

Emulsion copolymerization of acrylonitrile and butyl acrylate

3. Effect of the radical scavenger on the kinetics and polymerization behaviour

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A study of the emulsion copolymerization of acrylonitrile and butyl acrylate under batch conditions in the presence of *p*-benzoquinone is presented. Statistical copolymers are synthesized by the emulsion polymerization conducted to both low and high conversion using the anionic emulsifier.

It has been found that the copolymer formed at low conversion is enriched with acrylonitrile structural units both in the presence and in the absence of *p*-benzoquinone. Addition of a small amount of a radical scavenger significantly decreases the rate of polymerization and slightly decreases the size of polymer particles in the range of low surfactant concentration.

It is assumed that the initiation of the emulsion copolymerization is a two-step process. It starts in the aqueous phase by the primary radicals derived from the water-soluble initiator which add water-soluble monomer. These reactions lead to the formation of water-soluble or insoluble macroradicals which cause at low conversion the drift in copolymer composition. The second step occurs in micelles by radicals absorbed on the surface of micelles. It is expected that the polymer particles generated by homogeneous nucleation contribute to both the polymerization rate and copolymer composition.

Представлено изучение эмульсионной сополимеризации акрилонитрила и бутилакрилата в периодическом режиме в присутствии *p*-бензохинона. Статистические сополимеры синтезируются посредством эмульсионной полимеризации, ведущей как к низким, так и к высоким степеням конверсии с использованием анионных эмульгаторов.

Обнаружено, что сополимер, образующийся при низкой степени конверсии обогащен структурными единицами акрилонитрила как в присутствии, так и в отсутствии *p*-бензохинона. Добавка небольшого количества вещества, служащего в качестве ловушки радикалов, значительно понижает скорость полимеризации и ведет к некоторому уменьшению величины полимерных частиц при низкой концентрации поверхностно-активного вещества.

Предполагается, что иницирование эмульсионной сополимеризации является двухстадийным процессом. Он начинается в водной фазе первич-

ными радикалами, происходящими из водорастворимого инициатора, которые затем присоединяются к водорастворимому мономеру. Эти реакции приводят к образованию водорастворимых или нерастворимых макро-радикалов, которые вызывают при низкой степени конверсии изменение в составе сополимера. Вторая стадия протекает в мицеллах с участием радикалов, абсорбированных на поверхности мицелл. Ожидается, что частицы полимера, образовавшиеся в результате гомогенной нуклеации, оказывают влияние как на скорость полимеризации, так и на состав сополимера.

The introduction of nitrile groups into polymer chains improves chemical and thermal resistance of polymer. On the other hand, the introduction of nitrile groups into latex has negative effect on its colloidal stability. Copolymer latexes with the low acrylonitrile content are more stable than those with the high acrylonitrile content.

All features of the emulsion copolymerization seem to be closely related to the monomer distribution along the polymer chain, to molecular interaction within the latex particles, and to solubility of monomers in water and in their polymers.

Although a good deal of work has been done on the industrial use of the emulsion copolymerization process, only little work is done concerning the emulsion polymerization mechanism, especially at the beginning of polymerization. Experience shows that this stage called also the "stage 1" is very important due to formation of reaction loci. It is also known that the stage 1 is highly variable and dependent on the type of ingredients and reaction conditions and this is probably the reason why only little attention has been devoted to this study.

From these points of view we studied the free-radical emulsion copolymerization of acrylonitrile and butyl acrylate with the emphasis on the initial stage of polymerization process [1, 2]. As it has been reported [1], at the beginning of polymerization the copolymer enriched with acrylonitrile was generated. In the presence of a water-soluble radical trapper, the dependence of the copolymer composition on conversion showed nearly monotonic character even at low conversion [2]. Both facts favour the formation of macroradicals in the aqueous phase and their participation in the initiation within the monomer-swollen micelles or in nucleation of polymer particles by their separation from the aqueous phase above the critical value of the degree of polymerization.

The classical Mayo—Lewis model of copolymerization seems to be inadequate in high conversion region [3]. A relatively small amount of work has been devoted to high conversion emulsion copolymerization, in particular to systems with various water solubility of comonomers. It was reported that a monomer dissolved in water did not contribute to copolymer composition. Correction for dissolved monomer in water led to good agreement with the results obtained in mass and solution copolymerization [4]. To verify this observation the emulsion copolymerization of

monomers (butyl acrylate and acrylonitrile) with various water solubility is investigated.

