Emulsifier- free emulsion polymerization of styrene: effect of carboxylic acid monomer type on particle nucleation and growth

Mahdi Abdollahi[*], Ali Rahmatpour[1]

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 polystyrene latexes were prepared by emulsifier- free emulsion copolymerization of styrene with various carboxylic acid monomers (AA, MAA and IA). DLS analysis and SEM observations were used to investigate the effect of various carboxylic acid monomers on the particle formation and growth processes. It was found that number of particles per unit volume of aqueous phase (N_p) increases with increasing hydrophobicity of carboxylic acid monomers in order of IA < AA < MAA. There was significant difference in polymerization rate per particle (R_p/N_p) in all the experiments also. The results revealed that both particle nucleation and growth processes are 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 (d_{pswol}) of all the carboxylated polystyrene latexes at the same conversion of 0.4 was obtained to be 325.24, 199.30 and 661.02 nm for AA, MAA and IA respectively. Attempt was made to calculate the average number of propagating radicals per particle and to determine its relevance to the kinetics of particle growth by various carboxylic acid monomers.

Key words: Carboxylated polystyrene latex; Emulsifier- free emulsion polymerization; particle nucleation and growth, Dynamic light scattering

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.[1,2] 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 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 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 are often completely soluble in water. However, they will still partition to varying extents into

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[*] Corresponding author. Research Institute of Petroleum Industry, E-mail: abdollahim@ripi.ir
[1] Research Institute of Petroleum Industry

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.

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.[1-4] In addition, the particle growth process, i.e. polymerization rate per particle or equivalently average number of propagating radicals per particle is also affected by the presences of carboxylic acid monomers.[3, 5-8] Shoaf and Poehlein[7, 8] 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. The model was applied to two seeded carboxylated emulsion copolymerization systems, acrylic acid- styrene and methacrylic acid- styrene. Both experimental and predicted results revealed that the reaction behavior is greatly affected by the type of carboxylic acid monomer, partition of monomer between the various phases and locus of polymerization. The mechanism for acrylic acid- styrene system was more complicated than that or the methacrylic acid- styrene system. Evidence suggested that the primary reaction locus in the acrylic acid- styrene system shifts from the particles to the aqueous phase after the hydrophobic monomer (styrene) has been consumed. 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[5,6] evaluated the average number of propagating radicals 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 propagating radicals per particle in the seeded systems. Yuan et al[9-11] 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. The results indicated that, in the absence of micelles, the water soluble oligomers will grow in the aqueous phase and result in more acrylic acid block dyad sequence units in the oligomer chains, owing to the higher acrylic acid concentration there. When micelles exist, the water soluble oligomers will grow in both the aqueous phase and the organic phase. In this case, fewer acrylic acid dyads will be noted. Mahdavian and Abdollahi[3] 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 using dynamic light scattering (DLS) technique. It was observed that the number of particles 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 propagating 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 course of the free- emulsifier emulsion polymerization of styrene (St) in the presence of various carboxylic acid monomers. 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 nucleation and growth is evaluated. SEM observation is used to confirm data obtained by DLS and to investigate the variation of N_p as a function of mass conversion for various carboxylic acid monomers.

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 column. The purified styrene monomer was stored in a refrigerator until use. Acrylic acid (AA) (Aldrich) and methacrylic acid (MAA) (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 and itaconic acid (IA) monomer both from Merck Chemical Co. 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. Number- 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 number-average diameter of polymer particles (d_p) was determined from these measurements, which was then used to calculate N_p.

Polymerization procedures

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 have been mentioned in Table 1. The reactor was charged under nitrogen at room temperature with all ingredients. Then emulsion polymerization was started at 70 °C.

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

Ingredients	XPS1	XPS2	XPS3	XPS4
Distilled water (g)	420.000	420.000	420.000	420.000
Styrene (g)	100.000	100.000	100.000	100.000
Acrylic acid (g)[b]	4.000	--	---	--
Methacrylic acid (g)[b]	--	4.783	2.392	--
Itaconic acid (g)[b]	--	--	3.614	7.228
KPS (g)[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- 9 h (see Fig. 1)

[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 0.0547.

