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

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Abstract

Latexes of carboxylated styrene–butadiene rubber were prepared via batch emulsion copolymerization with different amounts of acrylic acid in the absence of emulsifier. The effect of acid monomer was investigated in the particle formation and growth. It was observed that the amount of acrylic acid strongly affected the particle formation. The number of particles and thus polymerization rate increased with increasing of the acid content. There was no significant difference in the polymerization rate per particle in all experiments. The results show 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. Several parameters such as polymerization rate and number of latex particle per unit volume of the aqueous phase were calculated. Attempt was made to evaluate the average number of growing chain per particle. Also average particle diameter of the above carboxylated SBR latexes was obtained through some calculations from the direct measurement of average particle diameter in the swollen state by light scattering technique for the first time.

Keywords: Carboxylated SBR latex; Emulsion polymerization; Particle nucleation and growth

1. Introduction

Carboxylated styrene–butadiene latexes (XSBR) are among the most important polymeric colloids, which are used as binder in paper coatings, carpet backing, paints and non-woven. It has been proved that incorporation of carboxylic acid groups in the polymeric chain has significant effect on colloidal properties of latex, processability and end-use (dry state) property [1].

Despite the presence of several studies on preparation and properties of XSBR latexes [2–8], there are few reports about the effect of carboxylic acid monomer on the nucleation process and particles growth in the literature [9,10]. 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 [11–16].

In emulsion polymerization, emulsifiers could be replaced partly or in some cases completely by monomers containing polar groups. The stabilization of particles in the latex is more effective when the stabilizing agent could be copolymerized or covalently bound to the particle surface instead of being adsorbed physically [9].

The mechanism of particle formation in non-micellar emulsion polymerization is homogeneous and/or coagulative nucleation. The comonomers, which are used in such systems, must have moderate to high solubility in water. XSBR and carboxylated acrylonitrile-butadiene (XNBR) rubbers are typical examples about preparation of latexes in the absence of emulsifier and presence of unsaturated carboxylic acid monomers. In such systems, particle nucleation and oligoradical formation occur simultaneously. The radicals grow up to a critical chain length and generate precursor particles after separation from aqueous phase [17]. These particles are unstable due to colloidal aspects and have to coagulate to form the stable primary particles in order to compensate with this instability. Then propagation is continued in the particles that have been stabilized by

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ionic charges of carboxyl groups and end groups of the initiator.

Here, we have performed emulsion copolymerization of styrene–butadiene–acrylic acid in emulsifier-free condition. Acrylic acid amount is the variable parameter and its role on the particle nucleation and growth has been investigated.

It is noteworthy that light scattering technique is not applicable for measurement of particle size (d_p) directly due to the swelling of particles with unreacted monomers. We have also developed this technique according to some corrections in order to determine the particle size of synthesized XSBR latexes straightly for the first time.

2. Experimental

2.1. Materials and equipments

Styrene (St) was purchased from Merck chemical Co. It was washed twice with NaOH solution (5% w/v) and dried over anhydrous calcium chloride and stored at 0 °C in dark bottles. Acrylic acid (AA) from BASF, potassium persulfate (KPS) from Merck and butadiene (BD) from Bandar Imam Petrochemical Co. (Iran) were used without further purification. Double distilled water was used in each polymerization recipe. Size of the particles was measured by a D5000 SIEMENS light scattering (90°).

Polymerization reactions were carried out in a stainless steel Buchi reactor equipped with mechanical stirrer and heating system with silicon oil circulation.

2.2. Procedure

Emulsifier-free batch emulsion polymerization reactions were carried out in a Buchi reactor equipped with a mechanical stirrer, which was set at 350 rpm (U-shaped shaft). 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.

Table 1
Recipe for batch emulsion copolymerization

	XSBR1	XSBR2	XSBR3
Distilled water (gr)	300.000	300.00	300.00
Styrene (gr)	42.914	42.914	42.914
Butadiene (gr)	28.571	28.571	28.571
Acrylic acid (gr)[a]	1.206	2.444	4.786
KPS (gr)	0.518	0.518	0.518

Mole ratio of St:BD is 1.00:1.28. Total solid content is about 20%. pH in all experiments was about 2.5 due to the presence of acrylic acid. Reaction time was 10–12 h.

