

Seeded Emulsion Polymerization of Styrene: Influence of Acrylic Acid on the Particle Growth Process

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Received 12 May 1999; accepted 15 October 1999

ABSTRACT: The seeded batch emulsion copolymerization of styrene and acrylic acid was studied. The polymerization rate was investigated with pH as the main parameter. Some attempts were made to evaluate the average number of growing chains per particle during Stage II of the emulsion polymerization process. The final latex products were characterized by means of conductometric aqueous titration and potentiometric titration in an organic solvent mixture. The distribution of the acid groups over the aqueous phase, the particle surface, and the interior of the particles together with the kinetic results provided insight into important features governing the incorporation of acrylic acid. The results indicate that pH is the dominating parameter for the incorporation process. An optimal incorporation on the surface of the particles is observed for a low value of pH. In that case, all the acid groups are protonated. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1186–1196, 2000

Key words: emulsion polymerization; styrene; acrylic acid; pH; polymerization rate

INTRODUCTION

Carboxylated latexes are produced by performing emulsion polymerization in the presence of carboxylic monomers. The final products have numerous advantageous properties.¹ The enhanced colloidal stability resulting from the presence of carboxylic groups on the outer surface of the latex particles justifies the use of small amounts of these functional monomers in industrial recipes. However, the use of such water-miscible monomers in emulsion polymerization is contradictory with the heterogeneous aspect of a process leading to water-insoluble polymers. Numerous studies have been performed to find out how carboxylic monomers are incorporated into emulsion polymers and to understand the role these mono-

mers play in emulsion. The challenge is to optimize the incorporation of the functional monomer into the polymer molecules because the incorporated carboxylic groups will ultimately reside in the outer shell of the particles.^{2,3} In addition to the conventional parameters to be defined in emulsion polymerization, the nature of the water-soluble carboxylic monomer makes the course of the process and its outcome very sensitive to pH. Not only is colloidal stability influenced but also the kinetics and the phase equilibria. The pH strongly influences the polymerization behavior of carboxylic monomers in water^{4,5} and their partitioning between the organic and aqueous phase of an emulsion system. The affinity of the polar monomer for the aqueous phase or the particle phase depends on the degree of dissociation of the carboxylic groups.⁶

Carboxylic monomers are found to play a major role in the nucleation process. The number of particles formed during the reaction is closely

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Journal of Applied Polymer Science, Vol. 76, 1186–1196 (2000)
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related to the amount and type of the carboxylic monomer, the pH, and the ionic strength.^{7,8} In addition, the particle growth process is also affected by the presence of carboxylic monomers. Shoaf and Poehlein^{9,10} developed a model that describes the kinetics of particle growth in emulsion copolymerization systems with carboxylic acids. These authors confirmed the influence of the events taking place in the aqueous phase on the basic mechanisms operating in the particle growth stage. In the presence of a completely water-miscible monomer, the events in the water phase should be emphasized.

The present article attempts to provide insight into the influence of some reaction parameters on the course of the emulsion polymerization of styrene (S) in the presence of acrylic acid (AA). Nucleation was avoided by performing seeded experiments. The variables investigated include pH, temperature, and particle diameter. Attention is focused on the effects on both the polymerization rate and the ultimate distribution of the functional monomer over the latex particles, which is a fingerprint of the events taking place during the reaction.

EMULSION COPOLYMERIZATION KINETICS

In copolymerization processes the reactivities of the monomers involved are generally different. As a consequence, the product of a batch process shows an intermolecular chemical composition distribution. A relation between the monomer composition at the locus of polymerization (f) and the momentary copolymer composition (F) is given by:

$$F_i = \frac{r_i f_i^2 + f f_j}{r_i f_i^2 + 2f_i f_j + r_j f_j^2} \quad (1)$$

Equation (1) is based on a simple kinetic scheme: monomer addition to a radical chain only depends on the nature of the radical end group and the propagating monomer.^{11,12} The reactivity ratios (r) of the monomers i and j are defined as:

$$r_i = \frac{k_{p,ii}}{k_{p,ij}} \quad (2)$$

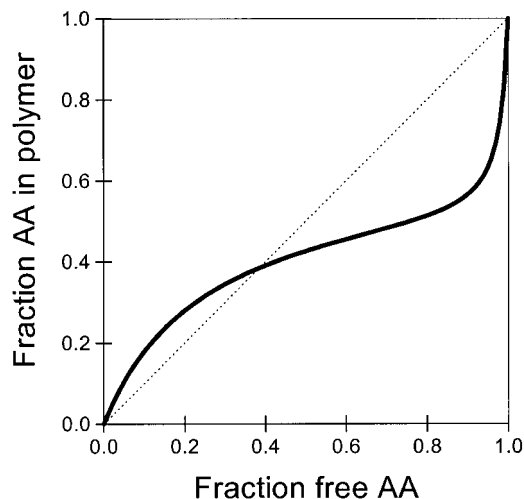


Figure 1 Calculated mole fraction of acrylic acid momentary built-in into the copolymer as a function of the mole fraction of free acrylic acid for the bulk copolymerization of styrene and acrylic acid. Calculation with eq. (1) and the constants given in Table II.

and

$$r_j = \frac{k_{p,ji}}{k_{p,ii}} \quad (3)$$

where $k_{p,ii}$ is the propagation rate coefficient for homopolymerization of monomer i and $k_{p,ij}$ is the rate coefficient for propagation of a terminal unit i with monomer j .