This paper, the third of the series, deals also with the effect of a radical scavenger on the polymerization kinetics.

The strong retardation effect of *p*-benzoquinone on the solution polymerization of methyl methacrylate has been described in paper [5]. On the other hand, when styrene was polymerized only inhibition effect was indicated [6]. The mechanism of the free-radical emulsion copolymerization of acrylonitrile and butyl acrylate in the presence of a radical scavenger (*p*-benzoquinone) was studied by conventional gravimetric and gas chromatography methods.

Theoretical

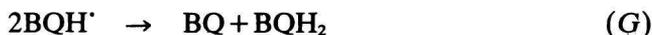
p-Benzoquinone has been reported to be good scavenger for alkyl and aryl radicals [7, 8]. The result of these reactions was the formation of mono-, di-, and trialkylquinones and a small amount of hydroquinone. The mechanism of reactions of *p*-benzoquinone with radicals is as follows: The initial step is an addition of a radical to *p*-benzoquinone giving the semiquinone radicals in any of their mesomeric, tautomeric, and acid-base forms. Then follows the reaction of radical with the second molecule of *p*-benzoquinone (BQ)



The kinetics of the semiquinone formation are of the first order with the half-lives being inversely proportional to *p*-benzoquinone concentration. In the absence of suitable radical scavengers the semiquinone disappears by a second-order disproportionation to yield in *p*-benzoquinone and hydroquinone



This process gives, however, rise to hydroquinone which is soluble in water and its consumption takes place by reactions with initiator fragments. The mechanism of these reactions is summarized in the following reaction scheme [9]



The reaction of hydroquinone and initiator fragments can lead to the stable products as has been reported in [2].

Experimental

Materials

Acrylonitrile (AN) and butyl acrylate (BA) monomers (certified grade, Chemical Works, Sokolov) were washed with 5 % aqueous sodium hydroxide solution to remove the inhibitor and with water to remove base, and dried over anhydrous calcium chloride (certified grade, Fluka A.G.). Monomers were distilled (BA under vacuum) under dry nitrogen, and the middle fractions *ca.* 70 % of the initial amount collected were stored in a refrigerator until used.

The surfactant used was reagent grade Dowfax 2A1 (sodium dodecylbenzenedisulfate, Dow Chemicals, Ltd.) in the form of 45 % aqueous solution.

Ammonium peroxodisulfate and *p*-benzoquinone, both anal. grade (supplied by Lachema, Brno), were used without further purification.

Acetone, toluene, 1,4-dioxan, *n*-octane, and methanol used for kinetic measurements were distilled before use. Twice-distilled water was used as the polymerization medium and for conductivity measurements.

Polymerization procedure

Emulsion copolymerizations of AN and BA were carried out at 70 °C. In all runs the recipe containing 140 g of water, 96.6 g of monomers, 0.027 g of *p*-benzoquinone, and 0.7725 g of ammonium peroxodisulfate was used. Concentrations of Dowfax 2A1 (DW) were used as given in legends to Figs. 1–4.

The conventional batch reactor was used to follow the kinetics of copolymerization process. The reaction ingredients were charged into glass bottle reactor under nitrogen in the order: 1. aqueous solution of surfactant and 2. monomer solution of *p*-benzoquinone. The mixture was then stirred for about 30 min at constant agitation rate at 70 °C. After this preemulsification period the aqueous solution of ammonium peroxosulfate was charged in. All polymerization runs were conducted in a nitrogen atmosphere. Other details of polymerization technique used have been given elsewhere [1, 10].