[a] $f_{AA}(\text{XSBR1}) = 0.018$; $f_{AA}(\text{XSBR2}) = 0.035$; $f_{AA}(\text{XSBR3}) = 0.066$.

3. Results and discussion

3.1. 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 to consider the weight of unreacted butadiene gas. Each sample was quenched immediately by addition of 0.5 ml of 1% (w/v) hydroquinone solution in methanol. Then, samples were dried at 60 °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. All of the obtained data have been figured out in next section.

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

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

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

Generally, when there exists 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 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)):

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

In which:

$$f_0 = \frac{f_0(\text{St})}{f_0(\text{BD})};\quad F = \frac{r_{\text{St}}f_0^2 + f_0}{r_{\text{BD}} + f_0};\quad \mu = \frac{M_M(\text{St})}{M_M(\text{BD})} \tag{2.2}$$

By substitution of the data available in Tables 1 and 2 in Eq. (2.2), f_0 and F were obtained 0.7813 and 0.4981, respectively. Thus $\theta(t)/X_{ov}(t)$ was equal to 1.0751

Table 2
Some useful parameters

	Monomer	Amount	Reference
M_M (g mol^{-1})	St	104.15	Merck catalogue
M_M (g mol^{-1})	BD	54.09	Merck catalogue
ρ_M (g cm^{-3})	St	0.906 (20 °C)	Merck catalogue
C_{MP} (mol dm^{-3})	–	5.5	[27]
r_{st}	St	0.5	[28]
r_{BD}	BD	1.4	[28]
K_p (dm^3 mol^{-1} s^{-1}) at 70 °C	St	477	[29]
K_p (dm^3 mol^{-1} s^{-1}) at 70 °C	BD	290	[30]
K_p (dm^3 mol^{-1} s^{-1}) at 25 °C	AA	41,000[a]	[31]

[a] Value extrapolated from K_{pAA} in acetic acid at 25 °C.

(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 ($dX_{ov}(t)/dt$) 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 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 acrylic acid amount could be neglected relative to styrene and butadiene due to its low amount or concentration.

Although the aqueous phase plays an important role in emulsion polymerization but 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]. 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 technique correctly, which will be discussed in next section.

3.2. Particle size and particle number determination

Generally, particle diameter (d_p) and particle size distribution (PSD) could be measured by SEM and TEM techniques. The above 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)).

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

In Eq. (4), ρ_P would be equal to 1 g/cm^3 for XSBR [12–16] and also P/W is a function of monomer to water ratio and conversion. So P/W in emulsifier-free systems could be calculated with an acceptable precision as below (Eq. (5)).

$$P/W = \frac{\mathrm{SC}(t)}{1 - \mathrm{SC}(\mathrm{final})} \tag{5}$$

We could use the following equation to obtain particles diameter swollen with monomer [11].

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

In intervals I and II of emulsion polymerization model introduced by Harkins [18], the monomer still exists as a separate phase and C_{MP} depends only on the particle diameter. 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 d_p by using of light scattering technique: (i) when the conversion is near 100%. Therefore, 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 light scattering analysis, which is slightly larger than those measured by SEM and TEM. (ii) When the conversion is low. In this case, light scattering analysis gives d_{pswol} and the particle size (d_p) measurement is not possible.

In this work, the final conversions in our experiments were in the range of 37–67% (Table 3). Hence, d_p could be calculated from Eq. (6) (d_{pswol} obtained from 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 light scattering technique, wherever the polymerization reaction has not reached to the complete conversion. Unreacted butadiene with boiling point of $-4.5\ ^\circ\mathrm{C}$ is evaporated during sampling. So the unreacted monomers will be styrene (major) and acrylic acid (minor). The percentage of acrylic acid relative to styrene in the feed is very few and also it does not incorporate into the particle phase and mainly remains in the aqueous phase. Therefore, the effect of unreacted acrylic acid in swelling of particles (d_{pswol}) and determination of d_p is negligible with correct approximation. Consequently M_M and ρ_M of styrene could be inserted in Eq. (6). C_{MP} could be considered constant in XSBR1 and XSBR2 as the particles' diameter are about the same with regard to the conversion range in which polymerization reactions were terminated in interval II. 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% in all experiments (interval II and C_{MP} were equal to 5.5 mol l^{-1}). The major problem, which arises here, is from the insertion of C_{MP} amount in Eq. (6). C_{MP} (5.5 mol l^{-1}) could be used up to 60% conversion (Fig. 2) and decrease with increasing of 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 XSBR3 according to the following relation:

