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Effect of carboxylic acid monomer and butadiene on particle growth in the emulsifier-free emulsion copolymerization of styrene–butadiene–carboxylic acid monomer

Mahdi Abdollahi [a,b,*], Maryam Sharifpour [b]

[a] Division of Polymer Science and Technology, Research Institute of Petroleum Industry (RIPI), P.O. Box 18745-4163, Tehran, Iran
[b] Department of Polymer Engineering, Faculty of Engineering, Tarbiat Modares University, P.O. Box 14155-143, Tehran, Iran

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Abstract

Carboxylated styrene–butadiene rubber (XSBR) latexes were prepared by emulsifier-free batch emulsion copolymerization of styrene and butadiene with different types of carboxylic acid monomers (AA, MAA, IA). It was found that the particle growth is dependent on the hydrophilic nature of carboxylic acid monomers. SEM studies showed that N_p is almost constant in the particle growth stage (conversion above 10%). Through some calculations by data obtained from DLS technique, average diameter of monomer swollen polymer particles of all the XSBR latexes at the same conversion of 0.4 was obtained to be 368.91, 174.17 and 437.15 nm for AA, MAA and IA, respectively. Several kinetic parameters related to the particle growth stage such as the average number of growing chain per particle were calculated to be 0.474, 0.370 and 1.685 for AA, MAA and IA, respectively. It was observed that these kinetic parameters increase with increasing average diameter of monomer swollen polymer particles, which is consistent with the emulsion polymerization kinetics. Moreover, results indicated that the polymerization rate per particle or equivalently the average number of the growing chain per particle (particle growth stage) decreases by replacing a part of styrene with butadiene in the emulsion copolymerization recipe of styrene–carboxylic acid monomer.

Keywords: Carboxylated SBR latex; Emulsifier-free emulsion copolymerization; Particle growth

1. Introduction

Water-soluble carboxylic acid monomers such as acrylic acid (AA), methacrylic acid (MAA) and itaconic acid (IA) are widely used in emulsion polymerization for the production of carboxylated latexes used for paper coatings, textile coatings and adhesives. The incorporation of the carboxyl groups on 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 [1,2]. Conventional emulsion polymer systems often use monomers that are relatively water-insoluble such as styrene, acrylonitrile and butadiene. The primary reaction locus is inside the polymer particles, and aqueous-phase polymerization is usually considered to be negligible. Many industrial reaction systems, however, employ one or more monomers that have a significant solubility in water. The concentration and extent of reaction of these water-soluble monomers in the aqueous phase may be significant, and conventional emulsion polymerization kinetics does not readily apply to these systems. Carboxylated styrene–butadiene rubber (XSBR) latexes comprise an important class of industrial emulsion polymer systems involving water-soluble carboxylic acid monomers [1,2]. Carboxylic acid monomers are often completely soluble in water. However, they will still partition to varying extents into the organic phase depending on their

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* Corresponding author. Department of Polymer Engineering, Faculty of Engineering, Tarbiat Modares University, P.O. Box 14155-143, Tehran, Iran. Tel.: +9821 55901021 51x5344.

E-mail addresses: m_abdollahi@modares.ac.ir, abdollahim@ripi.ir (M. Abdollahi).

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Nomenclature

$X_{ov}(t)$	overall mass conversion at time t
SC(t)	solid content at time t
SC(initial)	solid content at the beginning of reaction
SC(final)	solid content at the end of reaction
R_p	polymerization rate per unit volume of the continuous phase
$C_{M,0}$	initial monomer concentration (moles per unit volume of the continuous phase)
$\theta(t)$	overall molar conversion at time t
f_0	mole fraction of monomers i to j in the initial feed
F	instantaneous mole fraction of monomers i to j in the copolymer chain
$\overline{F}$	cumulative average mole fraction of monomers i to j in the copolymer chain at any conversion
$\overline{F}_i$	cumulative average mole fraction of monomer i in the copolymer chain at any conversion
μ	molecular weight ratio of monomers i to j
$\overline{n}$	average number of growing chain per particle
N_p	number of latex particles per unit volume of the aqueous phase
C_{MP}	overall monomer concentration in the polymer particles at interval II
N_{av}	Avogadro's number
P/W	weight ratio of polymer to water
M/W	weight ratio of monomer(s) to water
ρ_P	average density of the polymer
ρ_W	density of water
ρ_M	density of the swelling monomer at the liquid state
d_p	average particle diameter
d_{pswol}	average diameter of monomer swollen particles
M_M	molecular weight of the swelling monomer
F_i	instantaneous mole fraction of monomer i in the copolymer chain
f_i	instantaneous mole fraction of monomer i in the feed (unreacted monomer) at any conversion
f_i^0	f_i in the initial state
r_i	reactivity ratio of monomer i
$\overline{k}_p$	average propagation rates constant in the particle phase
$k_{p,ii}$	coefficient of propagation rate in homopolymerization of monomer i
$k_{p,jj}$	coefficient of propagation rate in homopolymerization of monomer j
α_i	partition coefficient of carboxylic acid monomer i between styrene and water
M_i	molecular weight of monomer i
$\overline{M}_M$	average molecular weight of the swelling monomer mixture in particle phase
ρ_i	density of monomer i at the liquid state
$\overline{\rho}_M$	average density of the swelling monomer mixture in particle phase
x_i	mole fraction of monomer i in the reaction mixture (particle phase)
ϕ_i	volume fraction of monomer i in the reaction mixture (particle phase)

relative hydrophobicity. In this case, significant amounts of carboxylic acid monomer may exist in both the organic and aqueous phases.

Despite the presence of several studies on preparation and properties of XSBR latexes [1–6], there are few reports about the effect of carboxylic acid monomer on the nucleation process and particles' growth in the literature [7–9]. These are among the most important parameters, which should be assigned in emulsion polymerization technique. However, in recent years due to high progresses in analytical techniques, investigation of these parameters has become plausible [10–16].

Although the conversion of monomer to polymer in conventional emulsion polymerization systems is believed to take place primarily in the monomer swollen polymer particles, the oligomeric radicals formed in the aqueous phase can play a major role in particle nucleation and stabilization and in the characteristics of the final latex products. The number of particles formed during the reaction is closely related to the amount and type of the carboxylic acid monomer, the pH and the ionic strength [9,16–18]. In addition, the particle growth process is also affected by the presence of carboxylic acid monomers [16,19,20]. Shoaf and Poehlein [19,20] developed a model that describes the kinetics of particle growth in seeded emulsion copolymerization of styrene with acrylic and methacrylic acids. 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 in order to predict reaction rates, copolymer composition, particle concentrations and particle size. Recently, Slawinski et al. [10–12] evaluated the average number of growing chains per particle during interval II of the emulsion polymerization process for seeded batch emulsion copolymerization of styrene and acrylic acid. The results indicate that pH generally has a minor influence on the polymerization rate and average number of growing chains per particle in the seeded systems. Yuan et al. [13–15] investigated experimentally the formation of water-soluble oligomers during the emulsion polymerization of styrene–butadiene–acrylic acid and determined their relevance to the kinetics and mechanism of particle nucleation and growth. Mahdavian and Abdollahi [16] investigated the effect of carboxylic acid monomer amount on both particle nucleation and growth in emulsifier-free batch emulsion copolymerization of styrene (St)–butadiene (Bu)–acrylic acid by DLS technique for the first time. It was observed that the number of latex particles per unit volume of the aqueous phase and thus polymerization rate increased with increasing the carboxylic acid monomer content. There was no significant difference in the polymerization rate per particle and thereby number of radicals per particle in all experiments. Therefore, results showed that in this case particle growth process is less dependent on the acrylic acid amount in comparison with its influence on nucleation stage and then particle number.

