.

expected from the distribution in the final products, hardly any surface acid was incorporated during polymerization at pH 7. At pH 2.5, the amount of surface acid groups remained low (10% of the initial acid) as well up to an overall conversion of 0.6. No clear trend could be observed in the conversion region between 0 and 0.6. Most of the surface acid groups were actually incorporated in the conversion region between 0.8 and 1.

### Two-step Seeded Emulsion Polymerization

Some experiments were performed in two steps: In the first step, all the reagents except AA were supplied to the reaction mixture. The second step started with the addition of AA to the reaction mixture. The total amount of AA supplied to the reaction mixture always corresponded to a molar ratio of AA and S in the final latex of 0.08 ( $x_{AA} = 0.08$ ). The moments at which AA was introduced into the reaction mixture were evaluated from experiments performed without AA and corresponded to the expected beginning of interval III, that is, 80-min reaction, and to an overall conversion of about 0.8, that is, 100-min reaction (see Figs. 2 and 3). For reactions performed at pH 7, some sodium carbonate was used in the first step. The pH of the buffered reaction mixture did not change upon adding AA in the second step. A pH of 2.5 during the second step was obtained by performing the first step without acid or buffering the system. The pH dropped to the value of about



**Figure 5** Overall conversion as a function of time for the seeded batch emulsion polymerization of S and AA at 70°C at (solid symbols) pH 2.5 and (open symbols) pH 7 with a shot of 5 g of AA (■) at 80 min and (▲) at 100 min.

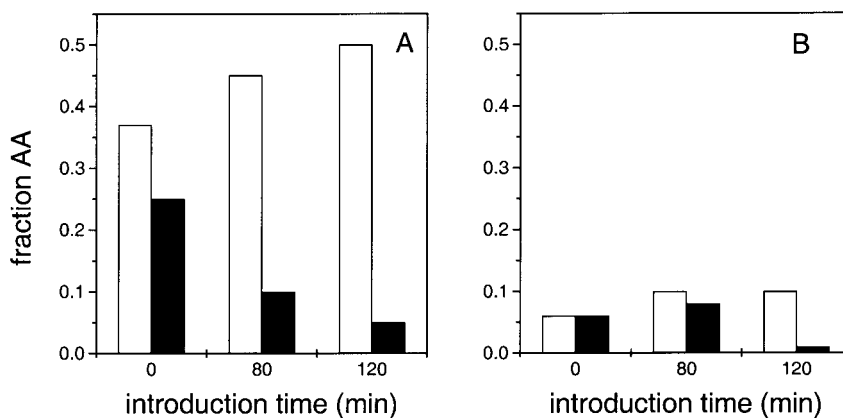
2.5 upon the addition of AA and remained constant. Secondary nucleation could be avoided in all the experiments performed in two steps. The conversion–time histories of the two-step polymerization experiments are shown in Figure 5. Figure 5 shows that the progress of the polymerizations after the addition of AA was hardly affected by the shot of functional monomer.

The results collected in Table IV and Figure 6 show the distribution of AA between the surface and the interior of the final latex particles at different pH values as a function of the AA introduction time. The results reveal that the pH had a strong influence on the acid distribution. At pH

7, the amounts of surface and buried acid groups were very low. More than 80% of the total AA remained in the aqueous phase whenever AA was supplied to the reaction mixture. The incorporation was more efficient at pH 2.5, as already observed for the single-step process. Moreover, regarding the introduction of AA into the reaction mixture resulted in a significant increase in the amount of surface acid groups and a decrease in the amount of buried acid groups in comparison with the single-step process. The introduction of AA in the final stage of the polymerization process therefore prevented AA to be buried in the interior of the particles. However, the results show that entry of AA-rich but still S-containing oligomeric radicals followed by further polymerization in the outer shell of the particles still occurred, leading to latex particles rich in fixed surface acid groups. Supplying AA to the system at overall conversions above 0.5 also means that the acid groups eventually incorporated on the surface during the polymerization could not be buried by further growth of the latex particles, since in interval 3 of the emulsion polymerization, the particle diameter does not increase any more.