$$C'_{MP} = (1 - [(67.3 - 60)/(100 - 60)])5.5 = 4.5\ \text{mol l}^{-1}$$

Table 3
Known and obtained data of the batch emulsion copolymerization

	XSBR1[a]	XSBR2[a]	XSBR3[b]
f_{AA}	0.018	0.035	0.066
SC[c]	0.074	0.110	0.138
X_{ov}[c]	0.372	0.546	0.673
P/W	0.080	0.123	0.160
d_{pswol} (nm)	313.3	329.7	273.6
d_p (nm)	224.5	236.3	214.6
N_p (dm^{-3})	1.35×10^{16}	2.83×10^{16}	3.09×10^{16}

[a] $C_{MP} = 5.5$ mol l^{-1}.
[b] $C'_{MP} = 4.5$ mol l^{-1}.
[c] At the final conversion.

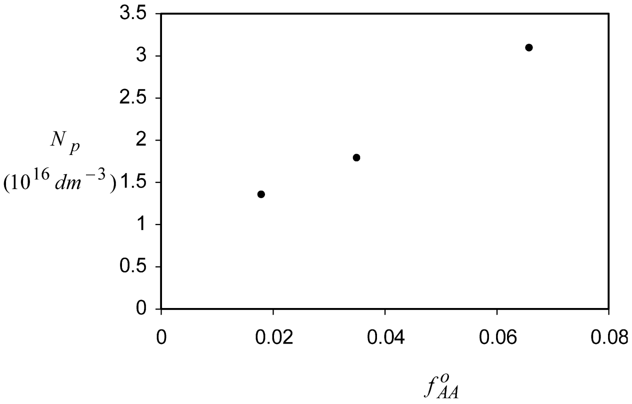

Fig. 1. Changes in number of latex particles per unit volume of the aqueous phase with variation in the initial mole fraction of acrylic acid.

Hence, the obtained d_{pswol} and d_{p} have been mentioned in Table 3.

3.3. Estimation of $\bar{K}_{\mathrm{p}}$ in emulsifier-free emulsion copolymerization of styrene–butadiene–acrylic acid

In order to analyze the kinetics of reaction we could determine $\bar{n}$ by knowing R_{p}, N_{p}, $\bar{K}_{\mathrm{p}}$ 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 [19,20]. According to this model, $\bar{K}_{\mathrm{p}}$ in the copolymerization reaction could be obtained as below (Eq. (7)).

$$\bar{K}_{\mathrm{p}} = \frac{r_i f_i^2 + 2 f_i f_j + r_j f_j^2}{\dfrac{r_i f_i}{K_{p,ii}} + \dfrac{r_j f_j}{K_{p,jj}}} \tag{7}$$

Generally, due to the difference in reactivity ratio of monomers (Table 2), F_{i} is not equal to f_{i} and these parameters depend on conversion amount. This behavior is called as composition drift. Mole fractions of monomers in the droplets and particles phase are the same for monomers with low solubility in water [21]. Hence, the data available in Table 2 and Eq. (7) could be used for investigation of the effect of instantaneous mole fraction of free monomers on $\bar{K}_{\mathrm{p}}$ in copolymerization of styrene–butadiene in the particle phase.

The composition drift has very little effect on $\bar{K}_{\mathrm{p}}$ in emulsion copolymerization of styrene–butadiene according to the results obtained from Eq. (7). Thus in the early stage of polymerization, $\bar{K}_{\mathrm{p}}$ that controls the kinetic of polymerization in particle phase could be estimated logically from initial mole fraction of monomers.

The effect of acrylic acid concentration on $\bar{K}_{\mathrm{p}}$ could be neglected due to its little amount in the recipe and its very little concentration in the particle phase consequently (high solubility in aqueous phase). Therefore, $\bar{K}_{\mathrm{p}}$ was found to be $364\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ in our experiments with regard to the above assumption and data available in Tables 1 and 2.

