Investigation into the effect of carboxylic acid monomer type on the particle nucleation in the emulsifier- free emulsion copolymerization of styrene and butadiene

Mahdi Abdollahi[1], Ali Rahmatpour[1], Navid Naderpour[2], Malek Abbas Gholamzadeh Alam[2]

Division of Polymer Science and Technology, Research Institute of Petroleum Industry (RIPI), P. O. Box 18745-4163, Tehran, Iran; E-mail: abdollahim@ripi.ir

Abstract
Carboxylated styrene- butadiene rubber (XSBR) latexes were prepared by emulsifier- free emulsion copolymerization of styrene and butadiene with various carboxylic acid monomers. The effect of various carboxylic acid monomers on the particle formation process was investigated. It was observed that the type of carboxylic acid monomer strongly affected the particle nucleation. Number of particles and thus polymerization rate increased with increasing hydrophobicity of carboxylic acid monomers. There was significant difference in the polymerization rate per particle. Results showed that particle nucleation and growth are dependent on the hydrophilic nature of carboxylic acid monomers. Average particle diameter of XSBR latexes in the dry state was obtained through some calculations from the direct measurement of average particle diameter in the monomer- swollen state by dynamic light scattering technique. Several parameters such as polymerization rate, number of latex particles per unit volume of the aqueous phase and polymerization rate per particle were calculated.
Key words: XSBR latex; Emulsifier- free emulsion copolymerization; particle nucleation

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 [1-3]. 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. Conventional emulsion polymer systems often use monomers that are relatively water- insoluble such as styrene, acrylonitrile and butadiene. 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 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 latexes comprise an important class of industrial emulsion polymer systems involving water- soluble carboxylic acid monomers. Carboxylic acid monomers (such as AA and IA) are often completely soluble in water. However, they will still partition to varying extents into the organic phase depending on their 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 [1-8], there are few reports about the effect of carboxylic acid monomer on the nucleation process and particles growth in the literature [9-11]. These are among the most important parameters, which should be assigned in

---

[1] Corresponding Author; Research Institute of Petroleum Industry; E-mail: abdollahim@ripi.ir
[1] Research Institute of Petroleum Industry
[2] Bandar Imam Petrochemical Complex

emulsion polymerization technique. However, in recent years due to high progresses in analytical techniques, investigation of these parameters has become plausible [12–18].

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 [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 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 [12-14] 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 [15-17] 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 [18] investigated the effect of carboxylic acid monomer amount on both particle nucleation and growth in emulsifier- free batch emulsion copolymerization of styrene- butadiene- acrylic acid by dynamic light scattering technique for the first time. It was observed that the number of particles and thus polymerization rate increased with increasing of 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. The 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.

The present article attempts to provide insight into the influence of carboxylic acid monomer type on 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, dynamic light scattering technique is used here to obtain average diameter of monomer swollen polymer particles from which the influence of carboxylic acid monomer type on particle nucleation and growth is evaluated.

Experimental
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 A°, 155 m^2/g surface area, Aldrich) column. The purified styrene monomer was stored in a refrigerator until use. Acrylic acid (AA) from Aldrich and methacrylic acid (MAA) from Merck were distilled under vacuum to remove the inhibitor. The purified carboxylic acid monomers were stored at about 14 ^{o}C under running tap water. Potassium persulfate (KPS) as initiator, itaconic acid (IA) monomer both 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 was measured by a D5000 SIEMENS dynamic light scattering (90°) at ambient temperature (20 $^{\circ}$C).

Polymerization procedure

Emulsifier- free batch emulsion polymerizations were carried out according to procedure reported in the literature [23] 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 have been mentioned in Table 1. The reactor was charged under nitrogen at room temperature with all 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.

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

Ingredients (gr)	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 hrs depending on the type of carboxylic acid monomer used in the recipe (see Fig. 2).
[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.