## DISCUSSION

The present study confirms the influence of pH on the distribution of acid groups in the final latex products. In agreement with previous observations,<sup>7</sup> the lowest pH resulted in the highest acid group incorporation in the polymer molecules ul-



**Figure 6** Two-step seeded batch emulsion polymerization of S and AA at 70°C. Incorporation of AA in the final latex products as a function of the introduction time. Reactions carried out at an AA/S molar ratio of 0.08/0.92 at (A) pH 2.5 and (B) pH 7. (Black bars) buried acid; (open bars) surface acid.



timately present in the latex particles and on their surface. The determination of the acid-group distribution in the latex products during the course of the reaction shows that AA was mainly incorporated after the monomer droplets disappeared. Shoaf and Poehlein<sup>15,19</sup> studied the S/AA system and developed a model for predicting batch copolymerization rates in seeded emulsion polymerizations. These authors reported that the primary locus of polymerization probably shifts from the particle phase to the aqueous phase after S has almost completely been consumed and they defined an interval IV in the emulsion polymerization process accounting for this typical behavior. Yuan<sup>20</sup> studied the emulsion copolymerization of S and butadiene in the presence of AA and reported a shift in the main polymerization locus as well in the last stage of the process, with most of the functional monomer still being present in the aqueous phase. Nomura et al.<sup>21</sup> studied the seeded emulsion polymerization of S and AA and reported that when the number of seed particles was higher than a certain critical value the contribution of the polymerization of AA to the overall rate of polymerization was negligible for S conversions below 0.75. Guillaume et al.<sup>22</sup> studied the emulsifier-free emulsion copolymerization of S and butyl acrylate in the presence of methacrylic acid and investigated the location of the functional monomer in the latex as a function of conversion. These authors reported that a significant amount of unreacted methacrylic acid was still present in the reaction mixture in the last stage of the process. The authors also further observed that a relatively large amount of acid was incorporated on the surface of the latex particles at overall conversions larger than 0.8.

Our results are in good agreement with those reported in all the studies mentioned here and suggest that during the last stage of the process a considerable amount of AA monomer is still present in the aqueous phase and contributes to a large extent to the incorporation of carboxylic acid groups onto the surface of the latex particles.

During the earlier stages of the emulsion copolymerizations, our experiments reveal that the overall rate of polymerization is not significantly dependent on  $x_{AA}$ . This typical result points to the particle phase to be the main locus of polymerization. This may be supported by realizing that an increase in  $x_{AA}$  leads to an increase in the rate of polymerization in the aqueous phase as a result of a considerable increase in  $\bar{k}_{p, aq}$  and  $f_{AA}$  in the aqueous phase (see Table III and Fig. 1). How-

ever, this increase in the aqueous phase polymerization rate can plausibly have no influence on the overall polymerization rate. Indeed, a constant rate of polymerization per particle follows from a constant value of the average number of growing chains per particle and a constant value of the average propagation rate coefficient in the particle phase. The average propagation rate coefficient in the particle phase may be expected to increase only slightly on increasing  $x_{AA}$ , since the resulting molar ratio of AA and S in the particle phase remains very low (see Shoaf et al.<sup>6</sup>).

The number of growing chains per particle strongly depends on the entry rate of oligomeric radicals into the latex particles.<sup>18</sup> Upon increasing the AA concentration in the aqueous phase, both the rate of polymerization and the number of oligomeric radicals in the aqueous phase increase, leading eventually to homogeneous nucleation and the formation of a second population of latex particles (see results in Table IV). However, the entry rate may be expected to be less dependent on the AA concentration. The reason for this may be found in  $z$ , the critical chain length of the oligomeric radical at which entry occurs.<sup>23</sup> If the AA fraction in the aqueous phase increases, the fraction of AA built into aqueous-phase copolymers will increase (see Table III and Fig. 1). Consequently, the  $z$  value may increase considerably. Although there are more AA-containing radicals, a smaller fraction of it will reach the  $z$  value necessary for entry. Other radicals will terminate before reaching this critical value and form AA-rich water-soluble polymer chains. As a consequence, not only does the polymerization rate remain constant, but also the amount of AA in the aqueous phase after complete reaction increases. Our experimental results actually confirm this behavior with a more efficient incorporation of AA on the surface of the latex particles at low  $x_{AA}$ , although the absolute amount of AA units incorporated on the surface increases with  $x_{AA}$ . The use of smaller amounts of AA leads to a higher probability of entry of oligomeric radicals as compared to termination during the whole polymerization process and results in the limited formation of a water-soluble acid-rich polymer and the high incorporation yield observed at low  $x_{AA}$ . However, the determination of the total amount of acid groups incorporated on the surface of the particles is not sufficient to elucidate the complex process of carboxylation of latex particles, unless it is combined with the determination of the num-