3.4. Effect of acrylic acid on nucleation and particle growth

Jacobi [22] and Priest [23] published the first reports on the mechanism of homogeneous nucleation. Fitch et al. [17] and Ugelstad et al. [24] proposed the quantitative theory for this phenomenon. The theoretical point of view of the homogeneous nucleation was presented as Hansen–Ugelstad–Fitch–Tsai (HUFT) theory. 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 compose primary 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. According to the above explanation, it is necessary to know the role of water-soluble monomers in emulsifier free systems in which stabilization is their main problem.

As a result, we examined the effect of acrylic acid amount on the homogeneous and/or coagulative nucleation stage in our polymerization process (Table 1). It should be noted that in all experiments, there was no problem concerning stability of the obtained latexes. The results of light scattering analysis reveal the narrow particle size distribution. Some useful information has been summarized in Table 3.

It could be observed that particles size decreases with respect to the number of particles per unit volume of the aqueous phase (N_{p}) by increasing the amount of acrylic acid from sample XSBR1 to XSBR3 (Table 3).

Correspondingly, number of latex particles per unit volume of the aqueous phase (N_{p}) will increase remarkably with increasing in the acrylic acid amount (Fig. 1). This could be anticipated to the increase in number of precipitating oligoradicals during nucleation stage and do

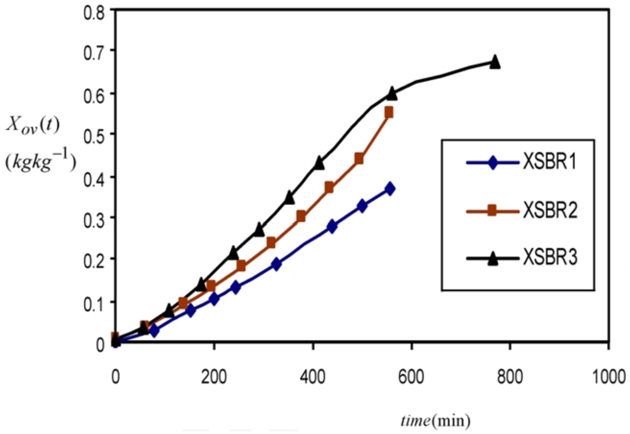

Fig. 2. Overall conversion versus time in batch emulsion copolymerization of styrene–butadiene–acrylic acid.

not allow permission of particles to limited flocculation in the growth step. Some evidence for this behavior could also be found in the progress of reaction (Fig. 2). The polymerization performed with a smaller amount of acrylic acid had a significantly lower reaction rate. It is evident that the polymerization rate has direct proportionality with acrylic acid amount since (i) logically it should generate more particles and (ii) the K_p of acrylic acid is very high at low pH (Table 2).

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. Consequently, despite the significant increase in R_p with increasing of acrylic acid amount in different samples, observed changes in R_p/N_p (particle growth process) was little in comparison to N_p (particle nucleation process).

It is deduced from the above data that acrylic acid amount has little effect on particle growth process (R_p/N_p) and it mainly affects on the nucleation process and eventually the particle number.

3.5. Effect of acrylic acid on the efficiency of radical entrance into the particles

Rate of emulsion polymerization in interval II (conversion range of about 0.1–0.4) was almost constant in our system with a proper presumption (Fig. 2). It could be considered that nucleation has been occurred before conversion of about 0.1 [14]. Therefore, we assumed N_p was constant in interval II of emulsion polymerization and R_p/N_p was calculated during particle growth. The results, which have been plotted in Fig. 3, show that R_p/N_p and $\bar{n}$ decrease with a smooth slope by increasing the acrylic acid amount in the feed.

According to Eq. (3), variation in R_p/N_p could be related to the influence of acid content on either $\bar{K}_p$ or $\bar{n}$. The influence of acrylic acid on C_{MP} is ruled out due to the low amounts of acrylic acid used in the recipes and its less solubility in particle phase. However, on the basis of above discussion, the effect of acrylic acid 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 acrylic acid content on $\bar{n}$. This parameter was calculated by knowing of C_{MP} (Table 2), R_p/N_p (Eq. (3)) and $\bar{K}_p$ ($\bar{K}_p = 364\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$) (Table 4).