Results and discussion

Polymerization rate study

The variations of the conversion with time of the emulsion copolymerization of acrylonitrile and butyl acrylate initiated by the water-soluble initiator (ammonium peroxodisulfate) in the presence of a small amount of *p*-benzoquinone are illustrated in Fig. 1. The conversion curves are sigmoid, *i.e.* the rate of polymerization is very low for a relatively long time and then gradually increases with the reaction time. It is interesting that only small induction periods, if any, are observed. The low rate of polymerization in the initial stage of polymerization is

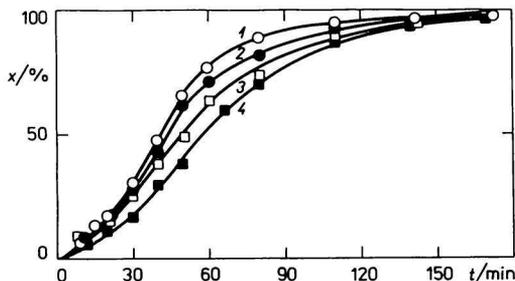


Fig. 1. Variation of the monomer conversion in the emulsion copolymerization of acrylonitrile and butyl acrylate with the reaction time and the concentration of surfactant.

Recipe: 140 g of water, 19 g of AN, 76.6 g of BA, $[BQ] = 2.27 \times 10^{-6} \text{ mol cm}^{-3}$ oil phase, $[(NH_4)_2S_2O_8] = 2.28 \times 10^{-5} \text{ mol cm}^{-3}$ water, temperature 70°C . $[DW] \cdot 10^5 / (\text{mol cm}^{-3} \text{ water})$: 1. 7.32, 2. 2.87, 3. 1.18, 4. 0.63.

due to (i) the nature of the emulsion polymerization and (ii) the inhibition action of a radical scavenger.

During the initial interval the generation of polymer particles takes place in the reaction system. The generation of polymer particles occurs either in the monomer-swollen micelles by the entry of the primary [11, 12] and oligomer [13] radicals and/or by the homogeneous nucleation [14–16]. The generation of polymer particles in the emulsion polymerization of water-insoluble monomer proceeds by micellar mechanism. On the other hand, the generation of polymer particles in the emulsion copolymerization of acrylonitrile and water-insoluble vinyl monomer may proceed by both mechanisms. These aspects are discussed later.

Kinetic data summarized in Tables 1–3 show that *p*-benzoquinone (BQ) remarkably decreases also the rate of polymerization during the stage 2. The decrease is more pronounced in the range of high surfactant concentration and at higher content of butyl acrylate in the reaction system.

Acceleration of the polymerization rate is attributed to the growth of the number of polymer particles. As soon as the number of polymer particles has been fixed the polymerization rate is nearly constant (stage 2).

Kinetic data show that the interval 2 of emulsion polymerization of AN and BA is situated in the range of conversion from 30 to 65 %, which seems to be not long enough. This behaviour seems to be function of: (i) accumulation of radicals within polymer particles, (ii) the change in the monomer concentration within polymer particles, and (iii) free-radical desorption. In the case of water-soluble oligomer radicals, the growing radicals of AN can transfer themselves out of the particles. Due to this fact, even if the number of polymer particles is kept constant, the rate of polymerization may decrease.

Table 1

Copolymerization kinetic data
Rate of polymerization in interval II of emulsion polymerization

$\frac{[DW] \cdot 10^5}{\text{mol cm}^{-3} \text{ water}}$	$\frac{R_p \cdot 10^3}{\text{mol}/((\text{dm}^3 \text{ of water}) \text{ s})}$			
	a, 1	b, 1	a, 2	b, 2
7.32	35.3	26.3	2.2	4.1
2.87	17.0	23.4	1.9	3.6
1.18	13.3	18.1	1.5	3.2
0.63	8.7	10.9	1.4	2.5

a) The initial monomer feed composition $[AN]/[BA]=0.6$ (mole ratio), b) the initial monomer feed composition $[AN]/[BA]=2.4$ (mole ratio).

1. Without BQ [1], 2. $[BQ]=2.27 \times 10^{-6} \text{ mol cm}^{-3}$ oil phase.

Table 2

The fractional rate of copolymerization (at maxima of curves presented in Fig. 2)

$\frac{[DW] \cdot 10^5}{\text{mol cm}^{-3} \text{ water}}$	$\frac{(dx/dt)/(1-x)_{\text{max}} \cdot 10^2}{\text{min}^{-1}}$			
	a, 1	b, 1	a, 2	b, 2
7.32	50.7	63.0	5.1	11.6
2.87	27.5	43.0	3.5	9.8
1.18	25.0	33.0	2.8	6.6
0.63	17.5	26.0	2.5	4.6

The same footnote as in Table 1.