Figure 1 shows the mole fraction of AA momentary built into the copolymer as a function of the mole fraction of free AA at the locus of polymerization for the monomer pair S-AA. Figure 1 was calculated with eq. (1) and reactivity ratios for bulk polymerization as reported by Kim¹³ (see Table II). Figure 1 shows that at low mole fractions of AA the amount of AA built-in into the copolymer is somewhat favored over the amount of S incorporated. As a consequence, in batch processes started with rather low mole fractions of AA, the AA is expected to be incorporated into the polymer in the early stages of the process.

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

$$R_p = \frac{\bar{k}_p \bar{n} N_p C_{Mp}}{N_{av}} \quad (4)$$

where \bar{k}_p is the average propagation rate constant at the locus of polymerization being the particle

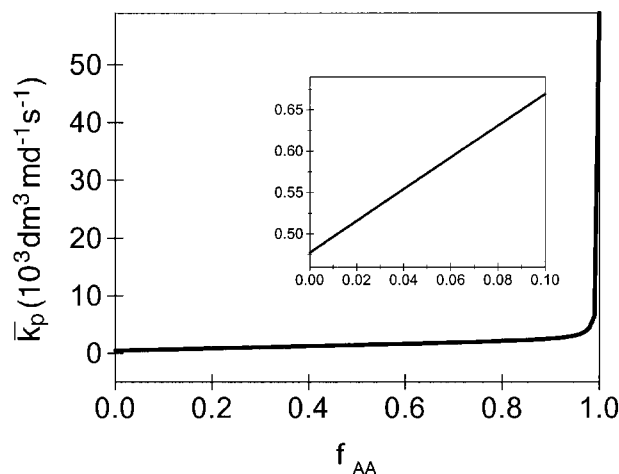


Figure 2 Calculated average propagation rate coefficient for the bulk copolymerization of styrene and acrylic acid at 70°C as a function of the acrylic acid mole fraction in the monomer feed. Calculation with eq. (5) and the constants given in Table II.

phase, \bar{n} is the average number of growing chains per particle, C_{M_p} is the overall monomer concentration in the particles, N_p is the number of latex particles per unit volume of the aqueous phase, and N_{av} is Avogadro's number.

Using the simple ultimate copolymerization model, eq. (5) can be derived for the average propagation rate constant \bar{k}_p :

$$\bar{k}_p = \frac{r_i f_i^2 + 2f_i f_j + r_j f_j^2}{(r_i f_i / k_{p,ii}) + (r_j f_j / k_{p,ij})} \quad (5)$$

For the emulsion copolymerization of S and AA, \bar{k}_p depends therefore on the reactivity ratios and the mole fraction of both monomers in the particle phase. Kim¹³ reported that the copolymerization of AA with S is strongly dependent on the solvent. Because the polymerization in the particle phase corresponds more or less to a bulk system, the reactivity ratios for bulk copolymerization are an obvious choice for an estimation of \bar{k}_p . Figure 2, calculated with eq. (5) and the parameters collected in Table II, shows the average propagation rate constant at 70°C as a function of f_{AA} the mole fraction of free AA at the locus of polymerization.

Shoaf and Poehlein⁶ reported the partition of AA in emulsion copolymerization systems. These authors investigated the partitioning of AA in conditions similar to emulsion copolymerizations and found a strong influence of monomer to water

ratio, pH, and ionic strength. Their work confirms that at low pH values, AA is rather hydrophilic and resides preferably in the water phase. At pH values above 5, AA is deprotonated and hardly any functional monomer is found in the organic phase. Figure 2 shows that in the low f_{AA} region, f_{AA} has a relatively limited influence on \bar{k}_p .

EXPERIMENTAL

Materials

The monomers S (Merck) and AA (Fluka) were distilled under reduced pressure and stored at 5°C before use. The initiator used was sodium persulfate (Fluka). 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 colloiddally stabilize the growing particles while preventing secondary nucleation. The pH of the reaction mixtures was about 2.5 due to the presence of acrylic acid. For reactions performed at a pH of about 7, some sodium carbonate (Merck) was used. The ionic strength was adjusted with sodium chloride (Merck) and based on a constant overall concentration of sodium ions in all the experiments. All the chemicals were laboratory grade.