Recently, the effect of various carboxylic acid monomers on both particle nucleation and growth has been investigated in emulsifier-free emulsion copolymerization of styrene–carboxylic acid monomer [21]. It has been observed that the carboxylic acid monomer type has a significant effect on both particle nucleation (number of latex particles per unit volume of the aqueous phase) and growth (polymerization rate per particle or equivalently average number of the growing chain per particle).

In the previous study, we examined the effect of carboxylic acid monomer type on the homogeneous/or coagulative nucleation stage in emulsifier-free emulsion copolymerization of styrene–butadiene–carboxylic acid monomer [22]. Results indicated that number of latex particles per unit volume of aqueous phase increases with increasing the hydrophobicity of carboxylic acid monomer in the order of IA < AA < MAA. This was attributed to the increase in number of precipitating oligoradicals during nucleation stage and don't permission of particles to limited coagulation in the growth step [22]. In the continuum of this work, present article attempts to provide insight into the influence of carboxylic acid monomer type on the particle growth in the free-emulsifier emulsion copolymerization of styrene (St)–butadiene (Bu)–carboxylic acid monomer. Size of monomer swollen polymer particles in the reaction conditions is one of the important parameters that control the efficiency of radical entry into the particles and radical exit coefficient from the particles. For this reason, DLS technique is used here to obtain average diameter of monomer swollen polymer particles from which the influence of carboxylic acid monomer type on particle growth is evaluated. Furthermore, the effect of butadiene monomer on particle growth is investigated by comparing results obtained here for XSBR latexes and those obtained previously for carboxylated polystyrene latexes [21] at the same reaction conditions.

2. Experimental

2.1. Materials and equipments

Styrene (St) monomer from Merck Chemical Co. was washed three times with a 5% aqueous solution of sodium hydroxide followed by three times washing with distilled water and then dried over anhydrous calcium chloride. To remove the inhibitor completely, styrene was passed through activated aluminum oxide (Brockmann I standard grade, basic, ~150 mesh, 58 Å, 155 m^2/g surface area, Aldrich) column. The purified styrene monomer was stored in a refrigerator until use. AA from Aldrich and MAA from Merck were distilled under vacuum to remove the inhibitor. The purified carboxylic acid monomers were stored at about 14 °C under running tap water. Potassium persulfate (KPS) as initiator from Merck Chemical Co. IA monomer from Merck Chemical Co. and butadiene (Bu) from Bandar Imam Petrochemical Co. (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 equipped with mechanical stirrer and heating system with silicon oil circulation. Average diameter of the monomer swollen polymer particles (d_{pswol}) was measured by a D5000 SIEMENS dynamic light scattering (DLS) (using a He–Ne laser as light source with wavelength of 632.8 nm under scattering angle of 90°) at ambient temperature (20 °C) immediately after diluting the latexes up to about 0.01% solid content with double distilled water. Direct inversion technique (cumulants analysis) was used for obtaining average diameter and polydispersity. The polydispersity is defined as the standard deviation of the particle size distribution divided by the average value. In particle size measurements by scanning electron microscopy (SEM) (Model Stereoscan 360, Cambridge Instrument Co.), one drop of diluted latex was placed on the sample holder and then freeze-dried under vacuum for removing the water and unreacted monomers (which swell the particles). Typically 500–1000 particles were measured on the micrographs. The average diameter of polymer particles (d_p) was determined from these measurements, which was then used to calculate N_p.

2.2. Polymerization procedures [23]

Emulsifier-free batch emulsion polymerizations were carried out in a Buchi reactor equipped with an anchor shape mechanical stirrer, which was set at 300 rpm. All of the reactions were performed at 70 °C under N_2 atmosphere. The amounts of monomers and initiator in any experiment are mentioned in Table 1. The reactor was charged under nitrogen at room temperature with all ingredients, except for Bu. The inert gas in the headspace 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

Table 1
Recipe for emulsifier-free batch emulsion copolymerization of styrene and butadiene with various carboxylic acid monomers[a]

Ingredients (g)	XSBR1	XSBR2	XSBR3	XSBR4
Distilled water	420.000	420.000	420.000	420.000
Styrene (St)	60.000	60.000	60.000	60.000
Butadiene (Bu)	40.000	40.000	40.000	40.000
Acrylic acid (AA)[b]	4.000	–	–	–
Methacrylic acid (MAA)[b]	–	4.783	2.392	–
Itaconic acid (IA)[b]	–	–	3.614	7.228
KPS[c]	0.728	0.728	0.728	0.728

[a] Total solid content is about 20%. pH in all experiments was about 2.5 due to the presence of carboxylic acid monomer. Reaction time was 7–12 h depending on the type of carboxylic acid monomer used in the recipe.

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

[c] Mole ratio of initiator to monomers was constant in all experiments.

pressure never exceeded 5 bar in the reactor during polymerization.

3. Results and discussion

3.1. Determination of conversion and polymerization rate

Solid content (SC) of latex during the progress of reaction was measured gravimetrically according to ASTM D1417 (method B). Samples of about 5–6 g were withdrawn from the bottom of reactor in a closed vial. After weighing, each sample was quenched immediately by the addition of 1 ml of 1% (w/v) hydroquinone solution in methanol. Then, samples were dried at 80 °C under reduced pressure condition until the weight of dried samples become constant. Solid content at time t ($\mathrm{SC}(t)$) was calculated by dividing the weight of dried sample to that of initial sample. It should be noted that the weight of dried samples was corrected by considering the amount of hydroquinone added to each sample (0.01 g). Overall mass conversion ($X_{\mathrm{ov}}(t)$) was calculated according to the following equation (Eq. (1)) for each sample. All of the obtained data are figured out in the next section.

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

Overall polymerization rate per unit volume of the continuous phase (R_{p}) in a batch emulsion polymerization could be determined by Eq. (2).

$$R_{\mathrm{p}}(t)=C_{\mathrm{M},0}\frac{\mathrm{d}\theta(t)}{\mathrm{d}t}\cong C_{\mathrm{M},0}\frac{\mathrm{d}X_{\mathrm{ov}}(t)}{\mathrm{d}t} \tag{2}$$

Generally, when there is more than one monomer in the system, R_{p} should be obtained with respect to molar conversion of monomers. We studied the kinetics of reaction in the range of 0.1–0.44 of mass conversion and according to some calculations; it was observed that the difference between molar and mass conversions is less than 7%. $X_{\mathrm{ov}}(t)$ is obtainable experimentally and $\theta(t)$ could be calculated according to the following equation (Eq. (2.1)):

$$\theta(t)=X_{\mathrm{ov}}(t)\frac{(1+F)(f_0\mu+1)}{(f_0+1)(1+F\mu)} \tag{2.1}$$

in which:

$$f_0=\frac{f_0(\mathrm{St})}{f_0(\mathrm{Bu})};\quad F=\frac{r_{\mathrm{St}}f_0^2+f_0}{r_{\mathrm{Bu}}+f_0};\quad \mu=\frac{M_{\mathrm{M}}(\mathrm{St})}{M_{\mathrm{M}}(\mathrm{Bu})} \tag{2.2}$$