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

Determination of conversion

Solid content (SC) of latex during the progress of reaction was measured gravimetrically according to ASTM D1417 (method B). Overall mass conversion ($X_{ov}(t)$) was calculated according to the following equation (Eq. (1)) for each sample. All of the obtained data have been figured out in next section.

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

Results and Discussion
Determination of polymerization rat

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

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

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 kinetic of reaction in the range of 0.1- 0.4 of mass conversion. Due to low amounts of carboxylic acid monomers in the polymerization recipe, difference between molar and mass conversions will be negligible.[3] It should be noted that the conversion rate ($dX_{ov}(t)/dt$) was obtained from the slope of linear part of the weight conversion versus time curve in the interval II of emulsion copolymerization, i.e. in the conversion range of 0.1- 0.4. This has ignorable deviation from that obtained in molar conversion versus time curve. As a consequence, we could consider R_p based on overall mass conversion (practically obtainable) in our equations.

Although the aqueous phase plays an important role in emulsion polymerization but the particle phase is mostly the major locus for polymerization progress. Hence, the participation of propagation in aqueous phase and its effect on R_p could be neglected.[3,5,6] So R_p is calculated from Eq. (3).

$$R_p = \frac{\bar{k}_p \bar{n} N_p C_{MP}}{N_{av}} \tag{3}$$

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

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 on dry state. Number of latex particles per unit volume of the aqueous phase could be calculated form 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 1.044 g/cm^3 for carboxylated polystyrene[6,12] 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 below (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.[3,13]

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

In intervals I and II of emulsion polymerization model introduced by Harkins,[14] 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.[12] 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%. Then, 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. In this case, 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).

Table 2: Some useful parameters used in the calculations

Parameter	Monomer	Amount	Reference
M_M (g mol^{-1})	St	104.15	Chemical catalogue
ρ_M (kg m^{-3})	St	9050 (20 ^{o}C) 8618 (70 ^{o}C)	15
ρ_p (kg m^{-3})	St	1044 (50 ^{o}C)	6, 12
C_{MP} (mol dm^{-3})	St	5.5	6, 12
r_{St} , r_{AA}	St, AA	0.4, 0.04	6, 16
r_{St} , r_{MAA}	St, MAA	0.25, 0.55	17, 18
r_{St} , r_{IA}	St, IA	0.35, 0.37	19
k_p(dm^3 mol^{-1} s^{-1}) at 70°C	St	480	20
k_p(dm^3 mol^{-1} s^{-1}) at 70°C	AA	59200	21
k_p(dm^3 mol^{-1} s^{-1}) at 70°C	MAA	1208	22
k_p(dm^3 mol^{-1} s^{-1}) at 70°C	IA	35.6[a]	23
α_{MAA} [b]	MAA	1.01 (25 ^{o}C)	24
α_{AA} [b]	AA	0.102 (25 ^{o}C)	24
α_{IA} [b]	IA	0.01 (50 ^{o}C)	25

[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.

In addition to withdrawing the samples for conversion analysis, a separate sampling for DLS analysis and SEM observations were carried out at various time intervals for all 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 are calculated from experimental data obtained in steady state conditions, i.e. interval II, of emulsion polymerization wherever the N_p is constant. However, the samples available for DLS analysis as well as SEM observations were samples with mass conversions of 8.8, 52.5, 67.8, 97.9, 98.8, 99.7 and 100 %. The sample with mass conversion of 52.5% was selected for DLS analysis (see Table 3) because this conversion is correspond to the interval III of emulsion polymerization wherever the N_p is constant (see next section). Hence, d_p could be calculated from Eq. (6) by d_{pswol} obtained from DLS analysis and available data for M_M, C_{MP} and ρ_M (Table 2). 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 DLS technique, wherever the polymerization reaction has not reached to the complete conversion. 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 partition coefficient (Table 2). 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 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 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- 40% conversion in all experiments (interval II of emulsion polymerization in which C_{MP} is equal to 5.5 mol dm^{-3})[12]. 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 40% conversion which corresponds to the end of interval II in emulsion polymerization (see Fig. 2) and then decrease with increasing the conversion. This means that C_{MP} is dependent on the conversion in interval III. Thus its amount should be corrected for calculation of d_p in experiment XPS2 according to the following relation:

