

Effect of the Carboxylic Acid Monomer Type on the Emulsifier-Free Emulsion Copolymerization of Styrene and Butadiene

Mahdi Abdollahi, Ali Rahmatpour, Ali Reza Khoshniyat

Division of Polymer Science and Technology, Research Institute of Petroleum Industry, P.O. Box 18745-4163, Tehran, Iran

Received 12 December 2006; accepted 14 March 2007

DOI 10.1002/app.26519

Published online 29 June 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Carboxylated styrene–butadiene rubber latexes were prepared through the emulsifier-free emulsion copolymerization of styrene and butadiene with various carboxylic acid monomers. The effects of various carboxylic acid monomers on the particle formation process were investigated. The type of carboxylic acid monomer strongly affected the particle nucleation. The number of particles and thus the polymerization rate increased with the increasing hydrophobicity of the carboxylic acid monomers. There was a significant difference in the polymerization rate per particle. The results showed that particle nucleation and growth were dependent on the hydrophilic nature of the carboxylic

acid monomers. The average particle diameter of the carboxylated styrene–butadiene rubber latexes in the dry state was obtained through some calculations using direct measurements of the average particle diameter in the monomer-swollen state by a dynamic light scattering technique. Several parameters, such as the polymerization rate, number of latex particles per unit of volume of the aqueous phase, and polymerization rate per particle, were calculated. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 828–836, 2007

Key words: emulsion copolymerization; kinetics (polym.); particle nucleation; radical polymerization

INTRODUCTION

Water-soluble carboxylic acid monomers such as acrylic acid (AA), methacrylic acid (MAA), and itaconic acid (IA) are widely used in emulsion polymerizations for the production of carboxylated latexes used for paper coatings, textile coatings, and adhesives.^{1–3} The incorporation of the carboxyl groups onto the latex particle surface, even in small amounts, provides many advantages, such as enhanced colloidal stability, mechanical and freeze–thaw stability, rheology, and adhesion to various substrates. Conventional emulsion polymer systems often use monomers that are relatively water-insoluble, such as styrene (St), acrylonitrile, and butadiene (Bu). Polymerization takes place inside the latex particles that form spontaneously in the first few minutes of the process, and aqueous-phase polymerization is usually considered to be negligible. These latex particles comprise many individual polymer chains. Many industrial reaction systems, however, employ one or more monomers that have significant water solubility. The concentration and extent of the reactions of these water-soluble monomers in the

aqueous phase may be significant, and conventional emulsion polymerization kinetics do not readily apply to these systems. Carboxylated latexes comprise an important class of industrial emulsion polymer systems involving water-soluble carboxylic acid monomers. Carboxylic acid monomers (e.g., AA and IA) are often completely soluble in water. However, they will still partition to various extents in the organic phase according to their relative hydrophobicity. In this case, significant amounts of carboxylic acid monomers may exist in both the organic and aqueous phases.

Despite several studies on the preparation and properties of carboxylated styrene–butadiene rubber (XSBR) latexes,^{1–8} there are few reports about the effects of carboxylic acid monomers on the nucleation process and particle growth in the literature.^{9–11} These are among the most important parameters that should be assigned in an emulsion polymerization technique. However, in recent years, because of great progress in analytical techniques, the investigation of these parameters has become plausible.^{12–18}

Although the conversion of a monomer to a polymer in conventional emulsion polymerization systems is believed to take place primarily in the monomer-swollen polymer particles, the oligomeric radicals that form in the aqueous phase can play a major role in particle nucleation and stabilization and in the characteristics of the final latex products. The

Correspondence to: M. Abdollahi (m_abdollahi@modares.ac.ir or abdollahim@ripi.ir).

number of particles that form during the reaction is closely related to the amount and type of the carboxylic acid monomer, the pH, and the ionic strength.^{11,18–20} In addition, the particle growth process is also affected by the presence of carboxylic acid monomers.^{18,21,22} Shoaf and Poehlein^{21,22} developed a model that describes the kinetics of particle growth in the seeded emulsion copolymerization of St with AA and MAA. These authors confirmed the influence of events taking place in the aqueous phase on the basic mechanisms operating in the particle growth stage. In the presence of a completely water-soluble monomer, the events in the water phase should be emphasized. Most of the reported studies in the literature for emulsion polymerization systems involving carboxylic acid monomers have focused on the overall kinetic scheme to predict the reaction rates, copolymer composition, particle concentrations, and particle size. Recently, Slawinski and coworkers^{12–14} evaluated the average number of growing chains per particle during interval II of the emulsion polymerization process for the seeded batch emulsion copolymerization of St and AA. The results indicate that the pH generally has a minor influence on the polymerization rate and average number of growing chains per particle in seeded systems. Yuan and coworkers^{15–17} investigated experimentally the formation of water-soluble oligomers during the emulsion polymerization of St, Bu, and AA and determined their relevance to the kinetics and mechanism of particle nucleation and growth. Mahdavian and Abdollahi¹⁸ investigated the effect of the amount of a carboxylic acid monomer on both particle nucleation and growth in emulsifier-free batch emulsion copolymerizations of St, Bu, and AA by a dynamic light scattering technique for the first time. It was observed that the number of particles and thus the polymerization rate increased with an increasing carboxylic acid monomer content. There was no significant difference in the polymerization rate per particle or therefore in the number of radicals per particle in all experiments. The results show that in this case the particle growth process is less dependent on the amount of AA in comparison with its influence on the nucleation stage and then the particle number.