From polymerization recipe (Table 1), f_0 (initial mole ratio of St to Bu) was obtained to be 0.7813. By substituting the obtained f_0 and monomer reactivity ratio data (Table 2) in Eq. (2.2), F was obtained to be 0.4981. Thus $\theta(t)/X_{\mathrm{ov}}(t)$ was equal to 1.0751 (Eq. (2.1)). As a consequence, we could consider R_{p} based on overall mass conversion (practically obtainable) in our equations with about 7% error, which is not really very critical. It should be noted that the conversion rate ($\mathrm{d}X_{\mathrm{ov}}(t)/\mathrm{d}t$) was obtained from the slope of linear part of the curve relating to the mass conversion versus time. This has ignorable deviation from that obtained in molar conversion versus time curve. Hence, the error in calculation of polymerization rate is much less than 7%. Also this is repeated for all procedures as the same and causes no serious problem in comparative studies. It should be noted that the effect of carboxylic acid monomer amount could be neglected relative to styrene and butadiene due to its low amount in the emulsion polymerization recipe as well as its low solubility in the particle phase (see the partition coefficients of carboxylic acid monomers in Table 2).

Table 2
Some useful parameters used in the calculations

Parameter	Monomer	Amount	Reference
M_{M} (g mol^{-1})	St	104.15	Chemical catalogue
	Bu	54.09	Chemical catalogue
ρ_{M} (kg m^{-3})	St	906 (20 °C)	[26]
		861.8 (70 °C)	[26]
	Bu	555.6 (70 °C)[a]	[27]
C_{MP} (mol dm^{-3})	St	5.5	[11,25]
r_{St}, r_{Bu}	St, Bu	0.5, 1.4	[28]
k_{p}(dm^3 mol^{-1} s^{-1}) at 70 °C	St	480	[29]
k_{p}(dm^3 mol^{-1} s^{-1}) at 70 °C	Bu	290	[30]
k_{p}(dm^3 mol^{-1} s^{-1}) at 70 °C	AA	59,200	[31]
k_{p}(dm^3 mol^{-1} s^{-1}) at 70 °C	MAA	1208	[32]
k_{p}(dm^3 mol^{-1} s^{-1}) at 70 °C	IA	35.6[b]	[33]
α_{MAA}[c]	MAA	1.01 (25 °C)	[34]
α_{AA}[c]	AA	0.102 (25 °C)	[34]
α_{IA}[c]	IA	0.01 (50 °C)	[35]
Water solubility (mM) at 70 °C	St	6.2	[14]
	Bu	50	[14]

[a] ρ_{Bu} at 70 °C was calculated via the given values of ρ_{Bu} at 15 and 50 °C [27] by assuming that relation between density and temperature is linear [26].

[b] Value reported for dimethyl itaconate. It is very likely that IA has a k_{p} value similar to that of dimethyl ester, although no study on this matter currently exists.

[c] α_{i} is the partition coefficient of carboxylic acid monomer i between styrene and water.

Although the aqueous phase plays an important role in emulsion polymerization the particle phase is the major locus for polymerization progress. Hence, the participation of propagation in aqueous phase and its effect on R_{p} could be neglected [11,12,16]. So R_{p} is calculated from Eq. (3).

$$R_{\mathrm{p}}=\frac{\bar{k}_{\mathrm{p}}\bar{n}N_{\mathrm{p}}C_{\mathrm{MP}}}{N_{\mathrm{av}}} \tag{3}$$

The above equation (Eq. (3)) is used to determine $\bar{n}$. $\bar{k}_{\mathrm{p}}$ could be estimated in emulsion copolymerization correctly, which will be discussed in the next section.

3.2. Particle size and particle number determination

Generally, polymer particle diameter (d_{p}) and particle size distribution (PSD) could be measured by SEM and TEM techniques. These methods could be applied with accuracy when there are dried latexes. Number of latex particles per unit volume of the aqueous phase could be calculated from the following equation (Eq. (4)).

$$N_p = \frac{6P/W}{\frac{\rho_P}{\rho_W}\pi d_p^3} \tag{4}$$

In Eq. (4), ρ_P and ρ_W would be equal to 1 g/cm^3 for XSBR [10–16] and 1.00 g/cm^3 for water, respectively. P/W is a function of monomer to water ratio and conversion. So P/W in emulsion polymerization systems could be calculated as follows (Eq. (5)).

$$\frac{P}{W} = \frac{M}{W} X_{ov} \tag{5}$$

We could use the following equation to obtain monomer swollen particles' diameter in the batch emulsion polymerization [10,16].

$$d_{pswol}^3 = d_p^3 \left[1 - \frac{M_M C_{MP}}{\rho_M}\right]^{-1} \tag{6}$$

In intervals I and II of emulsion polymerization model introduced by Harkins [24], the monomer still exists as a separate phase and C_{MP} depends only on the particle diameter. It should be noted that for polymer particles greater than about 50 nm, C_{MP} is almost independent of particle diameter [25]. Monomer phase disappears in interval III and the overall conversion will be also an effective parameter on the C_{MP}.

Two situations can be considered in determination of polymer particles' diameter by using DLS technique: (i) when the conversion is near 100%, the measured particle sizes are almost equal to those obtained from SEM and TEM techniques. It is noteworthy that the hydrodynamic diameter of latex particles measured by DLS is slightly larger than those measured by SEM and TEM due to the swelling of carboxylic acid groups at the surface of latex particles. The diameter of polymer particles determined by SEM and TEM is measured on dry samples. (ii) When the conversion is low, DLS analysis gives d_{pswol} (real diameter of polymer particles swelled with monomers under the polymerization conditions) while SEM and TEM give d_p (diameter of dried polymer particles).

In addition to withdrawing the samples for conversion analysis, a separate sampling for DLS analysis and SEM observations was carried out at various time intervals for all the experiments. Then, suitable sample for particle size analysis by DLS was selected according to conversion–reaction time data so that the conversion of sample falls in the interval II of emulsion polymerization because the kinetic parameters such as R_p are calculated from experimental data obtained in steady state conditions, i.e. interval II, of emulsion polymerization. Hence, d_p could be calculated from Eq. (6) by d_{pswol} obtained from DLS analysis (Table 3) and available data for M_M, C_{MP} and ρ_M (Table 2). Then N_p would be obtained by substituting the calculated d_p in Eq. (4). This means that N_p is obtainable indirectly from the data obtained by DLS technique, wherever the polymerization reaction has not reached to the complete conversion. Unreacted butadiene with boiling point of −4.5 °C is evaporated after sampling. So, the unreacted monomers will be styrene (major) and carboxylic acid (minor). The percentage of carboxylic acid monomer relative to styrene in the feed is low and also it does not incorporate completely into the particle phase and mainly remains in the aqueous phase depending on its partition coefficient (Table 2). Therefore, the effect of unreacted carboxylic acid monomer in the swelling of particles (d_{pswol}) and determination of d_p is negligible. Consequently, M_M and ρ_M of styrene at 20 °C (temperature in which DLS analysis has been carried out) could be inserted in Eq. (6). C_{MP} in the interval II of emulsion polymerization could be considered constant because the polymer particles' diameter in all the experiments is large enough. Some useful parameters, available in the literature, are given in Table 2.