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.

Preparation of Latexes

A jacketed cylindrical stainless steel reactor, volume 5 dm³, equipped with a 12-blade turbine impeller placed at 0.33 of the liquid level from the bottom, was used to prepare a polystyrene seed latex. The particle size was varied by using different amounts of emulsifier. 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 second stage.

The seeded experiments were carried out in a jacketed cylindrical stainless steel/glass reactor, volume 1.2 dm³, equipped with a six-blade turbine impeller placed at 0.33 of the liquid level

Table I Standard Recipe for Carboxylated Batch-Seeded-Emulsion Polymerization of Styrene

Seed	10 g of solid polymer
Styrene	85 g
Acrylic acid	5 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 dodecylsulfate (SDS)	$5.5 \times 10^{-3} \text{ mol dm}^{-3}$
Sodium carbonate (Na_2CO_3)	$0/50 \times 10^{-3} \text{ mol dm}^{-3}$
Sodium chloride (NaCl)	$100 \times 10^{-3}/0 \text{ mol dm}^{-3}$
$C_{M,0}$	$0.985 \text{ mol dm}^{-3}$
AA/S mole ratio in initial monomer feed	0.08/0.92
AA content	$694 \mu\text{eq gpol}^{-1}$

from the bottom, a nitrogen inlet, and a sampling valve. Table I gives an overview of the recipes. All the ingredients except the initiator were supplied to the reactor. Before the addition of the initiator, the reaction mixture was equilibrated for about 30 min at reaction conditions expressed in temperature and stirring speed.

Particle Size Analysis

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

Latex Cleaning

Hollow-fiber membranes proved to be useful for cleaning latexes.¹⁷ The membrane used in this

study is a commercially available dialyzer (Lun Dia® Pro 500, Gambro, Sweden). It consists of a polyether carbonate membrane in a polycarbonate casing, molecular weight cut-off: 15,000 kg/kmol; effective membrane area: 1.2 m²; membrane thickness: 15 μm. After reaction, the latex product was diluted to about 5 wt % solids and pumped loopwise along the shell side of the membrane. The water-soluble species were extracted with deionized water pumped through the membrane. The conductivity of both the latex and the extract phase were monitored. The process was governed by mass transfer through the membrane and proved to be very efficient in removing considerable amounts of electrolyte within a short period of time. The conductivity of the latex phase as well as the extract phase did not change significantly after dialyzing for 2 h. At that point the latex could be used for seeded experiments. The same procedure was used to clean the carboxylated latex products. However, the carboxylated latexes could not be cleaned sufficiently in this way. Insufficient cleaning by dialysis was also reported by El Aasser.¹⁸ The cleaning procedure was completed with the ion-exchange technique described by Vanderhoff et al.¹⁹

Table II Values for Parameters Used in the Calculation of the Rate of Polymerization

Parameter	Monomer	Value	Source
k_p at 70°C ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	AA	59,200	14
	S	480	15
E_{act} (kJ mol^{-1})	AA	13.132	
	S	32.510	
r_{AA}	AA	0.04	13
r_{S}	S	0.4	
C_{MP} (mol dm^{-3})	S	5.5	16
$x_{\text{AA}}^{\text{org}}$	AA	0.12	6
ρ_{S} (kg m^{-3})	S	878	16
ρ_{PS} (kg m^{-3})	S	1044	16

Analysis of Carboxylated Latexes

The distribution of carboxylic groups in the final latex products is given by the amount of functional groups present in the aqueous phase, the outer surface of the particles, and the interior of the particles. The amount of carboxylic groups present at the surface of the particles can successfully be evaluated by means of aqueous conductometric titration of the latex after thorough cleaning. It is commonly given as a fraction of the AA used in the recipe. The titration of the emulsion

polymer by means of potentiometric titration in an organic solvent results in the total amount of carboxylic groups present on the particle surface and in the particles. The amount of buried groups can be obtained from the results of the titration procedures in water and in the organic solvent.

The experimental conditions and the interpretation of conductometric titrations are extensively described in literature.^{20–23} In the work presented in this article, the total amount of surface acid groups was computed from the results of the so-called back titration of a known amount of latex with a 0.05*N* solution of HCl in water.