Table 4
Kinetic parameters relating to emulsion copolymerization of styrene–butadiene–acrylic acid

	XSBR1	XSBR2	XSBR3
dX_{ov}/dt (s^{-1})	1.26×10^{-5}	1.55×10^{-5}	1.94×10^{-5}
$C_{M,O}$ (mol dm^{-3})	3.189	3.246	3.355
C_{MP} (mol dm^{-3})	5.50	5.50	4.50
R_p (mol dm^{-3} s^{-1})	4.018×10^{-5}	5.037×10^{-5}	6.514×10^{-5}
R_p/N_p (mol s^{-1})	2.98×10^{-21}	2.83×10^{-21}	2.11×10^{-21}
$\bar{n}$	0.90	0.84	0.64

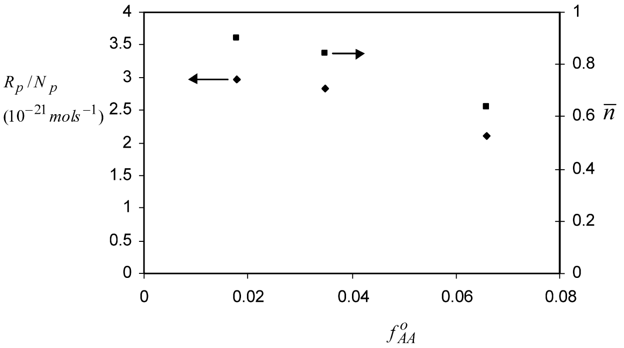

Fig. 3. Polymerization rate per particle and average number of growing radicals per particle versus initial mole fraction of acrylic acid in the feed.

All the data available in Table 4 show that the polymerization kinetic obeys Smith-Ewart kinetic (case 3) with $\bar{n} > 0.5$ [25]. In this condition, decrease in $\bar{n}$ with increasing of f°_{AA} means that acrylic acid amount influences the mass transfer phenomena and also termination rate mainly. This illustrates the low entrance rate of oligomeric radicals (formed in aqueous phase) into the latex particles or increases of free radical desorption rate from the latex particles. It is notable that in spite of increase in oligoradical concentration by increase in f°_{AA}, the entrance rate may be not affected because of the high solubility of oligoradicals in the aqueous phase. The probable reason that explains the increase in free radical desorption by increasing of acrylic acid concentration might be transfer reactions from oligoradicals to monomeric acrylic acid. The newly formed monomeric radicals have high solubility in water and cause the increase in desorption rate of free radicals from the particle phase.

The effect of higher rate of decomposition of persulfate should also be considered. Decrease in pH is the result of increase in acrylic acid amount. In this case, thermal decomposition of persulfate is facilitated [26]. More radical formation rate in aqueous phase that causes the higher entrance rate of oligoradicals to the latex particles will be also increased as a consequence. This competes with above discussions about $\bar{n}$ and means that lowering of pH has minor effect.

The above reasons could not explain the remarkable decrease in $\bar{n}$ due to the increase in acrylic acid amount. This would be described by the effect of acrylic acid on the nucleation process. N_p increases with increase in acrylic acid concentration (Fig. 1). By considering the similar conversion in these experiments (Table 1), particles' diameter decreases with increase in acrylic acid amount (with respect to increase in N_p) and surface area per particle will decrease as a result. This would cause the decrease in entrance efficiency of radicals to each 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 to the all particles ($\bar{n}N_p$) will increase and thus total polymerization rate will be increased (Eq. (3)).

4. Conclusion

Batch emulsion copolymerization of styrene–butadiene–acrylic acid in emulsifier-free condition led us to some useful information about the influence of acrylic acid on kinetics of reaction and particularly about the nucleation mechanism.

In this work, the modified obtained data from light scattering technique were used for particle size measurements of the XSBR latexes for the first time. The results were comparable with previous similar systems very well and confirmed the accuracy of our method.

It was found that average particles diameter at the same conversion had inverse proportionality with acrylic acid concentration (with respect to N_p). Beside that, particles number and polymerization rate increased with increasing of acrylic acid amount. Also the effect of acrylic acid on polymerization rate per particle (R_p/N_p) and average number of growing radicals per particle ($\bar{n}$) was investigated.