Table 3
Data obtained for particle nucleation stage of the emulsifier-free batch emulsion copolymerization of styrene–butadiene–carboxylic acid monomer

Parameter	XSBR1	XSBR2	XSBR3	XSBR4
C_{MP} (mol dm^{-3})[a]	5.5	5.5	5.5	5.5
X_{ov} (kg kg^{-1})[b]	0.2214	0.4372	0.4205	0.3283
M/W (kg kg^{-1})	0.2476	0.2495	0.2524	0.2553
P/W (kg kg^{-1})	0.0548	0.1091	0.1061	0.0838
d_{pswol} (nm)[c]	311.5	184.5	198.3	420.9
Polydispersity (%)[c]	2.45	2.29	2.24	2.51
d_p (nm)[d]	223.17	132.18	142.07	301.55
d_p (nm)[e]	220.69	129.43	–	297.86
N_p (dm^{-3})[d]	9.42×10^{15}	9.02×10^{16}	7.07×10^{16}	5.84×10^{15}

[a] These values are used in Eq. (6) to calculate d_p.
[b] Conversions corresponding to the samples used for DLS analysis.
[c] d_{pswol} and its polydispersity were obtained from DLS measurements.
[d] These values were calculated indirectly from DLS data (d_{pswol}).
[e] These data were obtained directly from SEM measurements.

It should be noted that R_p was obtained from the data in the range of 10–44% conversion in all experiments (interval II of emulsion polymerization in which C_{MP} is equal to 5.5 mol dm^{-3} [25]). The major problem, which arises here, is from the insertion of C_{MP} amount in Eq. (6). C_{MP} (5.5 mol dm^{-3}) could be used up to 50% conversion, which corresponds to the end of interval II in emulsion polymerization (see Fig. 1) and then decrease with increasing the conversion.

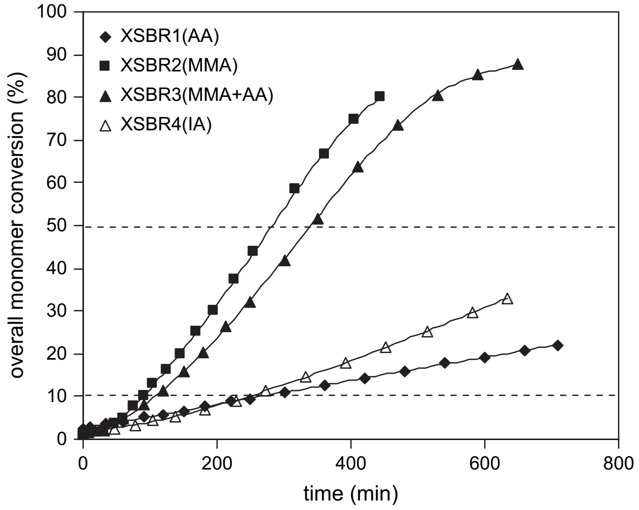

Fig. 1. Overall mass conversion as a function of reaction time in emulsifier-free batch emulsion polymerization of styrene–butadiene–carboxylic acid monomer.

This means that C_{MP} is dependent on the conversion in interval III. As conversion of the latex samples used in DLS analysis was below 44% in all the experiments (Table 3), C_{MP} corresponding to interval II of emulsion polymerization, i.e. 5.5 mol dm^{-3}, was inserted in Eq. (6) and then d_p was calculated. The obtained d_{pswol} and calculated d_p are mentioned in Table 3.

3.3. Estimation of $\bar{k}_p$ in emulsifier-free emulsion copolymerization of styrene–carboxylic acid monomer

In order to analyze the kinetics of reaction we could determine $\bar{n}$ by knowing R_p, N_p, $\bar{k}_p$ and C_{MP}. Subsequently the kinetics of reaction would be discussible according to Eq. (3).

The more conventional model for discussing the kinetics and chemical composition is the terminal model [36,37]. According to this model, $\bar{k}_p$ in the copolymerization reaction could be obtained as follows (Eq. (7)).

$$\bar{k}_p = \frac{r_i f_i^2 + 2 f_i f_j + r_j f_j^2}{\dfrac{r_i f_i}{k_{p,ii}} + \dfrac{r_j f_j}{k_{p,jj}}} \tag{7}$$

Mole fraction of monomers in the monomer droplets and polymer particles is the same for monomers with low solubility in water [38]. However, when water-soluble monomer (such as carboxylic acid monomers) is used together with water-insoluble monomer (such as styrene and butadiene) in the emulsion polymerization recipe, the mole fraction of water-soluble monomer in monomer droplets and polymer particles is determined by its partition coefficient in organic and aqueous phases. It is clear from partition coefficients of carboxylic acid monomers given in Table 2 that the amount of MAA, AA and IA in oil (styrene) phase is about 50, 9 and 1% of the initial amount, respectively. As a consequence, the effect of carboxylic acid monomer concentration in oil phase on $\bar{k}_p$ could be neglected due to its little amount in the recipe as well as its little incorporation into the polymer particle phase as a result of its high solubility in the aqueous phase except MMA. Although the initial concentration of MAA in oil phase is relatively high (about 50% of initial amount, i.e. 2.39 g or 0.020 mole fraction in experiment XSBR2 (Table 1)) the effect of its relatively high initial concentration in the oil phase on $\bar{k}_p$ could be neglected because the propagation rate constant ($k_{p,MAA}$) for MAA homopolymerization has no significant difference from that of St and Bu homopolymerizations at the same reaction temperature (Table 2). Therefore, $\bar{k}_p$ was calculated to be close to 364 dm^3 mol^{-1} s^{-1} (average propagation rate coefficient of the copolymerization of St and Bu) in all the experiments with regard to the above assumptions and the data available in Table 2.

3.4. Effect of carboxylic acid monomer on the particle growth

3.4.1. DLS studies

Jacobi [39] and Priest [40] published the first reports on the mechanism of homogeneous nucleation. Fitch and Tsai [41] and Ugelstad and Hansen [42] proposed the quantitative theory for this phenomenon. The theoretical point of view of the homogeneous and/or coagulative nucleation was presented as Hansen–Ugelstad–Fitch–Tsai (HUFT) theory. The mechanism of particle formation in non-micellar (such as 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 to their critical point in which they become insoluble in water phase. At this time they begin to precipitate and generate precursor polymeric particles. Then the monomers diffuse from their droplet phase and penetrate into the newly formed latex particles in order to swell them and propagate the polymerization reaction. These particles are colloidally unstable and have to coagulate to form the stable primary particles to compensate with 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 the above explanation, it is necessary to know the role of water-soluble monomers in emulsifier-free emulsion polymerization systems.

In the previous paper [22], we investigated the effect of carboxylic acid monomer on particle nucleation stage (i.e. on N_p) in emulsifier-free emulsion polymerization of styrene–butadiene–carboxylic acid monomer. It was observed that the number of particles per unit volume of the aqueous phase (Table 3) and thus polymerization rate (Fig. 1) increased with increasing the hydrophobicity of carboxylic acid monomer. In the continuum of work, we examined here the effect of various carboxylic acid monomers on the particle growth in emulsifier-free emulsion polymerization of styrene–butadiene–carboxylic acid monomer (Table 1). Also, the effect of butadiene monomer on particle growth was investigated by comparing the results obtained here for XSBR latexes and those obtained already for carboxylated polystyrene latexes [21] at the same reaction conditions. It should be noted that in all the experiments, there was no problem concerning stability of the obtained latexes. The results of DLS analysis revealed the narrow particle size distribution so that the polydispersity of polymer particles was always below 3%. Some useful information obtained in the previous study [22] is summarized in Table 3.