ber of oligomeric radicals that effectively entered the latex particles.

The last stage of the process seems to correspond to an enhanced capture of oligomeric radicals. During that stage, the concentration of S in the aqueous phase decreases and the oligomeric radicals may contain a larger fraction of AA units (see Fig. 1). However, our results point out a relatively high probability for entry of the AA-rich oligomeric radicals. Note that this means that there is a significant amount of growing AA-rich oligomeric radicals that survives termination in the aqueous phase and so reaches  $z$ , the critical chain length for entry. Moreover, it is rather probable that  $z$  increases significantly during the final stage of the reaction due to the decreasing S concentration in water.

At a pH value of 7, hardly any AA is incorporated into the final latex products in both the single-step and the two-step processes. The deprotonated AA units have the tendency to remain in the aqueous phase for hydrophilicity reasons and the entry of oligomeric radicals in the latex particles is, moreover, strongly hampered by electrostatic repulsion. Additionally, the pH of the reaction mixture may affect the reactivity ratios of S and AA and, therefore, the critical chain length for entry. The amount of acid groups incorporated in the first stage of the polymerization, until an overall conversion of about 0.7, is hardly different at pH 2.5 and pH 7, which is consistent with the similar polymerization rates observed. This indicates that in both cases the interfacial mass-transfer phenomena in the first stage of the polymerization process concern mainly oligomeric radicals rich in S.

Adding AA at the end of polymerization proved to be the most efficient method for the carboxylation of the latex particles at low pH. As already mentioned, although the S concentration decreases in the aqueous phase in the last stage of the process, our results show that the probability for AA-rich oligomeric radicals to enter the latex particles seems to be considerable. This result is in good agreement with the work of Emelie et al.,<sup>9</sup> who also investigated a two-step process for the emulsion copolymerization of methyl methacrylate and butyl acrylate in the presence of AA. These authors reported that the addition of the functional monomer at an overall conversion of 0.9 had hardly any effect on the distribution of acid groups in the final latex products unless a small amount of butyl acrylate was added together with AA, probably providing the oligo-

meric radicals with enough hydrophobicity to enter the latex particles. The amount of surface acid then increased while the amount of buried groups decreased.

At equivalent  $x_{AA}$ , a shot of AA in the last stage of the emulsion polymerization process resulted in an increased amount of available AA monomer units because of the retarded possible consumption of those units via propagation and termination of oligomeric radicals formed in the aqueous phase. However, the incorporation of carboxylic acid groups onto the surface of the latex particles seemed to be limited. Indeed, although the surface incorporation efficiency could be increased, the amount of AA units in the aqueous phase of the final latexes could not be minimized. This result indicates that the competition between entry and termination of AA-rich oligomeric radicals in the aqueous phase plays a crucial role in the formation of carboxylated latexes.

## CONCLUSIONS

Seeded emulsion polymerization experiments provide valuable information concerning the process of incorporation of carboxylic groups from acrylic acid into polystyrene latexes. The average number of growing chains per particle can be estimated from the experimental conversion-time histories. The amount of surface acid groups is valuable information to compare latex products.

Valuable additional mechanistic information can be obtained from the determination of the distribution of the carboxylic groups over the whole latex during the course of the emulsion polymerization process. The pH had generally a minor influence on the polymerization rate in the seeded systems but had a strong influence on the characteristics of the final latex products. The incorporation of acid groups on the surface of final latex particles was more efficient at lower pH. This behavior can partially be explained by the hydrophilic nature of the carboxylic species in their ionized form.