This article attempts to provide insight into the influence of the carboxylic acid monomer type on the emulsifier-free emulsion copolymerizations of St, Bu, and carboxylic acid monomers. The size of the monomer-swollen polymer particles under the reaction conditions is one of the important parameters that control the efficiency of radical entry into the particles and the radical exit coefficient from the particles. For this reason, a dynamic light scattering technique was used here to obtain the average diameter of monomer-swollen polymer particles, from which the

influence of the carboxylic acid monomer type on particle nucleation and growth was evaluated.

EXPERIMENTAL

Materials and equipment

St monomer from Merck Chemical Co. was washed three times with a 5% aqueous solution of sodium hydroxide and three times with distilled water and then dried over anhydrous calcium chloride. To remove the inhibitor completely, St was passed through an activated aluminum oxide column (Brockmann I standard grade, basic, ~ 150 mesh, 58 Å, 155 m²/g surface area; Aldrich). The purified St monomer was stored in a refrigerator until use. AA from Aldrich and MAA from Merck were distilled under a vacuum to remove the inhibitor. The purified carboxylic acid monomers were stored at about 14°C under running tap water. Potassium persulfate (KPS; used as an initiator) and IA monomer, both from Merck Chemical, and Bu, from Bandar Imam Petrochemical Co. (Tehran, Iran), were used without further purification. Double-distilled water was used in each polymerization recipe.

Emulsion polymerizations were carried out in a stainless steel Buchi reactor (Zurich, Switzerland) equipped with a mechanical stirrer and a heating system with silicon oil circulation. The average diameter of the monomer-swollen polymer particles was measured with a Siemens D5000 dynamic light scattering apparatus (Karlsruhe, Germany) (90°) at the ambient temperature (20°C).

Polymerization procedure

Emulsifier-free batch emulsion polymerizations were carried out according to a procedure reported in the literature²³ in a Buchi reactor equipped with an anchor-shaped mechanical stirrer, which was set at 300 rpm. All the reactions were performed at 70°C under an N₂ atmosphere. The amounts of the monomers and initiator in the experiments are listed in Table I. The reactor was charged under nitrogen at room temperature with all the ingredients, except for Bu. The inert gas in the head space was evacuated. The correct amount of freshly distilled liquid Bu was then added to the reactor from the weighed steel dosage vessel under pressure. The pressure never exceeded 5 bars in the reactor during polymerization.

RESULTS AND DISCUSSION

Determination of the conversion and polymerization rate

The solid content of each latex was measured during the progress of the reaction according to ASTM D

TABLE I
Recipe for the Emulsifier-Free Batch Emulsion
Copolymerization of St and Bu with Various Carboxylic
Acid Monomers^a

Ingredient	XSBR1	XSBR2	XSBR3	XSBR4
Distilled water (g)	420.000	420.000	420.000	420.000
St (g)	60.000	60.000	60.000	60.000
Bu (g)	40.000	40.000	40.000	40.000
AA (g) ^b	4.000	—	—	—
MAA (g) ^b	—	4.783	2.392	—
IA (g) ^b	—	—	3.614	7.228
KPS (g) ^c	0.728	0.728	0.728	0.728

^a The total solid content was about 20%. The pH in all experiments was about 2.5 because of the presence of a carboxylic acid monomer. The reaction time was 7–12 h, depending on the type of carboxylic acid monomer used in the recipe (see Fig. 2).

^b Equimolar amounts of the carboxylic acid monomers were used in all experiments so that the molar fraction of the acid monomers in all runs was equal to 0.0405.

^c The molar ratio of the initiator to the monomers was constant in all experiments.

1417 (method B) through the weighing of each sample in a closed vial. Each sample was quenched immediately by the addition of 1 mL of a 1% (w/v) hydroquinone solution in methanol. Then, the samples were dried at 80°C under reduced pressure, and the solid content at time t ($SC(t)$) was calculated. The overall mass conversion was calculated according to the following equation [eq. (1)] for each sample.¹⁸ The determination of the obtained data is discussed in the next section:

$$X_{ov}(t) = \frac{SC(t) - SC_{(initial)}}{SC_{(final)} - SC_{(initial)}} \quad (1)$$

where $X_{ov}(t)$ is the overall mass conversion at time t , $SC_{(initial)}$ is the solid content at the beginning of the reaction, and $SC_{(final)}$ is the solid content at the end of the reaction. The overall polymerization rate per unit of volume of the continuous phase (R_p) in a batch emulsion polymerization could be determined as follows:¹⁸

$$R_p(t) = C_{M,0} \frac{d\theta(t)}{dt} \cong C_{M,0} \frac{dX_{ov}(t)}{dt} \quad (2)$$

where $C_{M,0}$ is the initial monomer concentration (mol/L of continuous phase). Generally, when there is more than one monomer in the system, R_p should be obtained with respect to the molar conversion of the monomers. We studied the kinetics of the reaction in the range of 0.1–0.44 for the mass conversion; according to some calculations, the difference between the molar and mass conversions was less than 7%. $X_{ov}(t)$ was obtainable experimentally, and the overall molar conversion at time t [$\theta(t)$] could be

calculated according to the following equation:¹⁸

$$\theta(t) = X_{ov}(t) \frac{(1+F)(f_0\mu + 1)}{(f_0 + 1)(1 + F\mu)} \quad (3.1)$$

where

$$f_0 = \frac{f_0(\text{St})}{f_0(\text{Bu})}; \quad F = \frac{r_{St}f_0^2 + f_0}{r_{Bu} + f_0}; \quad \mu = \frac{M_M(\text{St})}{M_M(\text{Bu})} \quad (3.2)$$