C'_{MP}= (1- [(52.5-40)/(100-40)]) X 5.5 = 4.36 mol dm^{-3}

The obtained d_{pswol} and d_p have been mentioned in Table 3.

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

Parameter	XPS1	XPS2	XPS3	XPS4
C_{MP} (mol dm^{-3})[a]	5.5	4.36	5.5	5.5
X_{ov} (kg kg^{-1})[b]	0.2959	0.5248	0.3211	0.2798
M/W (kg kg^{-1})	0.2476	0.2495	0.2524	0.2553
P/W (kg kg^{-1})	0.0733	0.1309	0.0810	0.0714
d_{pswol} (nm)[c]	285.4	191.2	253.0	569.4
Polydispersity (%)[c]	2.64	2.38	2.56	2.84
d_p (nm[d])	204.3	151.6	181.1	407.7
d_p (nm)[e]	201.3	147.9	---	402.5
N_p (dm^{-3})[d]	1.57×10^{16}	6.88×10^{16}	2.49×10^{16}	1.93×10^{15}

[a] These values were 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.

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 terminal model.[26,27] According to this model, $\bar{k}_p$ in the copolymerization reaction could be obtained as below (Eq. (7)).

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

Mole fraction of monomers in the monomer droplets and polymer particles are the same for monomers with low solubility in water.[28] However, when water- soluble monomer (such as carboxylic acid monomers) is used together with water- insoluble monomer (such as styrene, which aqueous phase solubility for this

monomer at 50 ^{o}C is 4.5 mM[29]) 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 amount of MAA, AA and IA in oil (styrene) phase is about 50, 9 and 1% of 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 and its very little concentration in the polymer particle phase due to high solubility in 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 0.028 mole fraction in experiment XPS2 (Table 1)) but the effect of its relatively high initial concentration in oil phase on $\bar{k}_p$ could be neglected because the propagation rate constant ($k_{p,MAA}$) for MAA homopolymerization have not significant difference from that for St homopolymerization at the same reaction temperature (Table 2). Furthermore, monomer reactivity ratios data reported in literature (Table 2) suggest that the significant amount of MAA incorporates into the copolymer in the initial stage (below 10% conversion in the particle nucleation stage) of emulsion polymerization. Therefore, $\bar{k}_p$ was considered to be close to 480 dm^3 mol^{-1} s^{-1} (propagation rate coefficient of St homopolymerization) in all experiments with regard to the above assumptions and available data in Table 2.

Effect of Carboxylic Acid Monomer on Nucleation and Particle Growth

DLS studies: Jacobi[30] and Priest[31] published the first reports on the mechanism of homogeneous nucleation. Fitch et al[32] and Ugelstad et al[33] 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 to 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 previous paper,[3] we investigated the effect of carboxylic acid amount on particle nucleation stage in emulsifier- free emulsion polymerization of styrene- butadiene- acrylic acid. It was observed that the number of particles and thus polymerization rate increased with increasing the acrylic acid amount. In the present study, we examined the effect of various carboxylic acid monomers on the homogeneous and/ or coagulative nucleation stage as well as particle growth stage in emulsifier- free emulsion polymerization of styrene- carboxylic acid monomer (Table 1). 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 has been summarized in Table 3.