Table 3

Copolymerization kinetic data
Total monomer conversion (α) at maxima of curves presented in Fig. 2

$[DW] \cdot 10^5$ mol cm ⁻³ water	$\alpha_{\text{max}}/\%$			
	a, 1	b, 1	a, 2	b, 2
7.32	50.0	79.0	60.0	77.0
2.87	45.0	80.0	58.0	79.0
1.18	45.0	65.0	70.0	71.0
0.63	50.0	75.0	80.0	72.0

The same footnote as in Table 1.

Conversion vs. time curves (Fig. 1) were graphically differentiated to yield the fractional rate of polymerization shown in Fig. 2 and summarized in Tables 2 and 3, respectively. The dependence of the fractional rate on conversion is described by the curve with a maximum corresponding to a certain conversion. The position of maxima in the system with the monomer mole ratio $[AN]/[BA]=0.6$ is shifted by the addition of a radical scavenger from 50 % conversion (without an inhibitor) to the conversion range of 60–80 %. In the system with higher concentration of acrylonitrile ($[AN]/[BA]=2.4$) only a small shift of the maximum by addition of *p*-benzoquinone is observed.

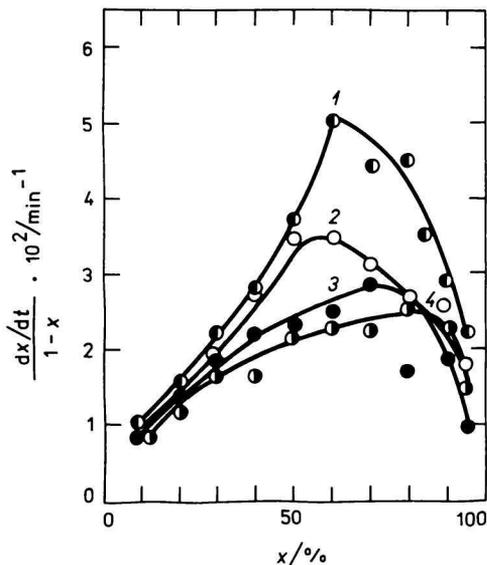


Fig. 2. Variation of the fractional rate of copolymerization $(dx/dt)/(1-x)$ of acrylonitrile and butyl acrylate with the concentration of surfactant and conversion.

$[DW] \cdot 10^5/(\text{mol cm}^{-3} \text{ water})$: 1. 7.32,
2. 2.87, 3. 1.18, 4. 0.63. Other conditions
as given in the legend to Fig. 1.

At some point the surfactant micelles disappear due to the depletion of the surfactant required to stabilize the polymer particles formed, marking the end of stage 1 and the beginning of stage 2. This point as shows the shape of curves in Fig. 2 is located in the conversion range of about 10 %.

At some point monomer droplets disappear marking the end of stage 2 and the beginning of stage 3. Using the high concentration of surfactant, high agitation rate, and the long preemulsification period, formation of emulsions with smaller droplet diameter takes place. This type of emulsions with an average droplet diameter of about 400 nm can significantly contribute to the overall polymerization rate. This may be the case of system with the highest surfactant concentration.

The shift of the fractional rate maximum caused by the addition of a radical scavenger indicates that not only disappearance of the oil droplets but also radical concentration and/or the reactivity of radicals can influence the polymerization behaviour in stages 2 and 3. In the presence of an oil-soluble radical scavenger the

polymerization rate within monomer droplets may be reduced and thus the shift and lower value of the maximum rate are observed. Besides, the shift of the maximum to the higher conversions compared with the system without inhibitor may be effected also by the retardation ability of both intermediates (semiquinones) and reaction products of BQ. It is reasonable to suppose that due to the low concentration of BQ dissolved in water and the high concentration of the water-soluble initiator, semiquinones should be deactivated through the reaction with primary radicals. In the monomer-swollen polymer particles, where a larger part of BQ and a lower part of radicals are located, deactivation of semiquinones should proceed through disproportionation. The intermediates formed during the polymerization can either terminate an active chain or desorb from the polymer particle. The change of the colour of polymerization reaction mixture as the reaction advances points to the possible formation of some reaction intermediates or reaction products of *p*-benzoquinone.