F is the molar fraction of monomer i to j in the copolymer chain, f_0 is the molar fraction of monomer i to j in the initial feed, r_i is the reactivity ratio of monomer i , μ is the molecular weight ratio of monomer i to j , and M_M is the molecular weight of the swelling monomer. Through the substitution of the data available in Tables I and II into eq. (3.2), f_0 and F were determined to be 0.7813 and 0.4981, respectively. Thus, $\theta(t)/X_{ov}(t)$ was equal to 1.0751 [eq. (3.1)]. As a result, we could consider R_p based on the overall mass conversion (practically obtainable) in our equations with about 7% error, which is not really very critical. The conversion rate [$dX_{ov}(t)/dt$] was obtained from the slope of the linear part of the curve related to the weight conversion versus the time. This had an ignorable deviation from that obtained in the curve of the molar conversion versus the time. Hence, the error in the calculation of the

TABLE II
Some Useful Parameters Used in the Calculations

Parameter	Monomer	Amount	Reference
M_M (g/mol)	St	104.15	Chemical catalogue
	Bu	54.09	Chemical catalogue
ρ_M (kg/m ³)	St	906 (20°C)	Chemical catalogue
	St, Bu	0.5, 1.4	13, 25
C_{MP} (mol/dm ³)	St	5.5	26
r_{St} r_{Bu}	St, Bu	0.5, 1.4	26
k_p (dm ³ mol ⁻¹ s ⁻¹) at 70°C	St	480	27
k_p (dm ³ mol ⁻¹ s ⁻¹) at 70°C	Bu	290	28
k_p (dm ³ mol ⁻¹ s ⁻¹) at 70°C	AA	59200	29
k_p (dm ³ mol ⁻¹ s ⁻¹) at 70°C	MAA	1208	30
k_p (dm ³ mol ⁻¹ s ⁻¹) at 70°C	IA	35.6 ^b	31
α_{MAA}^c	MAA	1.01 (25°C)	32
α_{AA}^c	AA	0.102 (25°C)	32
α_{IA}^c	IA	0.01 (50°C)	33

^a k_p is the coefficient of the propagation rate in homopolymerization.

^b The value reported for dimethyl itaconate. It is very likely that IA has a k_p value similar to that of the dimethyl ester, although no study on this matter currently exists.

^c α_i is the partition coefficient of carboxylic acid monomer i between St and water.

polymerization rate was much less than 7%. Also, this was repeated for all procedures and caused no serious problem in the comparative studies. The effect of the carboxylic acid monomer amount could be neglected with respect to St and Bu because it was low.

Particle size and particle number determination

Generally, the average particle diameter (d_p) of a polymer and the particle size distribution can be measured with scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. These methods can be applied with accuracy when there are dried latexes. The number of latex particles per unit of volume of the aqueous phase (N_p) can be calculated with the following equation:^{12,15,18}

$$N_p = \frac{6P/W}{\frac{\rho_p}{\rho_w} \pi d_p^3} \quad (4)$$

where P/W is the weight ratio of the polymer to water, ρ_p is the average density of the polymer, and ρ_w is the density of water. In eq. (4), ρ_p and ρ_w would be equal to 1 g/cm³ for carboxylated XSBR¹²⁻¹⁸ and 1.00 g/cm³ for water, respectively. P/W is a function of the monomer-to-water ratio and conversion. Therefore, P/W in emulsion polymerization systems can be calculated as follows:¹²

$$\frac{P}{W} = \frac{M}{W} X_{ov} \quad (5)$$

where M/W is the weight ratio of the monomer(s) to water. We could use the following equation to obtain the average diameter of monomer-swollen particles (d_{pswol}) in the batch emulsion polymerization:^{12,18}

$$D_{pswol}^3 = d_p^3 \left[1 - \frac{M_M C_{MP}}{\rho_M} \right]^{-1} \quad (6)$$

where ρ_M is the density of the swelling monomer and C_{MP} is the overall monomer concentration in the polymer particles in interval II. In intervals I and II of the emulsion polymerization model introduced by Harkins,²⁴ the monomer still exists as a separate phase, and C_{MP} depends only on the particle diameter. For polymer particles greater than about 50 nm, C_{MP} is independent of the particle diameter.²⁵ The monomer phase disappears in interval III, and the overall conversion will also be an effective parameter for C_{MP} .