Data summarized in Table 3 show that the number of latex particles per unit volume of the aqueous phase (N_p) increases remarkably with increasing the hydrophobicity of carboxylic acid monomers (see the partition coefficients of carboxylic acid monomers in Table 2) in the order IA < AA < (IA + MAA) < MAA [22]. This could be attributed to the increase in number of precipitating oligoradicals during nucleation stage and don't permission of particles to limited flocculation in the growth step. Some evidence for this behavior could also be found in the progress of reaction below 10% conversion, i.e. particle nucleation stage (Fig. 1). The polymerizations performed with most hydrophilic monomer, itaconic acid, had a significantly lower reaction rate. It is evident that the polymerization rate below 10% conversion (particle nucleation period) has a direct proportionality with hydrophobicity of carboxylic acid monomers since logically it should generate more stable primary particles. This matter has been explained comprehensively in the previous article [22].

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 (polymerization rate per particle) are given in Table 4. It is expected that at the same conditions of monomer to water ratio, diameter of polymer particles and number of polymer particles per unit volume of aqueous phase, the polymerization rate per particle decrease with increasing the hydrophilicity of carboxylic acid monomers due to the low efficiency of oligoradicals entry into the polymer particles. This expectable trend could not be seen for our experiments (Table 4) due to non-equal numbers of polymer particles per unit volume of water and thereby non-equal diameter of polymer particles. Trends observed here will be explained in detail in the next section. However, it may be deduced from the above data that carboxylic acid monomer type has a significant effect on both particle nucleation (N_p) and growth (R_p/N_p) processes.

3.4.2. SEM studies

In addition to one sample selected from each experiment for DLS analysis, all samples were used in SEM observations in order to further investigate the evolution of average diameter of polymer particles (d_p) with conversion from which N_p as a function of mass conversion was calculated via Eq. (4). Samples of experiments XSBR1, XSBR2 and XSBR4 were investigated in the SEM observations (Fig. 2) as the representative samples for emulsifier-free emulsion copolymerization of styrene and butadiene in the presence of AA, MAA and IA, respectively. The results of N_p versus mass conversion are given in Fig. 3. It should be noted that same as DLS results, the polydispersity of polymer particles' size in SEM measurements (Fig. 2) was always below 3%, indicating the narrow distribution of polymer particles' size.

Table 4
Kinetic parameters obtained for emulsifier-free emulsion copolymerization of styrene–butadiene–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})	1.577×10^{-21}	1.231×10^{-21}	1.308×10^{-21}	5.600×10^{-21}
$\overline{n}$	0.474	0.370	0.393	1.685
R_p/N_p (mol s^{-1})[a]	2.113×10^{-21}	4.275×10^{-21}	2.773×10^{-21}	28.79×10^{-21}
$\overline{n}$[a]	0.482	0.975	0.633	6.569

[a] Data reported for emulsifier-free emulsion polymerization of styrene–carboxylic acid monomer at the same reaction condition with the present work [21]. In the present work only a part of St was replaced with Bu in comparison with the previous work [21].

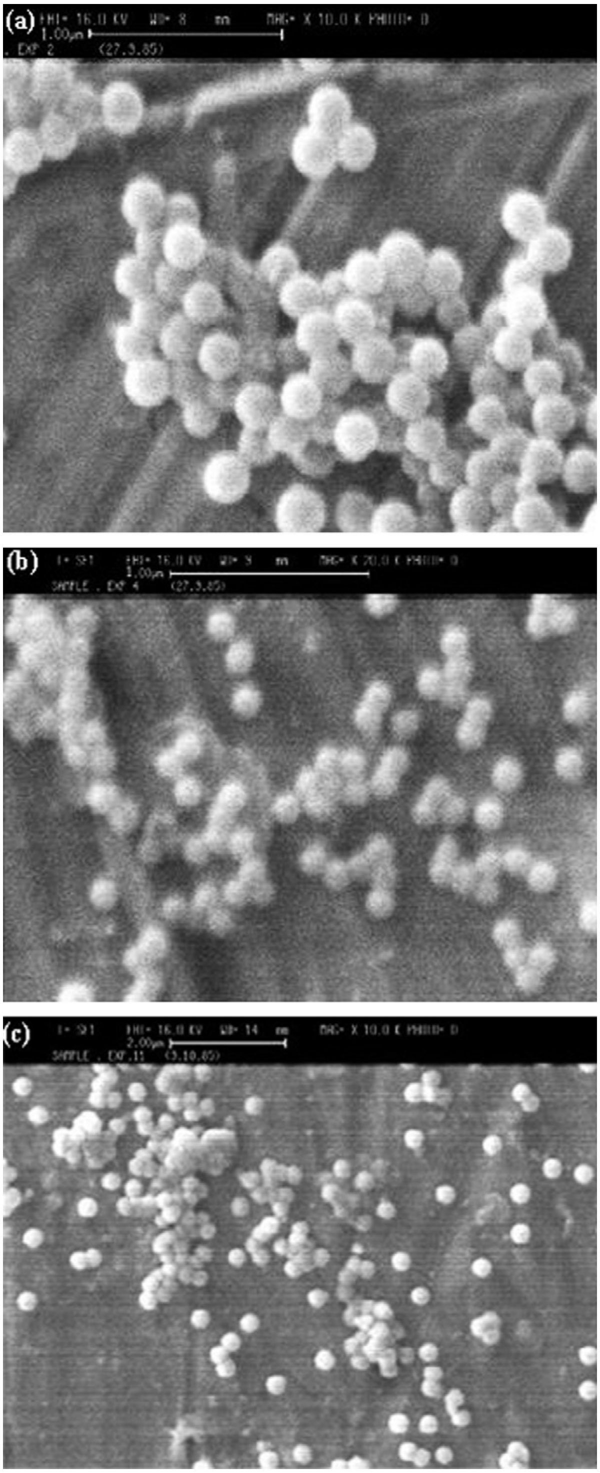

Fig. 2. SEM micrographs of latexes XSBR1 (a), XSBR2 (b) and XSBR4 (c) at the mass conversions of 22.14 (a), 43.72 (b) and 32.83% (c) (see Table 3).