Results and Discussion

Determination of conversion and polymerization rate

Solid content (SC) of each latex was measured during the progress of reaction according to ASTM D1417 (method B) by weighing of each sample in a closed vial. Each sample was quenched immediately by addition of 1 ml of 1% (w/v) hydroquinone solution in methanol. Then, samples were dried at 80 $^{\circ}$C under reduced pressure condition and SC(t) was calculated. Overall mass conversion was calculated according to the following equation (Eq. (1)) for each sample [18]. All of the obtained data have been figured out in next section.

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

Overall polymerization rate per unit volume of the continuous phase (R_p) in a batch emulsion polymerization could be determined by Eq. (2) [18].

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

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 kinetic 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%. $X_{ov}(t)$ is obtainable experimentally and $\theta(t)$ could be calculated according to the following equation (Eq. (2.1)) [18]:

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

In which:

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

By substitution of the data available in Tables 1 and 2 in Eq. (3.2), f_0 and F were obtained 0.7813 and 0.4981, respectively. Thus $\theta(t)/X_{ov}(t)$ was equal to 1.0751 (Eq. (3.1)). 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 ($dX_{ov}(t)/dt$) was obtained from the slope of linear part of the curve relating to the weight 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 or concentration.

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 form the following Equation (Eq. (4)) [12, 15, 18].

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

In Eq. (4), ρ_P and ρ_W would be equal to 1 g/cm³ for carboxylated XSBR [12-18] and 1.00 g/cm³ 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 below (Eq. (5)). [12]

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

We could use the following equation to obtain monomer swollen particles diameter in the batch emulsion polymerization [12, 18].

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

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 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 exist in determination of polymer particles diameter by using of dynamic light scattering technique: (i) when the conversion is near 100%. Then, the measured particle sizes are almost equal to

those obtained from SEM and TEM techniques. It is noteworthy that hydrodynamic particles diameter is measured by dynamic light scattering analysis, which is slightly larger than those measured by SEM and TEM. (ii) When the conversion is low. In this case, dynamic light scattering analysis gives d_{pswol} (real diameter of polymer particles under polymerization conditions) and d_p measurement is not possible.

In addition to withdrawing the samples for conversion analysis, a separate sampling for dynamic light scattering analysis was carried out at various time intervals for all experiments. Then, sample for particle size analysis 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 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) (d_{pswol} obtained from dynamic light scattering analysis) and then N_p would be obtained by substitution of the calculated d_p in Eq. (4). This means that N_p is obtainable indirectly from the data given by dynamic light scattering technique, wherever the polymerization reaction has not reached to the complete conversion. Unreacted butadiene with boiling point of -4.5 ^{o}C is evaporated after sampling. So, the unreacted monomers will be styrene (major) and carboxylic acid monomers (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 the its hydrophilic nature. Therefore, the effect of unreacted carboxylic acid monomer in swelling of particles (d_{pswol}) and determination of d_p is negligible. Consequently M_M and ρ_M of styrene in 20 ^{o}C (temperature in which dynamic light scattering 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 the all experiments is enough large. Some useful parameters, available in the literature, have been given in Table 2.

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. 2) and then decrease with increasing of the conversion. This means that C_{MP} is dependent on the conversion in interval III. As conversion of the latex samples used in dynamic light scattering analysis was below 44% in all experiments (Table 3), C_{MP} corresponding to the 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 d_p have been mentioned in Table 3.

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 ^{o}C)	Chemical catalogue
C_{MP} (mol dm^{-3})	St	5.5	[13,25]
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[a]	[31]
α_{MAA}[b]	MAA	1.01 (25 ^{o}C)	[32]
α_{AA}[b]	AA	0.102 (25 ^{o}C)	[32]
α_{IA}[b]	IA	0.01 (50 ^{o}C)	[33]

[a] 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.

[b] α_i is the partition coefficient of carboxylic acid monomer *i* between styrene and water.

Table 3: Known and obtained data 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
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}