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Appendix A

$X_{ov}(t)$	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
$C_{M,O}$	Initial monomer concentration
$\theta(t)$	Overall molar conversion at time t
f_0	Mole fraction of monomer i to j in the feed (unreacted monomer)
F	Mole fraction of monomer i to j in the copolymer chain
μ	Molecular weight ratio of monomer i to j
$\bar{K}_p$	Average propagation rates constant in the particle phase
$\bar{n}$	Average number of growing radicals per particle
N_p	Number of latex particles per unit volume of the aqueous phase
C_{MP}	Overall monomer concentration in the particles at interval II
C'_{MP}	Overall monomer concentration in the particles at interval III
N_{av}	Avagadro's number
P/W	Weight ratio of polymer 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 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)
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

References

[1] Chatterjee AK. Rubber Chem Technol 1983;56:995.

[2] Ceska GW. J Appl Polym Sci 1974;18:2493.

[3] Muroi S. J Appl Polym Sci 1966;10:713.

[4] Muroi S, Hosoi K, Ishikawa K. J Appl Polym Sci 1967;11:1963.

[5] Hoy KL. J Coat Technol 1979;51:27.

[6] Bassett DR, Derderian EJ, Johnston JE, MacRury TB. In: Basset DR, Hamielec AE, editors. Emulsion polymers and emulsion polymerization. ACS Symp Series 165: ACS; 1981. p. 263. Chapter 16.

[7] Bassett DR, Hoy KL. In: Fitch RM, editor. Polymer colloids, Vol. II. New York: Plenum Press; 1980. p. 1.

[8] Nishida S, El-Aasser MS, Klein A, Vanderhoff JW. In: Basset DR, Hamielec AE, editors. Emuldion polymers and emulsion polymerization. ACS Symp Series 165: ACS; 1981. p. 291. Chapter 18.

[9] Ceska GW. J Appl Polym Sci 1974;18:427.

[10] (a) Sakota K, Okaya T. J Appl Polym Sci 1976;20:3255. (b) Sakota K, Okaya T. J Appl Polym Sci 1976;20:3265.

[11] Slawinski M. Strategic aspects of incorporation of acrylic acid in emulsion polymers. PhD Thesis, Eindhoven University of Technology; 1999.

[12] Slawinski M, Schellekens MAJ, Meuldijk J, Van der Herk AM, German AL. J Appl Polym Sci 2000;76:1186.

[13] Slawinski M, Schellekens MAJ, Meuldijk J, Van der Herk AM, German AL. J Appl Polym Sci 2000;78:875.

[14] Yuan X-Y, Dimonie VL, Sudol ED, El-Aasser MS. Macromolecules 2002;35:8346.

[15] Yuan X-Y, Dimonie VL, Sudol ED, Roberts JE, El-Aasser MS. Macromolecules 2002;35:8356.

[16] Yuan X-Y, Dimonie VL, Sudol ED, El-Aasser MS. J Appl Polym Sci 2003;88:1988.

[17] Fitch RM, Tsai CH. In: Fitch RM, editor. Polymer colloids. New York: Plenum Press; 1971. p. 73.

[18] Harkins WD. J Am Chem Soc 1947;69:1428.

[19] Alfrey T, Goldfinger G. J Chem Phys 1944;12:205.

[20] Mayo FR, Lewis J. J Am Chem Soc 1944;66:1594.

[21] Verdurmen-Noel EFJ. Monomer partitioning and composition drift in emulsion copolymerization. PhD Thesis, Eindhoven University of Technology; 1994.

[22] Jacobi B. Angew Chem 1954;64:539.
[23] Priest WJ. J Phys Chem 1952;56:1077.
[24] Ugelstad J, Hansen FK. Rubber Chem Technol 1976;49:536.
[25] Smith WV, Ewart RH. J Chem Phys 1948;16:592.
[26] Lin H-R. Eur Polym J 2001;37:1507.
[27] Hawkett BS, Napper DH, Gilbert RG. J Chem Soc Faraday Trans 1980;76:1325.
[28] Meehan EJ. J Polym Sci 1946;1:318.
[29] Buback M, Gilbert RG, Hutchinson RA, Klumperman B, Kuchta F-D, Manders BG, O'driscoll KF, Russel GT, Schweer J. Macromol Chem Phys 1995;196:3267.
[30] Deibert S, Bandermann F, Schwee J, Sarnecki J. Makromol Chem Rapid Commun 1992;13:351.
[31] Gromov VF, Galperina NI, Osmanov TO, Khomikovskii PM, Abkin AD. Eur Polym J 1980;16:529.