Two situations exist in the determination of the diameter of polymer particles with a dynamic light scattering technique. First, when the conversion is nearly 100%, the measured particle sizes are almost equal to those obtained from SEM and TEM

techniques. The hydrodynamic particle diameter is measured by dynamic light scattering analysis and is slightly larger than those measured by SEM and TEM. Second, when the conversion is low, dynamic light scattering analysis gives d_{pswol} (the real diameter of polymer particles under polymerization conditions), and d_p measurement is not possible.

In addition to withdrawing the samples for conversion analysis, we carried out a separate sampling for dynamic light scattering analysis at various time intervals for all experiments. Then, a sample for particle size analysis was selected according to the conversion/reaction time data so that the conversion of the sample fell in interval II of the emulsion polymerization because the kinetic parameters were calculated from experimental data obtained under steady-state conditions, that is, interval II, of the emulsion polymerization. Hence, d_p could be calculated from eq. (6) (d_{pswol} was obtained from dynamic light scattering analysis), and then N_p could be obtained by the substitution of the calculated d_p value into eq. (4). This meant that N_p was obtainable indirectly from the data given by the dynamic light scattering technique as long as the polymerization reaction had not reached complete conversion. Unreacted Bu with a boiling point of -4.5°C was evaporated after sampling. Therefore, the unreacted monomers were St (major) and carboxylic acid monomers (minor). The percentage of the carboxylic acid monomer with respect to St in the feed was low, and it did not incorporate completely into the particle phase and mainly remained in the aqueous phase, depending on its hydrophilic nature. Therefore, the effect of the unreacted carboxylic acid monomer on the swelling of the particles (d_{pswol}) and the determination of d_p was negligible. Consequently, M_M and ρ_M of St at 20°C (the temperature at which the dynamic light scattering analysis was carried out) could be inserted into eq. (6). C_{MP} in interval II of the emulsion polymerization could be considered constant because the polymer particle diameter in all the experiments was large enough. Some useful parameters, available in the literature, are listed in Table II.

R_p was obtained from the data in the conversion range of 10–44% in all experiments (interval II of the emulsion polymerization in which C_{MP} was equal to 5.5 mol/dm³²⁵). The major problem arising here was from the insertion of C_{MP} into eq. (6). C_{MP} (5.5 mol/dm³) could be used up to a 50% conversion, which corresponded to the end of interval II in the emulsion polymerization (shown later in Fig. 2), and then decreased with increasing conversion. This meant that C_{MP} was dependent on the conversion in interval III. As the conversion of the latex samples used in the dynamic light scattering analysis was below 44% in all experiments (Table III), C_{MP}

TABLE III
Known and Obtained Data for the Emulsifier-Free Batch Emulsion Copolymerization of St, Bu, and Carboxylic Acid Monomers

Parameter	XSBR1	XSBR2	XSBR3	XSBR4
C_{MP} (mol/dm ³) ^a	5.5	5.5	5.5	5.5
X_{ov} (kg/kg) ^b	0.2214	0.4372	0.4205	0.3283
M/W (kg/kg)	0.2476	0.2495	0.2524	0.2553
P/W (kg/kg)	0.0548	0.1091	0.1061	0.0838
d_{pswol} (nm) ^c	311.5	184.5	198.3	420.9
d_p (nm)	223.17	132.18	142.07	301.55
N_p (dm ⁻³)	9.42×10^{15}	9.02×10^{16}	7.07×10^{16}	5.84×10^{15}

^a These values were used in eq. (6) to calculate d_p .

^b Conversions corresponding to the samples used for dynamic light scattering analysis.

^c d_{pswol} was obtained with a dynamic light scattering technique.

corresponding to interval II of the emulsion polymerization, that is, 5.5 mol/dm³, was inserted into eq. 6, and then d_p was calculated. The obtained d_{pswol} and d_p values are listed in Table III.

Effect of the carboxylic acid monomers on nucleation and particle growth

Jacobi³⁴ and Priest³⁵ published the first reports on the mechanism of homogeneous nucleation. Fitch and Tsai³⁶ and Ugelstad and Hansen³⁷ proposed the quantitative theory for this phenomenon. The theoretical point of view of homogeneous and/or coagulative nucleation has been presented as the Hansen-Ugelstad-Fitch-Tsai theory. The mechanism of particle formation in nonmicellar (e.g., emulsifier-free) emulsion polymerization is homogeneous and/or coagulative nucleation. According to this theory, monomeric units in the aqueous phase are added to the radicals until the obtained oligoradicals reach the critical point at which they become insoluble in the water phase. At this time, they begin to precipitate and generate precursor polymeric particles. Then, the monomers diffuse from their droplet phase and penetrate the newly formed latex particles to swell them and propagate the polymerization reaction. These particles are unstable because of colloidal aspects and have to coagulate to form the stable primary particles to compensate for this instability. Then, propagation is continued in the particles that have been stabilized by ionic charges of carboxyl groups and end groups of the initiator. According to this explanation, it is necessary to know the role of water-soluble monomers in emulsifier-free systems in which stabilization is the main problem.