The potentiometric analysis of emulsion polymers is less straightforward. There is no standard method because the experimental conditions mainly depend on the type of polymer and its solubility in a solvent suitable for potentiometric measurements.^{24,25} The following procedure was applied. A proper amount of latex was dissolved in THF and water to get 150 mL of a mixture containing between 0.5 and 1 g of polymer in a 80/20 volume ratio THF/water. The slightly cloudy solution was acidified with 0.2 mL of an aqueous 1*N* HCl solution. After 30 min equilibration, the mixture was titrated with a 0.05*N* solution of NaOH in water. Incremental volumes were added at constant time intervals and the pH was recorded with a Ross® Sure-Flow™ Model 8172 electrode from Orion Research. The drift in pH that often occurs in nonaqueous potentiometric titrations was minimized. Two equivalence points could be distinguished from the curves representing the pH as a function of the total volume of the NaOH solution added and the first derivative of these curves. The first equivalence point corresponded to the HCl added to the system and was the starting point for the neutralization of the weak acid groups. The second equivalence point corresponded to the complete neutralization of the carboxylic groups present in the polymer.

Because all the methods involving acid–base chemistry are very sensitive to the presence of CO₂,²⁶ every experiment was performed under an argon atmosphere.

RESULTS

Overall Polymerization Rate

The parameters that are varied in the seeded emulsion copolymerization of S and AA are the size of the seed latex particles, the pH, and the

temperature of the reaction mixture (see Table III). Each experiment is checked for secondary nucleation with TEM. The particle growth in seeded systems must indeed occur in the absence of particle formation, which would seriously hamper the interpretation of our results. TEM results showed that a secondary generation of latex particles was never formed. A typical example of conversion-time histories of the seeded emulsion copolymerization of S and AA is shown in Figure 3.

The overall polymerization rate per unit volume of the aqueous phase, R_p , can be calculated with eq. (4) and from the conversion-time history in a batch process with 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 I) 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 our study, R_p is calculated with eq. (6) from the conversion-time histories in the conversion region between 0 and 0.4 (see Fig. 3). In the time interval corresponding to this conversion region, unreacted monomer is still present in the reaction mixture as a separate phase and $C_{M,p}$ corresponds to the overall monomer in the particle phase. The assumption is made that $C_{M,p}$ is constant for conversions up to about 0.6 (see Table II).

Shoaf and Poehlein⁶ and Lange and Poehlein²⁷ measured x_{AA}^{org} , the fraction of AA in the organic phase of a water/S/AA mixture. For the reaction conditions used in this study, the value of x_{AA}^{org} given in Table II was assumed to be reasonable to estimate the AA distribution between water, the monomer droplets, and the monomer-swollen latex particles. Assuming that the organic phase consists of free monomer only, we used the value of x_{AA}^{org} reported in Table II to estimate f_{AA} , the mole fraction of free AA in the monomer-swollen particles. The fraction of AA in the monomer-swollen particles is always smaller than 0.015, so \bar{k}_p can be approximated by the propagation rate constant for the homopolymerization of S (see Fig. 2).

Effect of Particle Size

From the polymerization rate calculated from the conversion-time history up to a conversion of

Table III Results from All Runs

	T (°C)	pH	R_p/N_p (10^{-21} mol/s)	\bar{n}	Surface AA ^a	Buried AA ^a	Free AA ^a
34-nm seed latex, $N_p = 5.4 \times 10^{17}$ dm ⁻³ , $d_{\text{pswol}} = 75$ nm, $A_p = 9540$ m ² dm ⁻³							
S34-50L	50	2.5	0.17	0.08	36	18	46
S34-50H	50	7.0	0.26	0.12	6	—	—
S34-50L ^{'b}	50	2.5	0.27	0.13	57	13	30
S34-50H ^{'b}	50	7.0	0.26	0.12	9	—	—
S34-75L	75	2.5	0.72	0.14	51	25	24
S34-75H	75	7.0	0.70	0.14	6	5	89
50-nm seed latex, $N_p = 1.7 \times 10^{17}$ dm ⁻³ , $d_{\text{pswol}} = 110$ nm, $A_p = 6460$ m ² dm ⁻³							
S50-60L	60	2.5	0.70	0.22	48	22	30
S50-60H	60	7.0	0.69	0.22	6	6	88
S50-60L ^{'b}	60	2.5	0.82	0.26	51	19	30
S50-60H ^{'b}	60	7.0	0.85	0.27	3	10	87
S50-70L	70	2.5	1.14	0.26	51	—	—
S50-70H	70	7.0	1.11	0.25	8	—	—
97-nm seed latex, $N_p = 2.3 \times 10^{16}$ dm ⁻³ , $d_{\text{pswol}} = 210$ nm, $A_p = 3185$ m ² dm ⁻³							
S97-70L	70	2.5	3.53	0.82	37	25	38
S97-70H	70	7.0	4.40	1.00	6	—	—
S97-80L	80	2.5	7.50	1.20	41	25	34
S97-80H	80	7.0	4.56	0.75	6	5	89
100-nm seed latex, $N_p = 2.1 \times 10^{16}$ dm ⁻³ , $d_{\text{pswol}} = 210$ nm, no AA added							
B100-70L	70	2.5	3.90	0.9	—	—	—
B100-70H	70	7.0	3.90	0.9	—	—	—

^a Expressed in percentage of the initial amount of acid groups.