It is clear from Fig. 3 that at the very beginning of the emulsifier-free emulsion polymerization (below about 10% conversion), a large number of precursor particles are formed by homogeneous nucleation mechanisms, and their concentration increases with conversion. This results in a rapid increase in the number of polymer particles. With further growing the polymer particles, surface area of them increases significantly and thereby polymer particles become unstable. At this time, limited coagulation occurs (in order to stabilize the growing

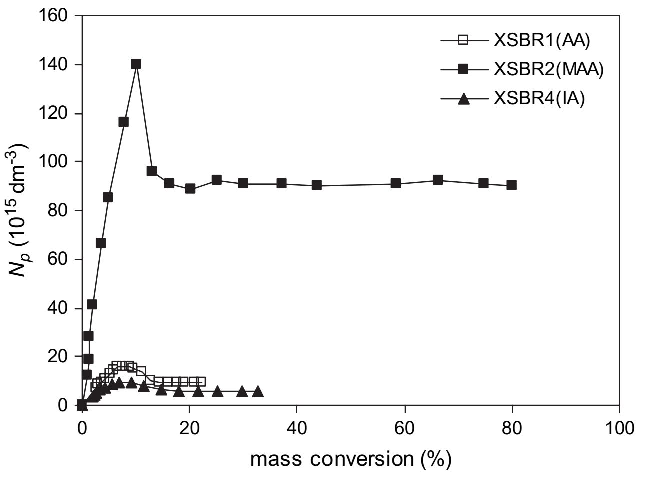

Fig. 3. N_p versus mass conversion for the emulsifier-free emulsion copolymerization of styrene and butadiene in the presence of AA (XSBR1), MAA (XSBR2) and IA (XSBR4).

particles, which lead to the observed decrease in N_p) until a new stabilization condition is reached. Similar results have been observed for the emulsion copolymerization of styrene–butadiene–acrylic acid in the presence of sodium lauryl sulfate emulsifier with the concentration below critical micelle concentration (CMC) [14]. Investigating the effect of carboxylic acid monomers on N_p (kinetic parameter in the particle nucleation stage) is not the aim of present study because this effect has been studied in the previous article [22]. The results in Fig. 3 show that homogeneous-coagulative particle nucleation is occurred in the conversions below about 10% and then N_p become almost constant in the particle growth stage of emulsifier-free emulsion copolymerization of styrene–butadiene–carboxylic acid monomer. Constant N_p in the particle growth stage allows us to calculate the steady state $\bar{n}$ in the interval II of emulsion polymerizations (see next section). Moreover, comparing d_p obtained directly from SEM technique and d_p calculated from DLS data (d_{pswol}) for the same samples (Table 3) shows no significant difference between them. This means that according to Eq. (6), d_p can be calculated by d_{pswol} data obtained from DLS measurements providing that the true value of C_{MP} for the corresponding emulsion polymerization system is known. Therefore, DLS technique was used here to measure d_{pswol} during the interval II of emulsion polymerization from which kinetic parameters in the particle growth stage (R_p/N_p and $\bar{n}$) as well as the effect of carboxylic acid monomers and butadiene on these kinetic parameters were evaluated (see next sections). Slightly greater d_p values in DLS measurements (Table 3) are reasonable because DLS method measures hydrodynamic diameter of monomer swollen polymer particle from which d_p is calculated while SEM measures d_p on the dry state.

3.5. *Effect of carboxylic acid monomer on the efficiency of radical entry into the particles*

Rate of emulsion polymerization in interval II (conversion range of about 0.1–0.5) was almost constant in our system with a proper presumption (Fig. 1). It could be considered that particle nucleation has been occurred before conversion of about 0.1 [13–15]. Therefore, we assumed that N_p is constant in interval II of emulsion polymerization [13–15] and R_p/N_p was calculated during particle growth. The results, which are given in Table 4, show that R_p/N_p and $\bar{n}$ decreases in the order of XSBR4(IA) $\gg$ XSBR1(AA) $>$ XSBR3(MAA + IA) $>$ XSBR2(MAA).

According to Eq. (3), variation in R_p/N_p could be related to the influence of carboxylic acid monomer type on either $\bar{k}_p$ or $\bar{n}$. The influence of carboxylic acid monomer type on C_{MP} is ruled out due to the low amounts of carboxylic acid monomer used in the recipes and its less solubility in particle phase. Moreover, on the basis of discussion in the previous section, the effect of carboxylic acid type on $\bar{k}_p$ is probably very limited and it could not explain the differences in the observed polymerization rates per particle. So the results would be attributed to the influence of carboxylic acid monomer on $\bar{n}$. This parameter was calculated by knowing C_{MP} (Table 2), R_p/N_p (Table 4) and $\bar{k}_p$($\bar{k}_p = 364$ dm^3 mol^{-1} s^{-1}at 70 °C) via Eq. (3). The results are shown in Table 4.

By performing the experiments in the same experimental conditions in regard to the number of polymer particles per unit volume of aqueous phase, diameter of polymer particles and monomer to water ratio, i.e. seeded emulsion polymerization, it is expected that the polymerization rate per particle (R_p/N_p) and average number of the growing chain per particle ($\bar{n}$) decrease with increasing the hydrophilicity of carboxylic acid monomer due to the low efficiency of oligoradicals' entry into the polymer particles. It is clear that critical polymerization degree of oligoradicals formed in the aqueous phase depends directly on the hydrophilicity of carboxylic acid monomers. Higher critical polymerization degree of oligoradicals formed in the aqueous phase can result in the increased concentration of oligoradicals in the aqueous phase and thereby oligoradicals may be terminated before entering into the polymer particles. As a consequence, the efficiency of oligoradicals entry into the polymer particles decreases. It should be noted that although the concentration of carboxylic acid monomeric free radicals formed by transfer reactions in the particle phase increases with increasing the hydrophobicity of carboxylic acid monomer but at the same diameter of monomer swollen polymer particles, it is expected that desorption rate of free radicals from polymer particles will not increase significantly because the water solubility of free radicals decreases with increasing the hydrophobicity of carboxylic acid monomer. In the present study, diameter of polymer particles in all the experiments is not same (Table 3) and thus our results should be explained by considering simultaneously the effect of carboxylic acid monomer type as well as the polymer particles' diameter on R_p/N_p and $\bar{n}$ as follows.

There is a way to better understand the effect of carboxylic acid monomer on the polymerization rate per particle and average number of the growing chain per particle without performing the seeded emulsion polymerization. Since polymerization rate per particle in the batch emulsion polymerization is controlled by hydrophilicity of oligoradicals formed in the aqueous phase and diameter of the monomer swollen polymer particles, one can observe truly the effect of hydrophilicity of carboxylic acid monomers on the polymerization rate per particle providing the real diameter of polymer particles under experimental conditions, i.e. the monomer swollen polymer particles' diameter is also considered.

To calculate the average diameter of the monomer swollen particles (d_{pswol}), it was assumed that the number of particles in the interval II of emulsion polymerization (conversion range of 0.1–0.5) is constant and equal to the calculated values in Table 3. This is true because the number of latex particles per unit volume of aqueous phase remains constant in the intervals II and III of emulsifier-free emulsion polymerizations of St–Bu–carboxylic acid monomer [13–15]. Then, similar conversion of 0.4 (interval II) was considered for all experiments due to this fact that R_{p} in Table 4 has been obtained from polymerization rate data in the range of 0.1–0.44. By considering the overall conversion of 0.4 and N_{p} values in Table 3, d_{p} was calculated by Eq. (4) and was substituted in Eq. (6) to calculate d_{pswol}. The major problem, which arises here, is from the insertion of ρ_{M} and M_{M} in Eq. (6). In order to estimate real d_{pswol} under the reaction condition, average density ($\overline{\rho}_{\mathrm{M}}$) and molecular weight ($\overline{M}_{\mathrm{M}}$) of unreacted monomer mixture (both St and Bu) at reaction temperature (70 °C) should be inserted in Eq. (6). $\overline{\rho}_{\mathrm{M}}$ and $\overline{M}_{\mathrm{M}}$ of unreacted monomers in the reaction could be estimated by Eqs. (8) and (9) provided that mole and volume fractions of unreacted monomer mixture at mass conversion of 0.4 are known. It should be noted that the effect of carboxylic acid monomer on $\overline{\rho}_{\mathrm{M}}$ and $\overline{M}_{\mathrm{M}}$ of monomer mixture could be negligible due to its low amount in the copolymerization recipe as well as due to its low incorporation into the particle phase.