Data given in Table 3 reveals that the number of latex particles per unit volume of the aqueous phase (N_p) will increase remarkably with increasing the hydrophobicity of carboxylic acid monomers (see the partition coefficients of carboxylic acid monomers in Table 2) in the order of IA<AA<(IA+MAA)<MAA (Fig. 1). This could be attributed to the increase in number of precipitating oligoradicals during nucleation stage and prevention of particles from 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. 2). 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 stage)

increases with increasing the hydrophobicity of carboxylic acid monomers since logically it should generate more stable primary particles (see the next section). It should be noted that polymerization rate in the experiments XPS2 and XPS3 increase suddenly above about 60 % conversion due to the gel effect. R_p obtained from Eq. (2) in the conversion range of 0.1-0.4 (interval II of emulsion polymerization) and R_p/N_p (polymerization rate per particle) have been 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 decreases 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 above data that carboxylic acid monomer type has a significant effect on the both particle nucleation (N_p) and growth (R_p/N_p) processes.
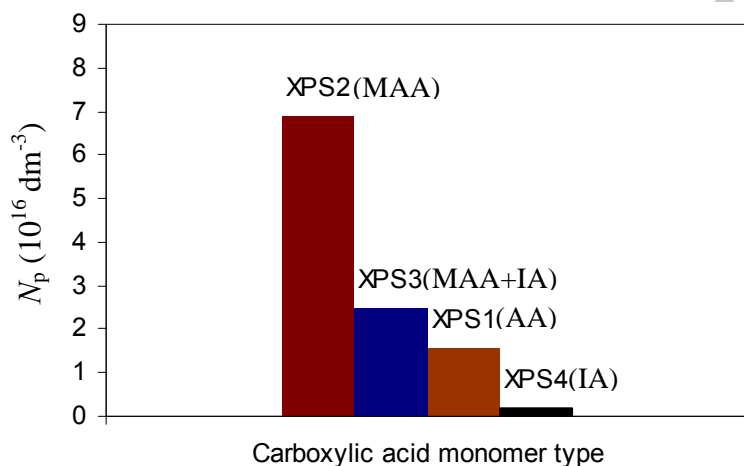

Fig. 1. Dependency of the number of the polymer particles per unit volume of the aqueous phase on the carboxylic acid monomer type
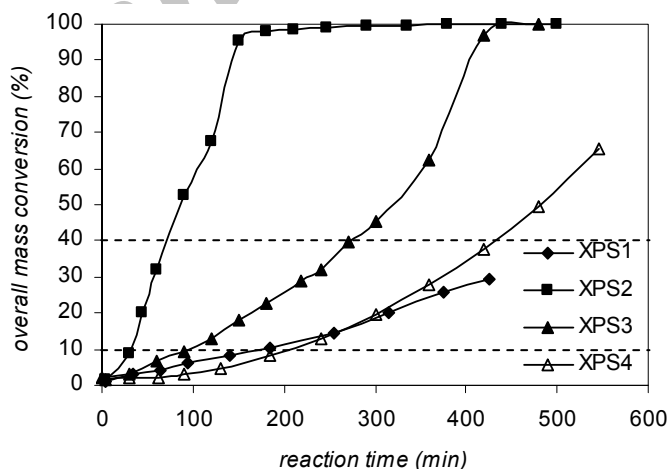

Fig. 2. Overall mass conversion as a function of reaction time in emulsifier- free batch emulsion polymerization of styrene- carboxylic acid monomer

Table 4. Kinetic parameters relating for particle growth stage of emulsifier- free emulsion copolymerization of styrene- carboxylic acid monomer

Parameter	XPS1	XPS2	XPS3	XPS4
dX_{ov}/dt (s^{-1})	1.372×10^{-5}	1.216×10^{-4}	2.860×10^{-5}	2.297×10^{-5}
$C_{M,0}$ (mol dm^{-3})	2.418	2.418	2.418	2.418
C_{MP} (mol dm^{-3})^a	5.5	5.5	5.5	5.5
R_p (mol dm^{-3} s^{-1})	3.318×10^{-5}	2.940×10^{-4}	6.916×10^{-5}	5.554×10^{-5}
R_p/N_p (mol s^{-1})	2.113×10^{-21}	4.275×10^{-21}	2.773×10^{-21}	2.879×10^{-20}
$\bar{n}$	0.482	0.975	0.633	6.569

^{a} These values were used in Eq. (3) to calculate steady state average number of growing radicals per particles ($\bar{n}$).