^b [SPS] = 20×10^{-3} mol dm⁻³.

about 0.4, the average number of growing chains per particle \bar{n} was estimated by using eq. (4) and proper values for $\bar{k}_p = k_{pS}$ and C_{Mp} (see Table II).

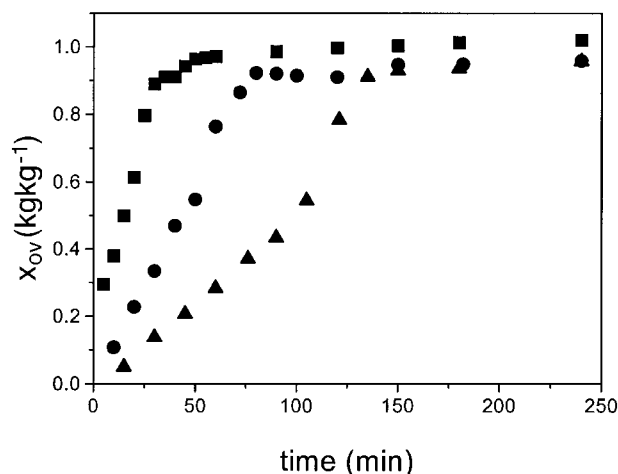


Figure 3 Overall conversion as a function of time for the batch-seeded-emulsion polymerization of styrene and acrylic acid. pH = 2.5 (recipe see Table I). (■) 34-nm seed, $T = 75^\circ\text{C}$, $N_p = 5.4 \times 10^{17}$ dm⁻³; (●) 50-nm seed, $T = 70^\circ\text{C}$, $N_p = 1.7 \times 10^{17}$ dm⁻³; (▲) 97-nm seed, $T = 70^\circ\text{C}$, $N_p = 2.3 \times 10^{16}$ dm⁻³.

The results collected in Table III and Figure 3 show that for an overall conversion of 0.4, the polymerizations started with a seed latex with a diameter of 34 or 50 nm obey zero–one kinetics with $\bar{n} < 0.5$. Polymerizations started with a seed latex with a diameter of 97 nm can roughly be approximated with Smith–Ewart Case 3 kinetics with $\bar{n} > 0.5$. Note that the polymerizations started with the seed latex with a diameter of 97 nm all showed an increase in the polymerization rate for overall conversions higher than 0.6 (see Fig. 4). This increase should be attributed to a gel effect.

Figure 5 shows \bar{n} as a function of d_{pswol} , the swollen particle diameter, for all the experimental conditions of pH, temperature, and initiator concentration collected in Table III. d_{pswol} was calculated at an overall conversion of 0.4, with the relation:

$$d_{\text{pswol}}^3 = \frac{1}{1 - (M_S C_{Mp} / \rho_S)} \left(d_{\text{pseed}}^3 + \frac{6}{\pi} \frac{6 M_S X_{\text{ov}} C_{M,0}}{1000 N_p \rho_{\text{PS}}} \right) \quad (7)$$

where d_{pseed} is the seed particle diameter, M_S ($M_S = 104$ g mol⁻¹) is the styrene molar mass,

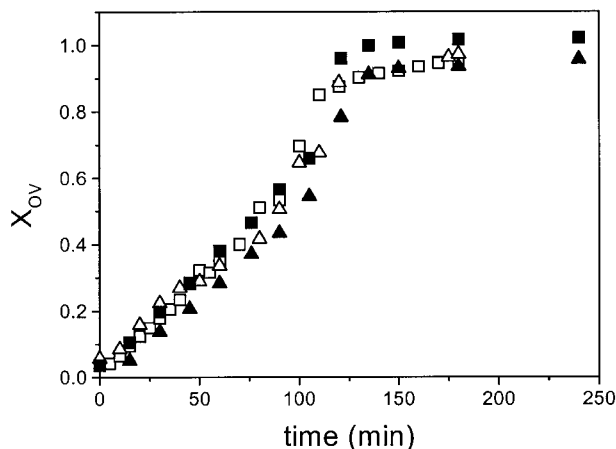


Figure 4 Overall conversion as a function of time for the batch-seeded-emulsion polymerization of styrene with (solid symbols) and without (open symbols) acrylic acid. 97-nm seed latex, $N_p = 2.3 \times 10^{16} \text{ dm}^{-3}$, $T = 70^\circ\text{C}$ (recipe see Table I). (■) pH = 2.5; (▲) pH = 7.

and ρ_S and ρ_{PS} are the densities of S and polystyrene, respectively (see Table II). Figure 5 shows that \bar{n} increases with particle size. This behavior is in good agreement with values of \bar{n} smaller or larger than 0.5 found experimentally.