The retardation effect of BQ is more pronounced in the systems with the high content of butyl acrylate in the feed. Butyl acrylate (as donor) in both monomer and polymer forms due to the donor-acceptor interaction with BQ [17] favours the assumption of localization of BQ within polymer particles. Thus, the higher concentration of BQ around reaction loci within polymer particle should lead to a decrease in the polymerization rate.

Copolymer composition studies

Variations of the cumulative copolymer composition, \bar{F}_{AN} , with conversion and the surfactant concentration in the presence of *p*-benzoquinone are presented in Fig. 3. The unexpected high values of the cumulative copolymer composition are observed in the range of low conversion. The similar behaviour has been observed in the system without inhibitor (Table 4).

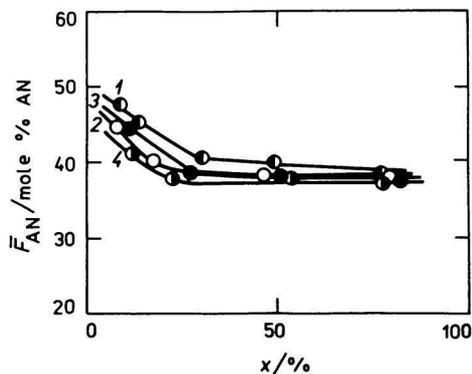


Fig. 3. Variation of the cumulative average mole fraction of acrylonitrile in the copolymer, \bar{F}_{AN} , with the concentration of surfactant and conversion.

[DW] · 10³ / (mol cm⁻³ water): 1. 7.32, 2. 2.87, 3. 1.18, 4. 0.63. Other conditions as given in the legend to Fig. 1.

Table 4

Copolymer composition data

[DW] · 10 ⁵ mol cm ⁻³ water	α %	\bar{F}_{AN} /mole % AN			
		a, 1	a, 2	b, 1	b, 2
7.32	7	47	48	77	82
7.32	15	43	45	73	77
7.32	20	40	43	72	75
7.32	50	38	40	70	71
7.32	80	37	39	68	70
2.87	7	45	46	75	80
2.87	15	42	43	73	77
2.87	20	40	40	72	73
2.87	50	37	39	69	71
2.87	80	36	39	68	70

The same footnote as in Table 1.

The instantaneous copolymer composition predicted from the single integrated copolymer composition equation [18] and literature reactivity ratios ($r_{AN} = 1.082$, $r_{BA} = 0.816$; [19]) calculated at the initial monomer feed compositions $[AN]/[BA] = 0.6$ and 2.4 is 42 mole % and 73 mole % of acrylonitrile structural units, respectively. The presence of water-insoluble butyl acrylate reduces AN monomer concentration in the aqueous phase or *vice versa* [1]. In the acrylonitrile—butyl acrylate system, correction for AN dissolved in water leads to the values of the instantaneous copolymer composition 37 mole % and 70 mole % for the systems with the mole ratio $[AN]/[BA] = 0.6$ and 2.4 , respectively.

The copolymer composition curves show that as reaction advances, the content of acrylonitrile in copolymer abruptly decreases until the plateau is reached (about 20 % conversion). The values of copolymer composition in the range of medium and high conversions lie between those calculated without and with correction for acrylonitrile dissolved in water. It is clear that acrylonitrile dissolved in water cannot participate in propagation reactions within the polymer particles. The higher content of acrylonitrile in copolymer in comparison with that found by calculation shows that there are some reactions which contribute to the copolymer composition (even at high conversion). This indicates that the homopolymerization of acrylonitrile in the aqueous phase takes place, which increases somewhat the content of acrylonitrile in copolymer. It is assumed that the acrylonitrile oligomer radicals either enter polymer radicals or precipitate themselves from the aqueous phase and in both cases contribute to the higher acrylonitrile content in copolymer.

In favour of this assumption tell the results of turbidimetric titration of polymer solutions and of extraction of the reaction product. These results indicate that the polymer formed at low and medium conversions contains only AN/BA copolymer.

Macromer studies

The complex character of the emulsion copolymerization of acrylonitrile and butyl acrylate follows from the high water solubility of AN. It is expected that the nucleation of new particles proceeds not only by the entry of free radicals from the aqueous phase to the monomer-swollen micelles but also by the homonucleation of separated propagating radicals from the aqueous phase. The separation of polymer radicals takes place above the critical value of the number-average degree of polymerization, $P_{n,m}$.