SEM studies: In addition to one sample selected from each experiment for DLS analysis, all the available samples were used in SEM observations in order to further investigating 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 XPS1, XPS2 and XPS4 were investigated in the SEM observations (Fig. 3) as the representative samples for emulsifier- free emulsion polymerization of styrene in the presence of AA, MAA and IA respectively. The results of N_p versus mass conversion are given in Fig. 4. It should be noted that Small and non- spherical particles in Fig. 3(a) and (b), especially in Fig. 3(a) may be attributed to the existence of a contamination in the SEM sample holder (mainly) or the precipitation of dead water soluble oligomers with many carboxylic acid monomer units during the freeze- drying of latex under vacuum because there was no peak in DLS analysis in the range of these small particles and particle size distribution was completely unimodal in the all experiments. Hence, these small and non-spherical particles are not related to the nucleated particles during emulsion polymerization and thus we did not measure the size of small particles in SEM micrographs. As a result, same as DLS results, the polydispersity of polymer particles size in SEM measurements (Fig. 3) was always below 3%, indicating the narrow distribution of polymer particles size.
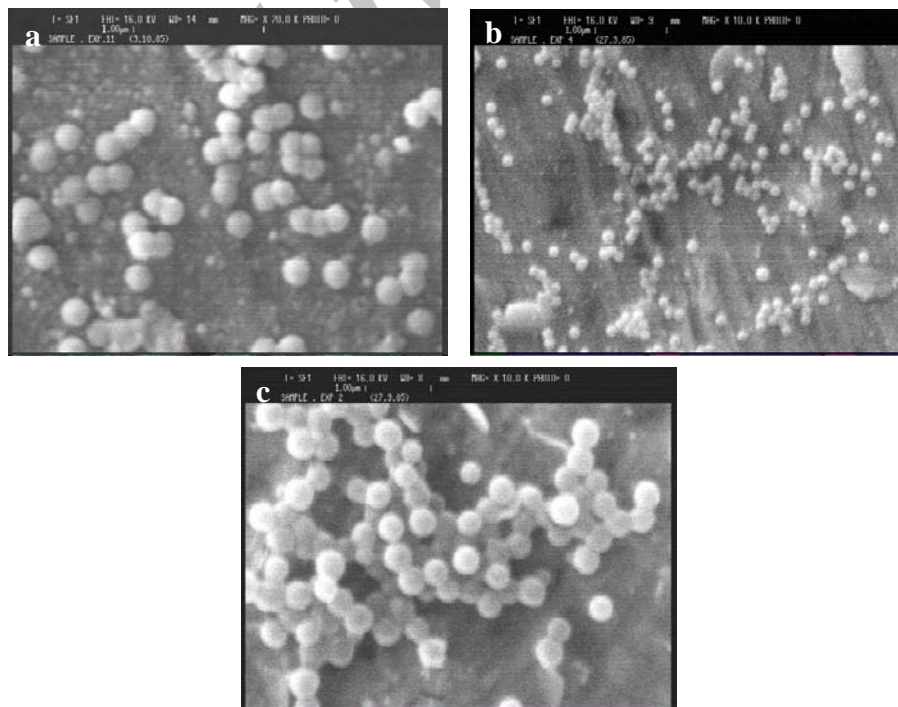
Fig. 3. SEM micrographs of latexes XPS1(AA) (a), XPS2(MAA) (b) and XPS4(IA) (c) at the mass conversions of 29.59 (a), 52.48 (b) and 27.98% (c) (see Table 3)