Influence of pH

The pH is expected to have a strong influence on the course of the emulsion polymerization process for the production of carboxylated latexes. Affecting the hydrophilicity of the functional monomer and oligomers bearing carboxylic groups, pH plays a considerable role in the kinetics of emulsion polymerization. During the particle growth stage, the pH mainly affects the aqueous-phase polymerization and the mass transfer (e.g., adsorption of oligomers, entry, and exit). The use of persulfate as initiator in our systems further complicated the interpretation of the results because the decomposition rate of persulfate is known to be strongly dependent on pH (see Kolthoff and Miller²⁸). These authors showed that the initiator decomposition is accelerated by hydrogen ions when the pH is < 3 due to an additional acid-catalyzed decomposition reaction which does not produce any free radical. Dos Santos et al.²⁵ studied the decomposition of persulfate in the pH range from 3 to 7 and found no influence of hydrogen ion concentration on the decomposition rate. Henton et al.²⁹ investigated the influence of AA on the decomposition of persulfate and observed an increased decomposition rate in the

presence of AA and partially neutralized AA in comparison with the decomposition in water buffered at equivalent pH values. However, the limitation of all the methods ever used to study the thermal decomposition of persulfate is that neither the rate of free-radical generation nor the efficiency can be directly measured. The effect of pH on the rate of free-radical production in water is therefore still difficult to quantify.

In the present work, the experimental conditions were chosen to ensure a complete protonation, pH 2.5, or neutralization, pH 7, of the carboxylic groups in both the monomer and the polymer. As references, two polymerization reactions were performed without the addition of AA, experiments B100-70L and B100-70H in Table III. These reactions were performed with another seed latex having equivalent characteristics in terms of particle size and amount of surfactant than the one used for the S97 experiments. The results in terms of the influence of pH on the polymerization rate in both series of experiments can therefore be compared. For the experiment performed at pH 2.5 without AA, the pH was adjusted by adding a proper amount of acetic acid to the initial reaction mixture. For the experiment at pH 7, sodium carbonate was used to adjust the pH. No difference was found in the overall polymerization rate between experiments B100-70L and B100-70H. One interpretation of this result is that the polymerization obeys Smith–Ewart Case 2 kinetics with $\bar{n} = 0.5$. For

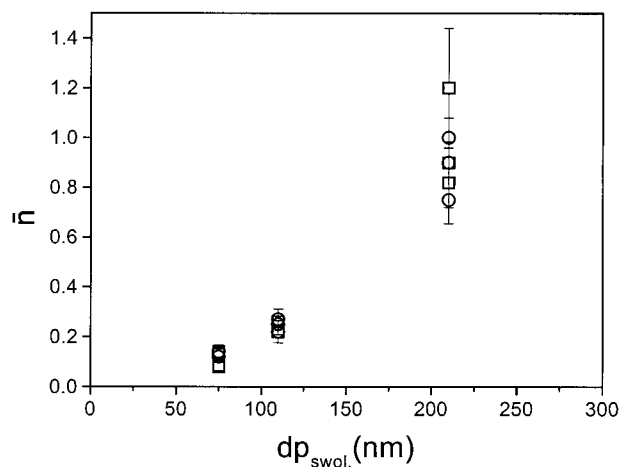


Figure 5 \bar{n} as a function of the diameter of the swollen latex particles at $X_{ov} = 0$ in the seeded-batch-emulsion polymerization of styrene and acrylic acid for all the initiator concentrations and temperature listed in Table III. (□) pH = 2.5; (○) pH = 7.

Case 2, kinetics the initiator decomposition rate has indeed no influence on the polymerization rate. However, the value of $\bar{n} = 0.9$ calculated from the actual polymerization rate using eq. (4) is larger than the Case 2 value of 0.5. Another interpretation is that the free-radical generation process is hardly affected by the pH. In the absence of significant aqueous-phase polymerization, equivalent free-radical generation rates result inevitably in equivalent overall polymerization rates. The latter interpretation is supported by the molecular weight distribution of the final latex products which was not significantly different for the experiment carried out at pH 2.5 and the experiment performed at pH 7.

The presence of AA in the S97 series at a temperature of 70°C had only a limited influence on the overall polymerization rate which was comparable to the rate of polymerization observed in the B100 series at both pH values investigated. The role of AA as well as the influence of pH on the course of the reaction in this particular situation was therefore questionable. Increasing the temperature to 80°C did not have the same influence on the polymerization rate at pH 2.5 and 7. The increase in polymerization rate at pH 2.5 was considerably larger than at pH 7. The different behavior of the polymerization rate at both pH values originates from a different influence of temperature on \bar{n} .