$$\overline{\rho}_{\mathrm{M}} = \phi_{\mathrm{i}}\rho_{\mathrm{i}} \tag{8}$$

$$\overline{M}_{\mathrm{M}} = x_{\mathrm{i}}M_{\mathrm{i}} \tag{9}$$

The instantaneous copolymer composition equation of Mayo–Lewis [36] is expressed as Eq. (10).

$$F_{\mathrm{i}} = \frac{r_{\mathrm{i}}f_{\mathrm{i}}^2 + f_{\mathrm{i}}f_{\mathrm{j}}}{r_{\mathrm{i}}f_{\mathrm{i}}^2 + 2f_{\mathrm{i}}f_{\mathrm{j}} + r_{\mathrm{i}}f_{\mathrm{j}}^2} \tag{10}$$

An integration of Eq. (10) leads to the Meyer–Lowry [43] equation as follows:

$$\theta(t) = 1 - \left(\frac{f_{\mathrm{i}}}{f_{\mathrm{i}}^0}\right)^{\alpha}\left(\frac{1-f_{\mathrm{i}}}{1-f_{\mathrm{i}}^0}\right)^{\beta}\left(\frac{f_{\mathrm{i}}^0-\delta}{f_{\mathrm{i}}-\delta}\right)^{\gamma} \tag{11}$$

where

$$\alpha = \frac{r_{\mathrm{j}}}{1-r_{\mathrm{j}}};\ \beta = \frac{r_{\mathrm{i}}}{1-r_{\mathrm{i}}};\ \gamma = \frac{1-r_{\mathrm{i}}r_{\mathrm{j}}}{(1-r_{\mathrm{i}})(1-r_{\mathrm{j}})} \text{ and } \delta = \frac{1-r_{\mathrm{j}}}{2-r_{\mathrm{i}}-r_{\mathrm{j}}}$$

According to the Meyer–Lowry equation, the overall monomer conversion (x) is related to the monomer composition in the reaction mixture and the monomer reactivity ratios.

A material balance in the following equation relates some of these parameters:

$$\overline{F}_{\mathrm{i}} = \frac{f_{\mathrm{i}}^0 - f_{\mathrm{i}}(1-\theta(t))}{\theta(t)} \tag{12}$$

According to some calculations, it was observed that mass conversion of 0.4 corresponds to the almost equimolar amounts of unreacted St and Bu in the reaction mixture (particle phase). First, by assuming f_{i}=0.5 overall molar conversion was calculated by Eq. (11) and data of Table 2 to be 0.451. Then, Eq. (12) was used to calculate $\overline{F}_{\mathrm{i}}(\overline{F}_{\mathrm{St}} = 0.572)$. Finally by insertion of the obtained $\theta(t)$ and $\overline{F}$ in Eq. (2.1), mass conversion was calculated to be 0.429.

Therefore, amounts of unreacted St and Bu in the reaction mixture at mass conversions of 0.4 were considered to be almost equimolar ($f_{\mathrm{St}} = f_{\mathrm{Bu}} = 0.5$). Now Eqs. (8) and (9) together with the data of Table 2 could be used to calculate $\overline{\rho}_{\mathrm{M}}$ (725.2 kg m^{-3}) and $\overline{M}_{\mathrm{M}}$ (79.12 g mol^{-1}), respectively. These values are inserted in Eq. (6) to calculate d_{pswol}. The results are given in Table 5.

Polymerization rate per particle and average number of the growing chain per particle ($\overline{n}$) as a function of monomer swollen polymer particles' diameter (d_{pswol}) are shown in Fig. 4. It is clear that $R_{\mathrm{p}}/N_{\mathrm{p}}$ and $\overline{n}$ increase with increasing d_{pswol} (real diameter of polymer particles during emulsion polymerization). This trend is consistent with emulsion polymerization kinetics in which polymerization rate per particle should be increased with increasing the monomer swollen polymer particles.

From Fig. 5 it is clear that the number of radicals entered into all the particles per unit volume of aqueous phase ($\overline{n}N_{\mathrm{p}}$)

Table 5
Diameter of monomer swollen polymer particles at mass conversion of 0.4 for emulsifier-free emulsion copolymerization of styrene–butadiene–carboxylic acid monomer

Parameter	XSBR1	XSBR2	XSBR3	XSBR4
P/W	0.0990	0.0998	0.1010	0.1021
N_{p} (dm^{-3})	9.42×10^{15}	9.02×10^{16}	7.07×10^{16}	5.84×10^{15}
d_{p} (nm)	271.80	128.33	139.72	322.08
d_{pswol} (nm)	368.91	174.17	189.64	437.15

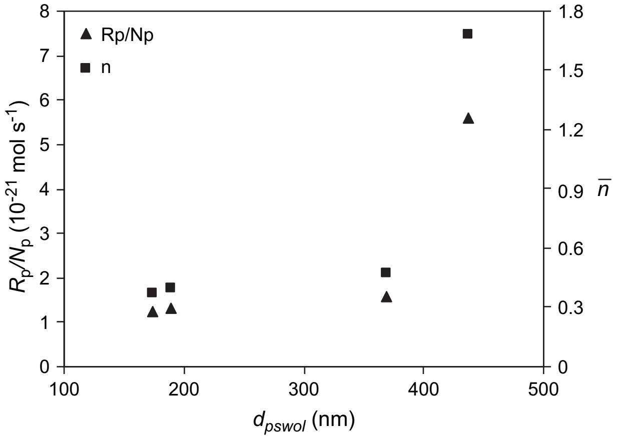

Fig. 4. Polymerization rate per particle and average number of growing chain per particle as a function of monomer swollen polymer particles' diameter (Table 5) in the emulsifier-free emulsion polymerization of styrene–butadiene–carboxylic acid monomer.

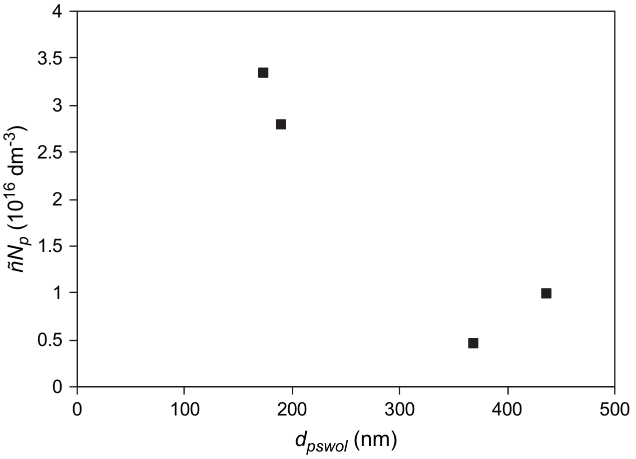

Fig. 5. Number of radicals entered into all the particles per unit volume of aqueous phase ($\bar{n}N_{\mathrm{p}}$) as a function of monomer swollen polymer particles' diameter (Table 5) in emulsifier-free emulsion copolymerization of styrene–butadiene–carboxylic acid monomer.

decreases initially with increasing the monomer swollen polymer particles (d_{pswol}) and then increases in the case of XSBR4(IA). Now trends observed for $R_{\mathrm{p}}/N_{\mathrm{p}}$ (or $\bar{n}$) and $\bar{n}N_{\mathrm{p}}$ can be explained logically as follow.