It is clear from Fig. 4 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 increase significantly and thereby polymer particles become unstable. At this time, limited coagulation occurs (in order to stabilize the growing particles, which leads 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) [11]. The results in Fig. 4 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- 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 by Eq. (3) (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) show 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 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.
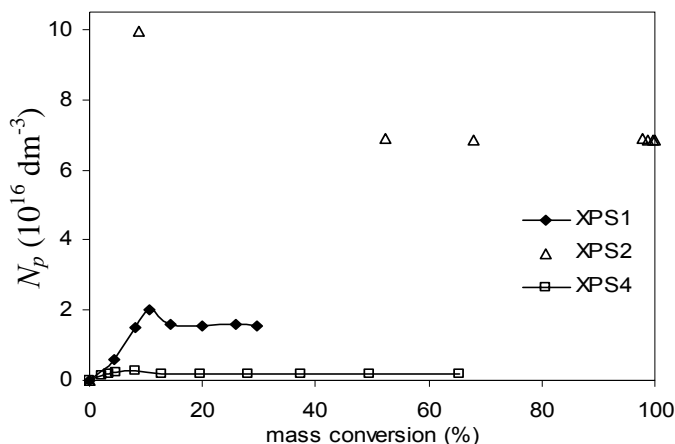

Fig. 4. N_p versus mass conversion for the emulsifier- free emulsion polymerization of styrene in the presence of AA (XPS1), MAA (XPS2) and IA (XPS4)

The function of the carboxylic acid monomer in emulsifier- free emulsion polymerization is twofold according to the mechanism of homogeneous/ coagulative nucleation. It delays the formation of polymer particles by precipitation of oligoradicals formed in aqueous phase after critical degree of polymerization (homogeneous nucleation) and lends stability to the polymer particles. The results in Table 3 and Fig. 4 indicate that the ability of the carboxylic acid monomers to generate particles is inversely related to their hydrophilicity (Table 2), with the most hydrophilic, itaconic acid, being least effective. The similar results

have been deduced from polymerization rate data for the emulsifier- free emulsion polymerization of styrene and styrene- butadiene in the presence of various carboxylic acid monomers,[34] however, attempts have not been made to estimate N_p and other kinetic parameters.

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- 0.4 on the bases of C_{MP} value reported for emulsion polymerization of styren[12]) was almost constant in our system as can be seen in Fig. 2. It could be considered that particle nucleation has been occurred before conversion of about 0.1 (Fig. 4).[9] Therefore, we assumed that N_p is constant in intervals II and III of emulsion polymerization and thus R_p/N_p was calculated during particle growth. The results, which have been given in Table 4, show that R_p/N_p decreases in order of XPS4(IA) >> XPS2(MAA) > XPS3(MAA+IA) > XPS1(AA).

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 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 of C_{MP} (Table 2), R_p/N_p (Table 4) and $\bar{k}_p$ ($\bar{k}_p$ = 480 dm^3 mol^{-1} s^{-1} at 70 ^{o}C, Table 2) via Eq. (3). The results are shown in Table 4.

With 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 propagating radical per particle ($\bar{n}$) decreases 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 the all experiments is not the 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 follow.

There is a way to better understanding the effect of carboxylic acid monomer on the polymerization rate per particle and average number of the propagating radical 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 that the real diameter of polymer particles under experimental conditions, i.e. the monomer swollen polymer particles diameter is considered also.

To calculate the monomer swollen particles diameter (d_{pswol}), it was assumed that the number of particles in the interval II of emulsion polymerization (conversion range of 0.1-0.4) is constant and equal to the calculated values in Table 3. This is true because the number of polymer particles remains constant in intervals II and III of emulsifier- free emulsion polymerizations (Fig. 4). Then, similar conversion of 0.4 (end of interval II on the bases of C_{MP} value of 5.5 mol.dm^{-3}) was considered for all the experiments due to this

fact that $\bar{n}$ in Table 4 have been obtained from polymerization rate data in the range of 0.1-0.4. With 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}. In order to estimate real d_{pswol} under the reaction condition, ρ_M of styrene at 70 ^{o}C (reaction temperature) (Table 2) was inserted in Eq. (6). The results are given in Table 5.