The course of polymerization in water is determined by the chemical structure and by the hydrophobicity of monomers and macroradicals. From the kinetic point of view the copolymerization in water is governed by the kinetics of a solution polymerization up to the stage at which the polymer separates from water.

The number-average degree of polymerization of AN—BA macromers (m) which separate from the aqueous phase can be estimated using the following equation [20, 21]

$$P_{n,m} = \frac{(r_{AN}[AN]^2 + 2[AN][BA] + r_{BA}[BA]^2)}{R_i^{0.5}(r_{AN}K_1^2[AN]^2 + 2\varphi K_1K_2r_{AN}r_{BA}[AN][BA] + r_{BA}K_2^2[BA]^2)^{0.5}} \quad (1)$$

where $[AN]$ and $[BA]$ are the amount-of-substance concentrations of monomers dissolved in the aqueous phase, K is the ratio of the rate constants for termination and propagation ($k_t^{0.5}/k_p$), R_i is the rate of initiation, φ is the ratio of the rate constants for cross- and selftermination ($k_{t,cross}/k_{t,1}^{0.5} \cdot k_{t,2}^{0.5}$), and 1 and 2 denote AN and BA, respectively.

For the initiation by thermal decomposition of persulfate the estimated value of R_i can be obtained from the following equation

$$R_i = 2fk_d[I] \quad (2)$$

where f is the initiator efficiency, k_d is the first-order decomposition rate constant, and $[I]$ is the initial amount-of-substance concentration of initiator. If we estimate k_d at 70 °C to be $7.0 \times 10^{-5} \text{ s}^{-1}$ [20, 21] and f is estimated to be 0.7 for the present system [22, 23], using the initiator concentration $[(\text{NH}_4)_2\text{S}_2\text{O}_8] = 2.48 \times 10^{-2} \text{ mol dm}^{-3}$ of the aqueous phase, the calculated rate of initiation is $2.37 \times 10^{-6} \text{ mol}/((\text{dm}^3 \text{ of water}) \text{ s})$. The estimated values of R_i , k_d , and f are physically reasonable, even if they are treated as parameters of an "ideal" solution polymerization.

In the emulsion polymerization, the magnitude of k_d is a function of the initiator

concentration, pH, temperature, and level and nature of other ingredients of the reaction system [24]. According to Vanderhoff [25], f is a decreasing function of the initiator concentration. It is reasonable to expect some decrease in the value of f in the presence of monomer, *i.e.* initiator waste reactions should be intensified by monomer soluble in water.

The degree of polymerization of macromers calculated according to eqn (1) using the following values: $K_1^2 = k_t/k_p^2 = 196.6$ [26]; $K_2^2 = 4.44$ [27]; $r_{AN} = 1.082$ and $r_{BA} = 0.816$ [19]; $[AN]_0 = 5.46 \times 10^{-1} \text{ mol dm}^{-3}$ of the aqueous phase, $[BA]_0 = 6.24 \times 10^{-3} \text{ mol dm}^{-3}$ of the aqueous phase (for the system with monomer mole ratio $[AN]/[BA] = 0.6$), and $\varphi = 1$ is 24. Taking $\varphi = 10$ the estimated value of $P_{n,m} = 23$, respectively.

In the system with the mole ratio $[AN]/[BA] = 2.4$, 1 dm^3 of water contains $7.218 \times 10^{-1} \text{ mol}$ of acrylonitrile and $7.8 \times 10^{-3} \text{ mol}$ of butyl acrylate. The estimated degree of polymerization taking $\varphi = 1$, or $\varphi = 10$ is for this system 34 or 33, respectively.

The values of $P_{n,m}$ of macromers together with solubility parameters of the monomers and their polymers are summarized in Table 5. It is supposed that the degree of polymerization at which the macromers are separated from the aqueous phase depends upon many factors: (i) water solubility of monomers and polymer formed, (ii) solubility of polymers in their monomers, (iii) the structure and the copolymer composition of macroradicals, *etc.*

In the dispersion polymerization of styrene (monomer insoluble in water) the oligomers had a degree of polymerization of about 7. Using methyl methacrylate (monomer partly soluble in water) the separation of propagating radicals from the aqueous phase occurred above the value of $P_{n,m} \sim 65$. The addition of water-soluble monomer like glycidyl methacrylate (15 mass %) to styrene causes the increase of the degree of polymerization from 7 up to 40.