All the data available in Table 4 show that the polymerization kinetics in experiments XSBR1–XSBR3 obeys Smith–Ewart kinetics (case 1) with $\bar{n} < 0.5$ while emulsion polymerization in experiment XSBR4 follows the Smith–Ewart kinetics (case 3) with $\bar{n} > 0.5$ [44]. In this condition, decrease in $\bar{n}$ with increasing the hydrophobicity of carboxylic acid monomer means that the type of the carboxylic acid monomer influences the mass transfer phenomena mainly and can be explained by increased concentration of carboxylic acid monomeric free radicals formed by transfer reaction from oligoradicals to the carboxylic acid monomers in the particle phase (see the partition coefficient of various carboxylic acid monomers in Table 2) as well as decreased diameter or equivalently decreased surface area per particle of monomer swollen polymer particles (Table 3). The newly formed monomeric radicals have a high solubility in water and can desorb from the particle phase. Moreover, addition of water-insoluble monomers (St and Bu) to the water-soluble carboxylic acid monomeric free radicals makes them water-insoluble, which compete with desorption of them from the polymer particles. The latter will be considerable relative to the former only when the diameter of monomer swollen polymer particles is small enough because the water-soluble monomeric free radicals can transfer easily from the particle phase into the aqueous phase. On the other hand, decreasing d_{pswol} decreases the surface area per particle which in turn decreases the efficiency of oligoradicals entry into each polymer particle. In brief, general trend of $R_{\mathrm{p}}/N_{\mathrm{p}}$ or $\bar{n}$ and $\bar{n}N_{\mathrm{p}}$values can be explained as follows.

General trend of $R_{\mathrm{p}}/N_{\mathrm{p}}$ or $\bar{n}$ values can be described by the effect of carboxylic acid monomer type on both particle nucleation and growth processes. N_{p} increases with decrease in hydrophilicity of carboxylic acid monomer (Table 3). Hence, by considering the similar conversion in these experiments, diameter of the monomer swollen polymer particles decreases with increase in hydrophobicity of carboxylic acid monomer (Table 5) and surface area per particle decreases as a result. This would cause the decrease in entrance efficiency of radicals into each particle and thereby decrease in polymerization rate per particle. It is notable that the increase in N_{p} will result in increase in total surface area. As a consequence, the total radicals entered into all the particles per unit volume of aqueous phase ($\bar{n}N_{\mathrm{p}}$) will increase and thus total polymerization rate will be increased (Eq. (3) and Fig. 1).

From the above discussion, remarkable increase in $\bar{n}N_{\mathrm{p}}$ for most hydrophilic carboxylic acid monomer (IA) in comparison with AA is unexpected but it can be explained by much higher value of $\bar{n}$ in the case of IA (Table 4) as follows. In the equimolar amount of carboxylic acid monomers, pH of aqueous phase in the styrene–butadiene–itaconic acid will be lower than styrene–butadiene–acrylic acid system because itaconic acid is bearing two carboxylic acid functional groups. IA has been shown to greatly induce the thermal decomposition of potassium persulfate initiator due to its carboxyl functional groups [45]. This may result in the increased entry of radicals into the polymer particles (Table 4) in addition to increased termination of these radicals in the aqueous phase. Furthermore, larger size of monomer swollen polymer particles in the particle growth stage (XSBR4, Table 5) can result in the increased efficiency of radical entry into each polymer particles. Some evidence for higher value of $\bar{n}$ in the case of IA (XSBR4) can also be observed in Table 4 as an increased rate of polymerization in the particle growth stage (conversion between 0.1 and 0.35 for XSBR4 in Fig. 1) relative to the particle nucleation stage (conversion below 0.1) in comparison with AA (XSBR1). It should be noted that the formation of itaconic acid monomeric free radicals in the particle phase by transfer reaction and thereby desorption of them from the polymer particles is negligible due to its very low solubility in the particle phase (Table 2).

3.6. *Effect of butadiene on the particle growth (R_p/N_p or $\bar{n}$)*

$R_{\mathrm{p}}/N_{\mathrm{p}}$ and $\bar{n}$ values in the emulsifier-free emulsion copolymerization of St–Bu–carboxylic acid monomer and St–carboxylic acid monomer are given in Table 4. The results for all of the various carboxylic acid monomers show that the presence of butadiene monomer in the emulsifier-free emulsion copolymerization recipe results in the decreased values of $R_{\mathrm{p}}/N_{\mathrm{p}}$ and $\bar{n}$. This can be attributed to the greater water solubility of butadiene monomer in comparison with styrene (Table 2). Yuan et al. [13–15] investigated the role of water-soluble oligomers in the emulsion copolymerization of St–Bu–AA. It was shown that at an emulsifier concentration below CMC, the fraction of Bu units in the water-soluble oligomer chains is comparable with the fraction of AA units, despite the low water solubility of Bu monomer relative to AA (Table 2), while the fraction of St units in the water-soluble oligomer chains is lowest due to the lower water solubility of St in comparison with Bu and AA. From the above discussion, it is expected that the molecular weight of oligoradicals should be increased by replacing a part of styrene with butadiene in emulsion polymerization recipe of styrene–carboxylic acid monomer. Consequently, probability of the termination rate of oligoradicals in the aqueous phase will be increased and thereby the efficiency of oligoradicals entry into the polymer particles will be decreased. Moreover, replacing a part of styrene with butadiene in emulsion polymerization recipe of styrene–carboxylic acid monomer will increase the desorption rate of free radicals from the polymer particle because transfer reaction from oligoradicals (entered into the particles) to the monomeric Bu in the particle phase will result in Bu monomeric radicals with higher water solubility than St monomeric radicals. Therefore, it can be concluded that emulsion copolymerization in the presence of butadiene monomer will lower the growth rate of polymer particles in the emulsion copolymerization of St–Bu–carboxylic acid monomer relative to St–carboxylic acid monomer.

4. Conclusions

Emulsifier-free batch emulsion copolymerization of styrene–butadiene–carboxylic acid monomer led us to some useful information about the influence of various carboxylic acid monomers on the kinetics of reaction. In this work, data obtained from DLS technique (d_{pswol}) were used to obtain average diameter of monomer swollen polymer particles from which the influence of carboxylic acid monomer type on particle growth was evaluated.

SEM studies showed that N_p is almost constant in the particle growth stage (conversion above 10%). This allows us to calculate the average number of growing chain per particle ($\bar{n}$). It was found that the average monomer swollen particles' diameter (d_{pswol}) at the same conversion had direct proportionality with hydrophilicity of carboxylic acid monomer type (with respect to N_p). The effect of various carboxylic acid monomers on polymerization rate per particle (R_p/N_p) and $\bar{n}$ was investigated as a function of d_{pswol} at the same conversion. It was observed that R_p/N_p and $\bar{n}$ increase with increasing d_{pswol}, which is consistent with emulsion polymerization kinetics. It was deduced that the carboxylic acid monomer type has a significant effect on both particle nucleation (N_p) and growth (R_p/N_p and $\bar{n}$) processes. Also, comparison of the results obtained here for XSBR latexes and those obtained already for carboxylated polystyrene latexes showed that kinetic parameters related to the particle growth stage (R_p/N_p and $\bar{n}$) decrease with replacing a part of styrene with butadiene in the emulsion polymerization recipe of styrene–carboxylic acid.

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