Average number of propagating radicals per particle ($\bar{n}$) as well as the number of propagating radicals into the all particles per unit volume of aqueous phase ($\bar{n}N_p$) as a function of monomer swollen polymer particles (d_{pswol}) are shown in Fig. 5. It is clear that with increasing d_{pswol} (real diameter of polymer particles during emulsion polymerization), number of propagating radicals per particle decrease slightly and then increase significantly in the case of IA (XPS4). According to emulsion polymerization kinetics, number of propagating radicals per particle should be increased with increasing the monomer swollen polymer particles. Nonconformity of experimental data and theoretical prediction can be attributed to the effect of carboxylic acid monomers on both particle nucleation (N_p) and growth (R_p/N_P and thus $\bar{n}$) (see the next section).

From Fig. 5 it is clear that the number of propagating radicals into the all particles per unit volume of aqueous phase ($\bar{n}N_p$) decreases initially with increasing the monomer swollen polymer particles (d_{pswol}) which related to the nature of carboxylic acid monomers and then increases slightly in the case of XPS4. Now, trends observed for R_p/N_p (or $\bar{n}$) and $\bar{n}N_p$ can be explained logically as follow.

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

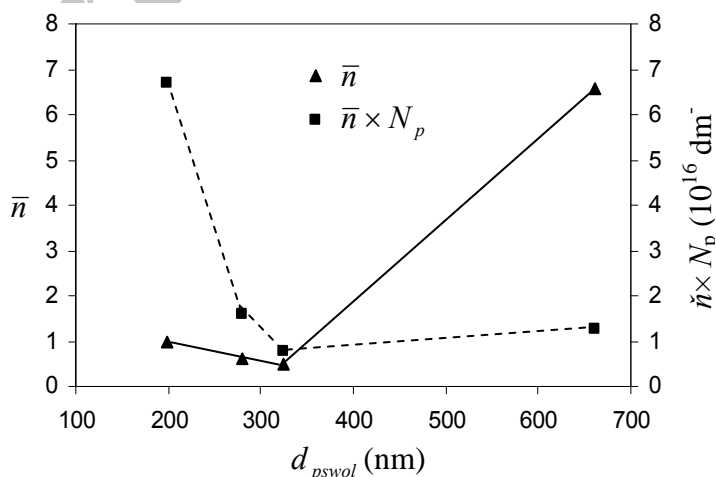| Parameter	XPS1	XPS2	XPS3	XPS4
P/W	0.0990	0.0998	0.1010	0.1021
N_p (dm^{-3})	1.57×10^{16}	6.88×10^{16}	2.49×10^{16}	1.93×10^{15}
d_p (nm)	225.95	138.46	194.91	459.24
d_{pswol} (nm)	325.24	199.30	280.55	661.02
$\bar{n}N_p$ (dm^{-3})	7.57×10^{15}	6.71×10^{16}	1.58×10^{16}	1.27×10^{16}

Fig. 5. Average number of propagating radicals per particle ($\bar{n}$) as well as the number of propagating radicals into the all particles per unit volume of aqueous phase ($\bar{n}N_p$) as a function of monomer swollen polymer particles (Table 5) in emulsifier- free emulsion polymerization of styrene- carboxylic acid monomer