In a previous article,¹⁸ we investigated the effect of the carboxylic acid amount on the particle nucleation stage in emulsifier-free emulsion polymerizations of St, Bu, and AA. The number of particles and thus the polymerization rate increased with increasing AA content. Here we examined the effect of the carboxylic acid monomer type on the homogeneous

and/or coagulative nucleation stage in emulsifier-free emulsion polymerizations of St, Bu, and carboxylic acid monomers (Table I). In all experiments, there was no problem concerning the stability of the obtained latexes. The results of the dynamic light scattering analysis reveal the narrow particle size distribution. Some useful information is summarized in Table III and plotted in Figure 1.

Figure 1 reveals that N_p increased remarkably with the increasing hydrophobicity of the carboxylic acid monomers (see the partition coefficients of the carboxylic acid monomers in Table II) in the order of IA < AA < (MAA + AA) < MAA. This could be attributed to the increase in the number of precipitating oligoradicals during the nucleation stage and not to the capacity of the particles for limited flocculation in the growth step. Some evidence for this behavior could also be found in the progress of the reaction below 10% conversion, that is, the particle nucleation stage (Fig. 2). The polymerizations that were performed with the most hydrophilic monomer, IA, had a significantly lower reaction rate. It is evident that the polymerization rate is directly proportional to the hydrophobicity of the carboxylic

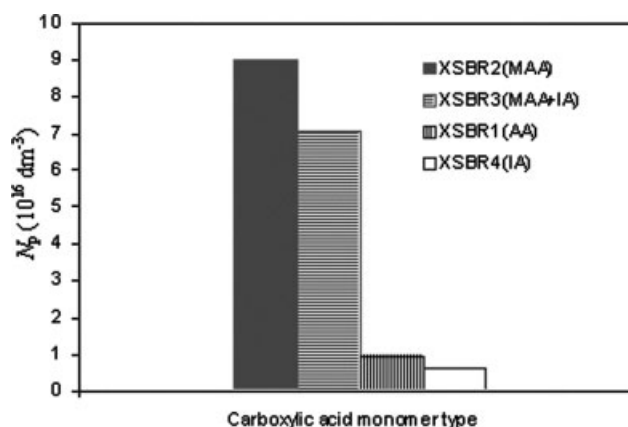


Figure 1 Dependence of N_p on the carboxylic acid monomer type.

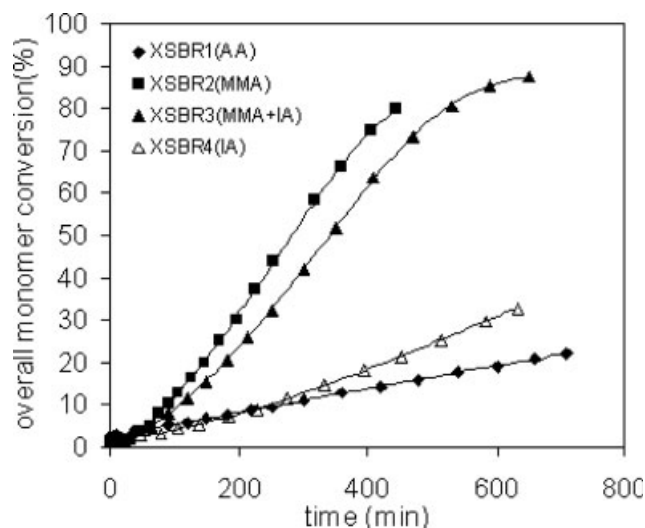


Figure 2 Overall mass conversion as a function of the reaction time in the emulsifier-free batch emulsion polymerization of St, Bu, and carboxylic acid monomers.

acid monomers because logically it should generate more stable primary particles (discussed later).

The function of a carboxylic acid monomer in an emulsifier-free emulsion polymerization is twofold according to the mechanism of homogeneous/coagulative nucleation. It induces the formation of polymer particles through the precipitation of oligoradicals formed in the aqueous phase after the critical degree of polymerization (homogeneous nucleation) and lends stability to the polymer particles. The results in Table III indicate that the ability of the carboxylic acid monomers to generate particles is inversely related to their hydrophilicity (Table II), with the most hydrophilic, IA, being least effective. Although similar results have been deduced from polymerization rates observed for emulsifier-free emulsion polymerizations of St and of St and Bu in the presence of various carboxylic acid monomers, values of N_p have not been calculated.³⁸

Qualitatively, the ability of carboxylic acid monomers to induce particle formation can be explained by the Hansen–Ugelstad–Fitch–Tsai theory. Persulfate radicals induce polymerization in the aqueous phase, producing highly carboxylated oligomers that precipitate at a critical degree of polymerization and nucleate to form polymer particles. Particle growth continues inside the particle. The particles maintain their stability from the hydrophilic shell provided by the carboxyl groups, which concentrate at the particle–water interface.