The AA was incorporated mainly in the last stage on the emulsion polymerization process at overall conversions higher than 0.7. At the beginning of the process, hardly any AA was incorporated at both pH 2.5 and pH 7. This might indicate that only S-rich oligomeric radicals enter the latex particles.

The use of smaller amounts of AA in the recipes resulted in the presence of a relatively small amount of acid-containing species in the aqueous phase of the final latexes. The consumption of AA through aqueous-phase polymerization and termination is minimized and the incorporation efficiency optimized.

The use of a two-step process in which AA was introduced in the last stage of the emulsion polymerization was a successful method to increase the amount of surface acid groups as compared with the single-step process. However, the amount of AA present in the water phase of the final latexes could not be minimized under these process conditions.

The present study indicates that the AA incorporation process is governed mainly by the aqueous-phase polymerization. A better knowledge of the main kinetic parameters in the aqueous phase and the influence of pH on these parameters is needed for better understanding of the carboxylation process.

## REFERENCES

- Blackley, D. C. In *Science and Technology of Polymer Colloids*; Poehlein, G. W.; Ottewill, R. H.; Goodwin, J., Eds.; NATO ASI Series; Nijhoff: Boston, 1983; Vol. 1, p 203.
- Ceska, G. W. *J Appl Polym Sci* 1974, 18, 2493.
- Egusa, S.; Makuuchi, K. *J Polym Sci A* 1982, 20, 863.
- Kabanov, V. A.; Topchiev, D. A.; Karaputadze, T. M. *J Polym Sci* 1973, 42, 173.
- Cutié, S. S.; Smith, P. B.; Henton, D. E.; Staples, T. L.; Powell, C. *J Polym Sci B* 1997, 35, 2029.
- Shoaf, G. L.; Poehlein, G. W. *Ind Eng Chem Res* 1990, 29, 1701.
- Slawinski, M.; Schellekens, M. A. J.; Meuldijk, J.; Van Herk, A. M.; German, A. L. *J Appl Polym Sci*, 2000, 76, 1186.
- Greene, B. W. *J Colloid Interf Sci* 1973, 43, 449.
- Emelie, B.; Pichot, C.; Guillot, J. *Makromol Chem* 1988, 189, 1879.
- Dos Santos, A. M.; McKenna, T. F.; Guillot, J. *J Appl Polym Sci* 1997, 65, 2343.
- Alfrey, T.; Goldfinger, G. *J Chem Phys* 1944, 12, 205.
- Mayo, F. R.; Lewis, J. *J Am Chem Soc* 1944, 66, 1594.
- Buback, M.; Gilbert, R. G.; Hutchinson, R. A.; Klumperman, B.; Kuchta, F.-D.; Manders, B. G.; O'Driscoll, K. F.; Russel, G. T.; Schweer, J. *Macromol Chem Phys* 1995, 196, 3267.
- Gromov, V. F.; Galperina, N. I.; Osmanov, T. O.; Khomikovskii, P. M.; Abkin, A. D. *Eur Polym J* 1978, 16, 529.
- Shoaf, G. L.; Poehlein, G. W. *J Appl Polym Sci* 1991, 42, 1239.
- Lane, W. H. *Ind Eng Chem* 1946, 18, 295.
- Hawkett, B. S.; Napper, D. H.; Gilbert, R. G. *J Chem Soc Faraday Trans* 1980, 76, 1323.
- Smith, W. V.; Ewart, R. H. *J Chem Phys* 1948, 16, 592.
- Shoaf, G. L.; Poehlein, G. W. *J Appl Polym Sci* 1991, 42, 1213.
- Yuan, X. Ph.D. Thesis, Lehigh University, 1996.
- Nomura, M.; Ichikawa, H.; Fujita, K.; Okaya, T. *J Appl Polym Sci* 1997, 35, 2689.
- Guillaume, J. L.; Pichot, C.; Guillot, J. *J Polym Sci A* 1988, 26, 1937.
- Maxwell, I. A.; Morrison, B. R.; Napper, D. H.; Gilbert, R. G. *Macromolecules* 1991, 24, 1629.