For the rest of the reactions performed in this study in the presence of AA, the pH appeared to have in most cases only a small influence on the polymerization rate. The rate in experiment S34-50 was however significantly lower at pH 2.5 than at pH 7. An additional experiment was performed in which the amount of initiator was doubled. The results are also reported in Table III. The polymerization rate and so \bar{n} increased a factor 1.5 at pH 2.5. Increasing the temperature to 75°C resulted in an increase in \bar{n} as well. These results seem to confirm that the polymerizations started with seed particles with a diameter of 34 nm obeyed Smith–Ewart Case 1 kinetics with R_p increasing with the initiator concentration. However, at pH 7, hardly any influence of temperature or initiator concentration could be observed on \bar{n} . In polymerizations started with 50 nm seed particles \bar{n} increased moderately upon temperature and initiator concentration at both pH values, indicating that the polymerization rate is not very sensitive to the rate of free-radical generation.

Incorporation of Acid Groups

The amount of acid groups present in polymer molecules which will ultimately reside in the outer shell of the surface (i.e., surface acid) as well as the amount of acid groups present inside the particles (i.e., buried acid) are strongly dependent on the pH of the reaction mixture (see Table III). There are two distinct situations. In products produced at pH 7, most of the acid groups remained in the aqueous phase and both the amount of surface acid and the amount of buried acid were small. Generally, <10% of the initial amount of AA was incorporated. This result is in agreement with the increased hydrophilicity of the functional monomer in its dissociated form. The carboxylic monomer concentration in the particle phase at pH 7 is considerably lower than at pH 2.5. Oligomeric radicals formed in water at pH 7 are also likely to be more hydrophilic than at pH 2.5 and therefore have a rather low tendency for entry. As a consequence, bimolecular termination of the oligomeric radicals in the aqueous phase at pH 7 may be expected to be more probable than at pH 2.5.

At pH 2.5 most of the acid was present as surface acid. Between 40 and 50% of the initial amount of AA was present in the outer shell of the particles. Additionally, a significant amount of AA (i.e., about 25%) was buried inside the particles. Experiment S34-50L showed clearly an increasing amount of surface acid when the initiator concentration was doubled and when the temperature was increased to 75°C (see Table III). This behavior is actually consistent with the simultaneously observed increase in \bar{n} . A higher rate of free-radical generation results in more AA-containing oligomeric radicals entering the particles and therefore more AA incorporated. The influence of temperature or initiator concentration on the AA incorporation was far less significant within runs performed with the other two seed latexes.

An influence of the seed particle diameter on the distribution over the outer surface of the particles and the surrounding continuous phase was observed at low pH when going from rather small seed particles (i.e., 34 and 50 nm) to larger ones (i.e., 97 nm). The amount of surface acid decreases from about 50 to 40%, whereas the amount of acid groups in the aqueous phase increases. The decrease in the amount of polymerized AA on the outer particle surface seems significant and is consistent with the difference in

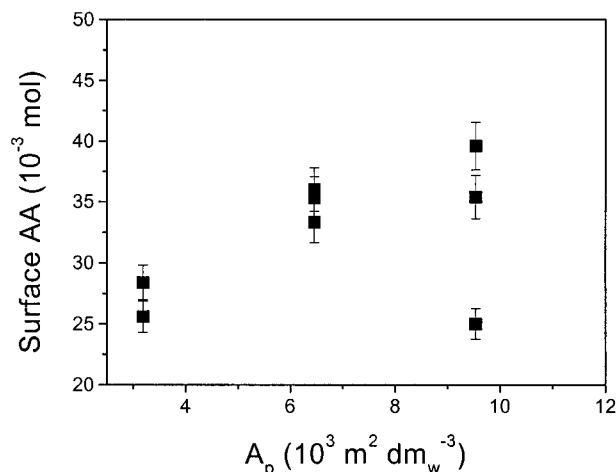


Figure 6 Amount of surface acid groups as a function of the total surface area of the swollen latex particles per unit volume of the aqueous phase at $X_{ov} = 0$ in the seeded-batch-emulsion polymerization of styrene and acrylic acid at pH 2.5 for all the initiator concentrations and temperature listed in Table III.

A_p . A_p is the specific particle surface area per unit volume of the continuous phase (see Table III). While changing the seed particle diameter, we have chosen to keep the volume fraction of the seed particles in the reaction mixture at a constant value, so the number of particles as well as the total particle surface per unit volume of the continuous phase decreases on increasing the diameter of the seed particles. Figure 6 shows the amount of surface acid groups at pH 2.5 as a function of the initial surface area of the swollen particles A_p given in Table III. The incorporation of the functional monomer on the surface increases with the particle surface area indicating that the rate of entry of oligomeric radicals in the particles increases with the surface area available.