Using the integrated copolymer composition equation [18], the copolymerization reactivity ratio of AN and BA comonomer system [19], and monomer concentration in the aqueous phase, the instantaneous values of the mole fraction $F_{AN,m}$ of acrylonitrile monomeric units in the copolymer referring to the macromer (which is formed until its precipitation) were calculated. For the system $[AN]/[BA] = 0.6$ the value of $F_{AN,m}$ was calculated to be 0.94. The system with higher acrylonitrile content ($[AN]/[BA] = 2.4$) produces macromers with the copolymer composition of about $F_{AN,m} \sim 0.99$.

From the kinetic point of view, the initial stage of formation of macromeric radicals is governed by the kinetics of a solution polymerization. At this stage, the length of macromer chains is regulated by the primary radical and monomer concentrations, and by the solubility of polymers in water and in their monomers.

Solubility parameter values δ show that the increase of AN fraction in both the monomer feed and the copolymer should produce macromers with longer chains.

Table 5

The number-average degree of polymerization of macromers, $P_{n,m}$, and the solubility parameter values of vinyl monomers (σ_m) and polymers (σ_p)

Monomer	Water solubility	σ_m^a	σ_p^a	$P_{n,m}$
	mass %	(cal/cm ³) ^{0.5}	(cal/cm ³) ^{0.5}	
Acrylonitrile	7.2 ^b	10.5	12.5	—
Vinyl acetate	2.5 ^c	9.0	9.4	54 ^d
Methyl methacrylate	1.5 ^c	8.8	9.1	65 ^e
Vinyl chloride	1.05 ^c	7.8	9.7	54 ^f
Butyl acrylate	0.1 ^b	8.8	8.8	—
Styrene	3.6×10^{-2c}	9.3	9.1	8 ^g
Glycidyl methacrylate (15 mass %)—styrene (85 mass %)	—	—	—	40 ^h
Acrylonitrile (20 mass %)— —butyl acrylate (80 mass %)	5.9 ^b	—	—	24 ^b
Acrylonitrile (50 mass %)— —butyl acrylate (50 mass %)	2.9 ^b	—	—	34 ^b

a) Ref. [28], b) this paper, c) Ref. [29], d) Ref. [30], e) Ref. [31], f) Ref. [32], g) Ref. [33, 34], h) Ref. [35].

Polyacrylonitrile and poly(butyl acrylate) differ, however, for their solubilities in acrylonitrile and butyl acrylate. AN and BA monomers dissolve or swell PBA. But, on the contrary, they do not dissolve or swell PAN. From this point of view, the increase of the content of AN structural units in copolymer may cause the decrease of the value of $P_{n,m}$.

In the presence of the surfactant the kinetics of macromer formation are supposed to be more complex. The surface-active compounds increase the solubility of monomers and polymers in the aqueous phase and thus increase the value of $P_{n,m}$. The way of the change of soluble oligomer radicals through water-insoluble macromeric radicals to active polymer particles is a continuous complex process depending on several factors.

Latex particle studies

Variations of the average particle size, the interface tension and conductivity of the final polymer latexes with the surfactant concentration and the monomer feed composition are presented in Fig. 4 and in Tables 6 and 7.

The average size of polymer particles prepared in the presence of *p*-benzoquinone using the low surfactant concentration is found to be smaller than the size of particles prepared without the radical scavenger. Under the high surfactant concentration conditions the size of polymer particles seems to be unaffected by BQ. It is seen that the size of latex particles is dependent on the value of the monomer feed composition. The particle size decreases with the increase of butyl acrylate monomer content in the feed. As expected, the size of particles decreases with the concentration of the surfactant.

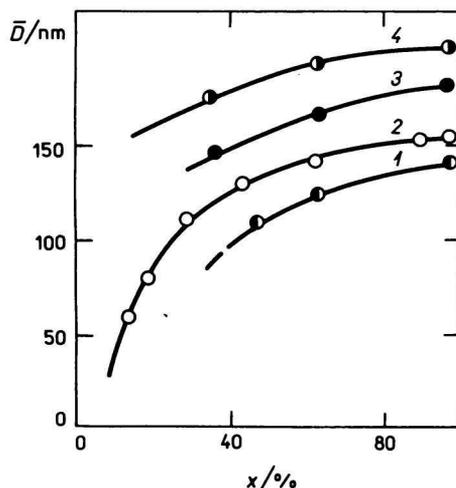


Fig. 4. Variation of the mean particle diameter, \bar{D} , with the concentration of surfactant and conversion.