As a result, to better understand the effect of carboxylic acid monomers on particle nucleation, it is necessary to consider the capacity of these monomers for both the formation and stabilization of polymer particles. It is clear that the critical polymerization degree of oligoradicals formed in the aqueous phase

depends directly on the hydrophilicity (i.e., water solubility) of carboxylic acid monomers. A higher critical polymerization degree of oligoradicals in the aqueous phase can result in an increased concentration of oligoradicals in the aqueous phase, and so oligoradicals may be terminated and remain water-soluble before either precipitation to form polymer particles or entry into the previously formed polymer particles. This results in decreased particle nucleation and decreased efficiency of oligoradical entry into the polymer particles. Also, dead water-soluble oligomers may cause destabilization of the particles through a bridging flocculation mechanism.¹⁷ Therefore, the ability of carboxylic acid monomers to form precursor particles is expected to be in the order of $MAA \gg AA > IA$, as shown in Figure 1. Depending on the nature of the carboxylic acid monomers, precursor particles may be coagulated to some extent to form stable primary particles. The more surface-bound carboxyl groups there are, the higher the stabilization ability is of the carboxylic acid monomers. Then, the number of the stable primary particles formed after the limited coagulation of precursor particles will be high. It has been observed that IA, being the most hydrophilic and having the least solubility in St (Table II), tends to distribute itself in favor of the aqueous serum phase, whereas AA, which has limited solubility in St and is sufficiently hydrophilic, tends to prefer the particle surface predominantly. MAA, being the most hydrophobic of the three carboxylic acid monomers studied and having good solubility in St, has been shown to be concentrated inside the particle core.³³ However, it has been reported that a significant amount of AA (ca. 50–65%, depending on the reaction temperature) reacts in a later stage (> 80% conversion) of the batch emulsion copolymerization of St, Bu, and AA.¹⁷ Also, the emulsion copolymerization kinetics of St with AA and MAA have been investigated, and it has been observed that the mechanism for the AA–St system is more complicated than that for the MAA–St system.²¹ Evidence suggests that the primary reaction locus in the AA–St system shifts from the particles to the aqueous phase after the hydrophobic monomer, St, has been consumed.^{21,22} Therefore, the effects of various carboxylic acid monomers on limited coagulation seem to be almost similar.

From this discussion, one can conclude that the number of polymer particles nucleated in the emulsifier-free emulsion copolymerization of water-insoluble monomers such as St and Bu in the presence of hydrophilic carboxylic acid monomers increases with the increasing hydrophobicity of the carboxylic acid monomers (Tables I–III). There are other factors influencing the capacity of a carboxylic acid monomer for particle nucleation. For example, the propagation rate coefficients of carboxylic acid monomers (Table II) and pH-induced thermal decomposition of

TABLE IV
Kinetic Parameters Related to the Emulsifier-Free Emulsion Copolymerization of St, Bu, and Carboxylic Acid Monomers

Parameter	XSBR1	XSBR2	XSBR3	XSBR4
dX_{ov}/dt (s^{-1})	4.550×10^{-6}	3.402×10^{-5}	2.832×10^{-5}	1.001×10^{-5}
$C_{M,0}$ (mol/dm^3)	3.265	3.265	3.265	3.265
R_p ($mol/dm^3 s^{-1}$)	1.485×10^{-5}	1.110×10^{-4}	9.244×10^{-5}	3.269×10^{-5}
R_p/N_p (mol/s)	1.577×10^{-21}	1.231×10^{-21}	1.308×10^{-21}	5.600×10^{-21}

the KPS initiator by carboxylic acid monomers³⁹ should be considered for the particle nucleation ability of these monomers, especially in the case of IA, because IA does not homopolymerize easily and bears two carboxylic acid functional groups, which result in a lower pH. These factors in the case of IA increase the concentration of radicals in the aqueous phase, and so a lower portion of these radicals is likely to precipitate to form precursor polymer particles because of termination reactions in the aqueous phase.

R_p , obtained from eq. (2) in the conversion range of 0.1–0.44 (interval II of emulsion polymerization), and R_p/N_p (i.e., the polymerization rate per particle) are given in Table IV. From the previous discussion, it was expected that with the same monomer-to-water ratio and same number of polymer particles per unit of volume of the aqueous phase, R_p/N_p would decrease with the increasing hydrophilicity of the carboxylic acid monomers because of the low efficiency of oligoradical entry into the polymer particles. This expected trend was not seen in our experiments (Fig. 3) because of the unequal numbers of polymer particles per unit of volume of water and therefore unequal polymer particle diameters. In addition, the significant increase in R_p/N_p in the case of IA (XSBR4) can be attributed to the larger size of the polymer particles as a result of the lower number of polymer particles, as discussed in detail in the next section. Some evidence for a high value of R_p/N_p in the particle growth stage for IA (experiment XSBR4) can also be found in the progress of the reaction (Fig. 2). A considerable increase in the polymerization rate in the particle growth stage (conversion = 0.1–0.35 for XSBR4 in Fig. 2) with respect to the particle nucleation stage (conversion < 0.1) may be due to the high efficiency of radical entry into the lower number of polymer particles nucleated in the particle nucleation period (Fig. 1) but larger size of the polymer particles in the particle growth period. It may be deduced from these data that the carboxylic acid monomer type has a significant effect on both particle nucleation (N_p) and growth (R_p/N_p) processes.

The rate of emulsion polymerization in interval II (conversion \approx 0.1–0.5) was almost constant in our system with the proper assumptions (Fig. 2). It could

be concluded that particle nucleation occurred before a conversion of about 0.1.¹⁵ Therefore, we assumed that N_p was constant in interval II of the emulsion polymerization, and R_p/N_p was calculated during particle growth. The results, which are plotted in Figure 3, show that R_p/N_p decreased in the order of XSBR4(IA) \gg XSBR1(AA) > XSBR3(MAA+IA) > XSBR2(MAA).