DISCUSSION

The role of AA in emulsion polymerization has been reported in numerous papers.^{3,7,8,25} Many authors reported that the polymerization rate is influenced by the pH of the reaction mixture. Because most of the studies concern *ab initio* reactions, the influence of pH on the polymerization rate is generally related to different numbers of particles present after the nucleation period.

Shoaf and Poehlein^{9,10} studied the S/AA system and developed a model to predict polymeriza-

tion rates for seeded-emulsion copolymerizations in a batch reactor. These authors reported that the primary locus of polymerization probably shifts from the particle phase to the aqueous phase after S was consumed. This typical behavior was accounted for by the definition of an interval IV in the emulsion polymerization process. However, Shoaf and Poehlein did not include the influence of pH. Additionally, the distribution of AA groups in the latex products was not investigated, although this distribution gives valuable information. These authors, however, attempted to model the styrene/methacrylic acid system at various degrees of neutralization. Evidence was found that the acid concentration in the organic phase decreases as expected when the acid is neutralized. Shoaf and Poehlein explained the decreased polymerization rate of S, as observed in their batch-seeded emulsion experiments, by a lower rate of capture of the partially neutralized oligomeric radicals. In our experiments, the influence of pH on the course of the reaction was not very pronounced. The kinetics is apparently dependent on the particle size only. In most cases, none or only a rather limited decrease in the polymerization rate is observed at higher pH. The systems we studied, however, are different because we used a polystyrene seed latex containing no carboxylic groups. Carboxylated seed latexes were also used by Coen et al.³⁰ to study the influence of pH on the emulsion polymerization of S. Poly(acrylic acid) as stabilizer played a crucial role in the mechanism of the polymerization, which is probably also the case in the work of Shoaf and Poehlein.^{9,10} Our systems actually describe the carboxylation process of polystyrene latexes and in this context the limited effect of pH on the polymerization rate is plausible.

\bar{n} increases with the particle diameter which is in agreement with the emulsion-polymerization theory reported by Ugelstad et al.³¹ (see Fig. 5). In most cases when \bar{n} was < 0.5 , there was no or only a limited dependence of the initiator concentration or the temperature on \bar{n} . This may indicate that termination of oligomeric radicals in the aqueous phase becomes dominant. The initiator efficiency decreases due to the production of more water-soluble dead oligomers. Similar results have been reported by Schoonbrood³² for the seeded emulsion copolymerization S and methyl acrylate.

However, the final latexes produced under different conditions of pH are far from similar. The distribution of acid groups was completely differ-

ent at pH 2.5 and 7 and was qualitatively in good agreement with the work of several authors.^{25,33,34} All these authors reported that a high pH retains the dissociated carboxylic groups in the water phase, whereas a lower pH increases the AA concentration in the organic phase. This can explain the difference in the amount of buried acid groups (assuming that the amount of buried groups is related to the partition coefficient) at different pH values. To the best of our knowledge, it was not reported earlier that the amount of surface acid at low pH is sensitive to the initiator level and the temperature and that it depends strongly on the particle surface area per unit volume of the continuous phase. This indicates that the functional groups on the surface of the latex particles must originate from effective entry of oligomeric radicals. At higher pH values, the experimental conditions had no influence on the incorporation of AA on the particle surface. The increased hydrophilicity of AA at pH >6 together with the additional electrostatic effects impede the effective entry of AA-containing oligomeric radicals.

Establishing a relation between the amount of incorporated acid and the mechanism of the polymerization is not straightforward. The following additional critical remark should be made. Our observations about the kinetics are valid in interval II of the emulsion polymerization only, whereas the distribution of acid groups is measured after complete reaction. If the interval IV hypothesis given by Shoaf and Poehlein^{9,10} is retained, it means that a significant amount of acid reacts in the aqueous phase after almost complete depletion of S in the system. The question is then in which stage of the process are the surface acid groups built-in into the particles.

CONCLUSIONS

Seeded-emulsion-copolymerization experiments of S and AA give valuable information about the process of incorporation of carboxylic groups in latex particles.

Provided the number of latex particles is kept constant throughout the reaction, the average number of growing chains per particle can be estimated from the experimental conversion-time histories.

Additional mechanistic information can be obtained from a good and detailed knowledge of the distribution of the carboxylic groups over the en-

tire latex system. The amount of surface acid groups is a valuable information to compare latex products.

The pH generally has a minor influence on the polymerization rate in the seeded systems. No evidence was found that the pH affects the rate of free-radical generation in emulsion polymerizations initiated with persulfate.

The pH has a strong influence on the characteristics of the final latex products. The incorporation of acid groups on the surface of latex particles was more efficient at lower pH. This behavior can partially be explained by the more hydrophilic nature of the carboxylic species in their ionized form.

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