$[DW] \cdot 10^5 / (\text{mol cm}^{-3} \text{ water})$: 1. 7.32, 2. 2.87, 3. 1.18, 4. 0.63. Other conditions as given in the legend to Fig. 1.

Table 6

Kinetic parameters of the final polymer latexes at the initial monomer mole ratio $[AN]/[BA] = 0.6$

$\frac{[DW] \cdot 10^5}{\text{mol cm}^{-3} \text{ water}}$	\bar{D}^1 nm		γ^2 mN m ⁻¹		Cond. ³ mS cm ⁻¹	
	a	b	a	b	a	b
7.32	120	120	44	44	7.1	7.1
2.87	150	150	55	53	5.5	6.3
1.18	195	180	59	56	5.1	5.3
0.63	220	200	61	58	5.0	5.1

1. The average particle diameter, 2. the interface tension, 3. conductivity.

a) Without *p*-benzoquinone, b) $[BQ] = 2.27 \times 10^{-6}$ mol cm⁻³ oil phase.

Table 7

Kinetic parameters of the final polymer latexes at the initial monomer mole ratio $[AN]/[BA] = 2.4$

$\frac{[DW] \cdot 10^5}{\text{mol cm}^{-3} \text{ water}}$	\bar{D}^1 nm		γ^2 mN m ⁻¹		Cond. ³ mS cm ⁻¹	
	a	b	a	b	a	b
7.32	190	190	35	35	8.0	8.0
2.87	230	220	50	50	6.3	6.3
1.18	240	240	56	58	5.5	5.2
0.63	295	280	60	62	5.2	5.0

The same footnote as in Table 6.

The measurements of the conductivity and the interface tension indicate the presence of the active species probably formed through the reaction of BQ with the radicals. These new species can contribute to the overall conductivity of the system by taking part in association with polymer, monomer, and surfactant molecules. This new association results in releasing the anionic surfactant to water [36]. The released emulsifier increases the conductivity of the system. The changes in conductivity values are small and they are observed only at low surfactant concentrations. The high concentration of surfactant overlaps the effect of BQ.

Kinetic data show that polymer latexes with higher content of acrylonitrile in copolymer exhibit higher values of conductivity and lower values of the interfacial tension. This indicates that a change in adsorption of surfactant on the polymer within polymer particles should occur. The process of adsorption is fairly complicated; it depends on many factors, e.g. the nature of the absorbent, the monomer

sequence in polymer, the molecular mass of the polymer, temperature, the effect of solvent, etc.

Among these factors, the solvolytic character of the monomer influences the adsorption of surfactant on the polymer in the following ways: One is the energetic factor, *i.e.* since a solvent molecule must replace surfactant molecules and *vice versa*, the difference in energy of interaction between adsorbent and solvent, and adsorbent and polymer molecule, will be important in determining the extent of adsorption. Another factor is the interaction of polymer—monomer, monomer—monomer, polymer—surfactant, and monomer—surfactant, which leads to the expectation that adsorption of surfactant on the polymer surface is the best from the poor solvent.

Apart from energetic reasons, the tighter coiling of the polymer within the latex particle in the poorer solvent would decrease the interaction activity of polymer surface.

According to this concept, it is expected that if polymer molecules favour the adsorption then also the swelling ability of latex particles increases. The particles with the thick adsorption layer of surfactant on the polymer surface should show a strong protection against flocculation. This case is most probably the emulsion polymerization of butyl acrylate [10] where stable particles were formed and in which the shape of curves of the particle size vs. conversion indicated no sign of coalescence.

On the other hand, the shape of the curves of the particle size vs. conversion illustrated in Fig. 4 indicates that the increase of the particle size through the whole range of conversion is most probably caused by coalescence of polymer particles themselves. As it has already been discussed, the high water solubility of acrylonitrile gives rise to generation of new particles by homonucleation of oligomer radicals which can be adsorbed by larger size particles and so the increase in the average particle size can be observed even at monomer-starved conditions.

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