All the data available in Table 4 show that the polymerization kinetic in experiments XPS2, XPS3 and XPS4 obeys Smith- Ewart kinetic (case 3) with $\bar{n} > 0.5$ while emulsion polymerization in experiment XPS1 follows the Smith- Ewart kinetic (case 2) with $\bar{n} \approx 0.5$.[35] For experiments XPS1, XPS2 and XPS3, decrease in $\bar{n}$ with increasing the hydrophilicity of carboxylic acid monomer means that nature of the carboxylic acid monomer influences the mass transfer phenomena and also termination rate mainly. This illustrates the low entry rate of oligomeric radicals (formed in aqueous phase) into the latex particles or increases of radical exit rate from the latex particles. The probable reason that explains the increase in radical exit by increasing hydrophilicity of carboxylic acid monomer might be transfer reactions from oligoradicals to carboxylic acid monomer. The newly formed monomeric radicals have high solubility in water and cause the increase in exit rate of free radicals from the particle phase. Thus, the greater value of $\bar{n}$ for XPS2 (MAA) relative to XPS1 (AA) (Table 4 and Fig. 5) can be attributed to the higher efficiency of oligoradicals entry into the polymer particle in the case of more hydrophobic MAA and to the influence of carboxylic acid monomer on radical exit from polymer particles because the transfer reaction to hydrophilic acrylic acid in XPS1 in comparison with the transfer reaction to hydrophobic methacrylic acid in XPS2 produces monomeric radicals with higher tendency to exit from polymer particles.

General trend of $\bar{n}N_p$ values related to the particle growth stage can be described by considering the effect of carboxylic acid monomer type on the nucleation process. N_p increases with decrease in hydrophilicity of carboxylic acid monomer (Fig. 1). Increase in N_p will result in increase in total surface area of polymer particles. As a consequence, the total oligoradicals entered into the all particles and thereby the number of propagating radicals into the all particles per unit volume of aqueous phase ($\bar{n}N_p$) will increase and thus total polymerization rate will be increased (Eq. 3 and Fig. 2).

From above discussion, increase in $\bar{n}N_p$ 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 follow. In the equimolar amount of carboxylic acid monomers, pH of aqueous phase in the styrene- itaconic acid will be lower than the styrene- 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.[36] 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 (XPS4, Table 5) can be result in the increased efficiency of radical entry into the each polymer particles and the concomitant decrease in the exit rate of radicals from the each polymer particles. Some evidence for higher value of $\bar{n}$ in the interval II of emulsion polymerization in the case of IA (XPS4) can also be observed in Fig. 2 as an increased rate of polymerization in the particle growth stage (conversion between 0.1-0.4) relative to the particle nucleation stage (conversion below 0.1) in comparison with AA (XPS1). 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).

Conclusion
Emulsifier- free batch emulsion copolymerization of styrene- carboxylic acid monomer led us to some useful information about the influence of various carboxylic acid monomers on the kinetics of reaction in terms of the particle nucleation and growth processes. In this work, data obtained from DLS technique (d$_{pswol}$) were used to calculate d_p and N_p (kinetic parameter relating to the particle nucleation stage) for

all the experiments from which the influence of carboxylic acid monomer type on particle growth stage (R_p/N_p and $\bar{n}$) 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 propagating radical per particle ($\bar{n}$). It was found that average monomer swollen particles diameter at the same conversion had direct proportionality with hydrophilicity of carboxylic acid monomer type. Beside that, number of polymer particles and polymerization rate decreased with increasing hydrophilicity of carboxylic acid monomer. Also the effect of various carboxylic acid monomers on polymerization rate per particle (R_p/N_p) and average number of propagating radicals per particle ($\bar{n}$) was investigated as a function of d_{pswol} at the same conversion. 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 or $\bar{n}$) processes.

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Appendix

$X_{ov}(t)$: 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

$\theta(t)$: Overall molar conversion at time t

$\overline{k}_p$: Average propagation rate coefficient in the particle phase

$\overline{n}$: Average number of propagating radicals 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

C'_{MP}: Overall monomer concentration in the polymer particles at interval III

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

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 feed (unreacted monomer)

r_i: Reactivity ratio of monomer i

$k_{p,ii}$: 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