A high value of R_p/N_p for the emulsion copolymerization of St and Bu in the presence of IA is not related indeed to the effect of IA on the efficiency of radical entry into the particles (growth stage) but is related to the effect of IA, the most hydrophilic carboxylic acid monomer, on the particle nucleation. As discussed in the previous section, the emulsifier-free emulsion copolymerization of St, Bu, and IA results in a lower number of primary particles being initially nucleated, and so larger polymer particles are formed. The larger the diameter is of the polymer particles, the higher the number is of the radicals that have entered the polymer particles. Thus, when experiments are performed under the same experimental conditions with respect to the number of polymer particles per unit of volume of the aqueous phase, the diameter of the particles, and the monomer-to-water ratio (i.e., seeded emulsion polymerization), R_p/N_p is expected to decrease with the increasing hydrophilicity of the carboxylic acid monomer. However, the diameters of the particles in all the

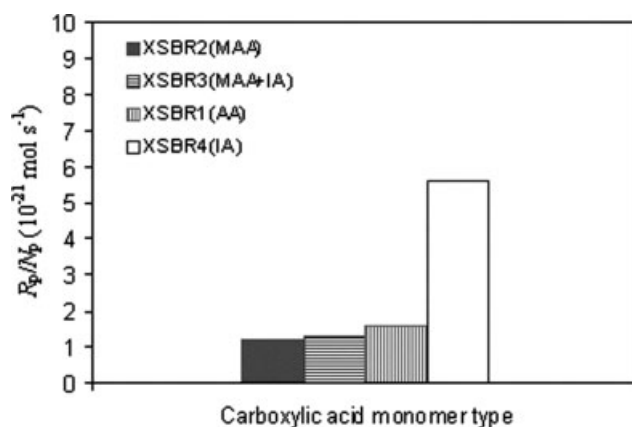


Figure 3 Dependence of R_p/N_p on the carboxylic acid monomer type.

experiments of this work were not the same. Thus, our results should be explained with consideration of the effects of the carboxylic acid monomer type and the particle diameter on R_p/N_p as follows.

The general trend of the R_p/N_p values can be described by the effect of the carboxylic acid monomer type on the nucleation process. N_p increases with a decrease in the hydrophilicity of the carboxylic acid monomer (Fig. 1). Hence, by considering the similar conversions in these experiments, we find that the particle diameter decreases with the decreasing hydrophilicity of the carboxylic acid monomer, and the surface area per particle will decrease as a result. This will cause a decrease in the entrance efficiency of the radicals into each particle and therefore a decrease in R_p/N_p . It is notable that the increase in N_p will result in an increase in the total surface area. As a result, the total number of radicals entering all particles per unit of volume of the aqueous phase will increase, and thus the total polymerization rate will be increased [eq. (3) and Fig. 2].

CONCLUSIONS

Emulsifier-free batch emulsion copolymerizations of St, Bu, and carboxylic acid monomers led us to some useful information about the influence of the carboxylic acid type on the kinetics of the reaction and particularly about the nucleation mechanism. In this work, data obtained with a dynamic light scattering technique were used for particle size measurements of XSBR latexes. The results were quite comparable to those of previous similar systems and confirmed the accuracy of our method.

It was found that d_{pswol} at the same conversion was directly proportional to the hydrophilicity of the carboxylic acid monomer type (with respect to N_p). Beside that, the number of polymer particles and polymerization rate decreased with the increasing hydrophilicity of the carboxylic acid monomer. Also, the effects of various carboxylic acid monomers on R_p/N_p were investigated. It was deduced that the carboxylic acid monomer type had a significant effect on both the particle nucleation (N_p) and growth (R_p/N_p) processes.

NOMENCLATURE

α_i	partition coefficient of carboxylic acid monomer i between styrene and water
AA	acrylic acid
Bu	butadiene
$C_{M,0}$	initial monomer concentration (mol/L of continuous phase)
C_{MP}	overall monomer concentration in the polymer particles in interval II

d_p	average particle diameter
d_{pswol}	average diameter of monomer-swollen particles
F	molar fraction of monomer i to j in the copolymer chain
f_0	molar fraction of monomer i to j in the initial feed
IA	itaconic acid
k_p	coefficient of the propagation rate in homopolymerization
KPS	potassium persulfate
μ	molecular weight ratio of monomer i to j
M/W	weight ratio of the monomer(s) to water
MAA	methacrylic acid
M_M	molecular weight of the swelling monomer
N_p	number of latex particles per unit of volume of the aqueous phase
P/W	weight ratio of the polymer to water
ρ_M	density of the swelling monomer
ρ_P	average density of the polymer
ρ_W	density of water
r_i	reactivity ratio of monomer i
R_p	polymerization rate per unit of volume of the continuous phase
$SC_{(t)}$	solid content at time t
$SC_{(initial)}$	solid content at the beginning of the reaction
$SC_{(final)}$	solid content at the end of the reaction
SEM	scanning electron microscopy
St	styrene
$\theta(t)$	overall molar conversion at time t
TEM	transmission electron microscopy
$X_{ov}(t)$	overall mass conversion at time t
XSBR	carboxylated styrene-butadiene rubber

References

- Chatterjee, A. K. *Rubber Chem Technol* 1983, 56, 995.
- Ceska, G. W. *J Appl Polym Sci* 1974, 18, 2493.
- Muroi, S. *J Appl Polym Sci* 1966, 10, 713.
- Muroi, S.; Hosoi, K.; Ishikawa, K. *J Appl Polym Sci* 1967, 11, 1963.
- Hoy, K. L. *J Coat Technol* 1979, 51, 27.
- Bassett, D. R.; Derderian, E. J.; Johnston, J. E.; MacRury, T. B. In *Emulsion Polymers and Emulsion Polymerization*; Bassett, D. R.; Hamielec, A. E., Eds.; ACS Symposium Series 165; American Chemical Society: Washington, DC, 1981; Chapter 16, p 263.
- Bassett, D. R.; Hoy, K. L. In *Polymer Colloids*; Fitch, R. M., Ed.; Plenum: New York, 1980; Vol. II, p 1.
- Nishida, S.; El-Aasser, M. S.; Klein, A.; Vanderhoff, J. W. In *Emulsion Polymers and Emulsion Polymerization*; Bassett, D. R.; Hamielec, A. E., Eds.; ACS Symposium Series 165; American Chemical Society: Washington, DC, 1981; Chapter 18, p 291.
- Ceska, G. W. *J Appl Polym Sci* 1974, 18, 427.
- Sakota, K.; Okaya, T. *J Appl Polym Sci* 1976, 20, 3255.
- Sakota, K.; Okaya, T. *J Appl Polym Sci* 1976, 20, 3265.

12. Slawinski, M. Ph.D. Thesis, Eindhoven University of Technology, 1999.
13. Slawinski, M.; Schellekens, M. A. J.; Meuldijk, J.; Van der Herk, A. M.; German, A. L. *J Appl Polym Sci* 2000, 76, 1186.
14. Slawinski, M.; Schellekens, M. A. J.; Meuldijk, J.; Van der Herk, A. M.; German, A. L. *J Appl Polym Sci* 2000, 78, 875.
15. Yuan, X.-Y.; Dimonie, V. L.; Sudol, E. D.; El-Aasser, M. S. *Macromolecules* 2002, 35, 8346.
16. Yuan, X.-Y.; Dimonie, V. L.; Sudol, E. D.; Roberts, J. E.; El-Aasser, M. S. *Macromolecules* 2002, 35, 8356.
17. Yuan, X.-Y.; Dimonie, V. L.; Sudol, E. D.; El-Aasser, M. S. *J Appl Polym Sci* 2003, 88, 1988.
18. Mahdavian, A.-R.; Abdollahi, M. *Polymer* 2004, 45, 3233.
19. Sakota, K.; Okaya, T. *J Appl Polym Sci* 1976, 20, 1745.
20. Yang, B.-Z.; Chen L.-W.; Chiu W.-Y. *Polym J* 1997, 29, 737.
21. Shoaf, G. L.; Poehlein, G. W. *J Appl Polym Sci* 1991, 42, 1213.
22. Shoaf, G. L.; Poehlein, G. W. *J Appl Polym Sci* 1991, 42, 1239.
23. Mahdavian, A. R.; Abdollahi, M. *React Funct Polym* 2006, 66, 247.
24. Harkins, W. D. *J Am Chem Soc* 1947, 69, 1428.
25. Hawkett, B. S.; Napper, D. H.; Gilbert, R. G. *J Chem Soc Faraday Trans* 1980, 76, 1323.
26. Meehan, E. J. *J Polym Sci* 1946, 1, 318.
27. 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.
28. Deibert, S.; Bandermann, F.; Schwee, J.; Sarnecki, J. *Makromol Chem Rapid Commun* 1992, 13, 351.
29. Gromov, V. F.; Galperina, N. I.; Osmanov, T. O.; Khomikovskii, P. M.; Abkin, A. D. *Eur Polym J* 1978, 16, 529.
30. Beuermann, S.; Paquet, D. A.; McMinn, J. H.; Hutchinson, R. A. *Macromolecules* 1997, 30, 194.
31. Yee, L. H.; Coote, M.; Chaplin, R. P.; Davis, T. P. *J Polym Sci Part A: Polym Chem* 2000, 38, 2192.
32. Sakota, K.; Okaya, T. *J Appl Polym Sci* 1976, 20, 2583.
33. Vijayendran, B. R. *J Appl Polym Sci* 1979, 23, 893.
34. Jacobi, B. *Angew Chem* 1954, 64, 539.
35. Priest, W. J. *J Phys Chem* 1952, 56, 1077.
36. Fitch, R. M.; Tsai, C. H. In *Polymer Colloids*; Fitch, R. M., Ed.; Plenum: New York, 1971; p 73.
37. Ugelstad, J.; Hansen, F. K. *Rubber Chem Technol* 1976, 49, 536.
38. Ceska, G. W. *J Appl Polym Sci* 1974, 18, 427.
39. Lock, M. R.; El-Aasser, M. S.; Klein, A.; Vanderhoff, J. W. *J Appl Polym Sci* 1990, 39, 2129.