

Emulsion polymerization of butyl acrylate

I. CAPEK, J. BARTOŇ, and E. OROLÍNOVÁ

*Polymer Institute, Centre for Chemical Research,
Slovak Academy of Sciences, CS-842 36 Bratislava*

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The mechanism of the water-soluble ammonium persulfate-initiated emulsion polymerization of butyl acrylate at 70 °C has been investigated.

It was found that at low conversions the viscosity-average relative molecular mass of polymer $\bar{M}_{r,v}$ is approximately inversely proportional to the 0.50 power of the initiator concentration. The viscosity-average relative molecular masses decrease, while the rate of initiation and polymerization increases with the concentration of surfactant.

The equilibrium monomer concentration in the particles in interval II of emulsion polymerization was constant and independent of surfactant concentration in the feed.

Radical concentration, number of particles per volume unit, and the ratio of the rate constants for propagation and termination (k_p/k_t) increase, while the mean particle radius and number of radicals per particle decrease with increasing concentration of surfactant in the feed.

A good agreement is observed between the estimated particle radius and those obtained by light scattering measurements of final polymer latexes.

Исследован механизм эмульсионной полимеризации бутилакрилата при 70 °C, инициируемой водорастворимым персульфатом аммония.

Найдено, что при низкой степени превращения среднемолекулярная относительная молекулярная масса полимера, определенная вискозиметрически, $\bar{M}_{r,v}$, приблизительно обратно пропорциональна корню квадратному из концентрации инициатора. Среднемолекулярная вискозиметрическая относительная молекулярная масса уменьшается, в то время как скорость инициирования и полимеризации возрастает с повышением концентрации эмульгатора.

Равновесная концентрация мономера в частицах во II фазе эмульсионной полимеризации была постоянна и не зависела от концентрации эмульгатора в исходной смеси.

Концентрация радикалов, число частиц в единице объема и величина отношения констант скоростей роста и обрыва (k_p/k_t) возрастают, а величина среднего радиуса частиц и число радикалов на одну частицу уменьшаются при возрастании концентрации эмульгатора в исходной смеси.

Наблюдалось хорошее согласование между оцененной величиной радиуса частиц и ее значениями, полученными на основании изучения конечных полимерных латексов методом светорассеяния.

No other area of polymerization has been the subject of so many studies, as that of emulsion polymerization [1]. This fact results from the character of emulsion polymerization arising from the specific nature of the monomers and the polymers produced, and from their influence on the course of the process itself.

It was found convenient to define three stages of emulsion polymerization [2]. In stage I, polymer particles are formed by the entry of radical from water into micelles accompanied by chain propagation, *i.e.* the particles are nucleated by radicals absorbed on the surface of the monomer-swollen soap micelles. During this period the number of particles gradually increases with conversion. The reaction stage I is highly depending on initiator type and concentration, monomer, and polymer type, degree of agitation, presence of oxygen, *etc.*

On the contrary, stage II is highly reproducible [3] with the fixed number of polymer particles. At this stage a polymer radical may grow undisturbed for a long time (till 100 s) until another radical enters the particle, which results in an immediate termination.

In stages I and II the reaction mixture consists of three phases: the aqueous phase, droplets of monomer, and monomer-swollen latex particles.

Beyond the stage II, when conversion is high enough, the monomer droplets disappear, and the reaction mixture becomes a two-phase system. At this stage (III) the unconverted monomer is present only in latex particles and in water (if it is soluble). Furthermore, the mutual radical termination is much suppressed, but diffusion of monomer to the site of the active radical still occurs. At very high conversion (above 95 %) the diffusion of monomer is supposed to become hindered and polymerization slows down.

In the last years the concept of the mechanism of emulsion polymerization [4] has been questioned and a new idea has been proposed by some workers [5—7]. For example, Roe [5] proposes the particle generation that is independent of the presence of micelles and occurs at each interaction of a dissolved free radical with a dissolved monomer molecule and continues until the emulsifier is depleted to a level the new particles of which cannot achieve stability by adequate adsorption of emulsifier.

During past few years, it was found out that Smith—Ewart basic assumptions were not applicable to all monomers and to all experimental conditions and therefore they were later reviewed and modified by Gardon [8]. It was assumed that initiation of the emulsion polymerization of vinyl monomers would take place in the monomer-loaded detergent micelles but not in the aqueous phase.

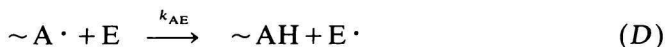
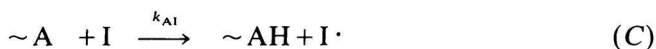
All those assumptions are still open to experimental verification. In the present paper, we report on the results of the emulsion polymerization of sparingly soluble butyl acrylate initiated by ammonium persulfate by conventional methods.

Theoretical

The chain propagation step within the polymer particle involves monomer addition as in the mass radical polymerization according to the scheme (A)



and chain transfer to monomer, initiator, and emulsifier (schemes (B—D))



Propagation and transfer rate constants are defined in eqns (A—D), respectively.

The rate of transfer in the free-radical emulsion polymerization is given by the following equation

$$R_{tr} = k_{AA}[A \cdot][A] + k_{AI}[A \cdot][I] + k_{AE}[A \cdot][E] \quad (1)$$

Here the square brackets denote concentration and $[A \cdot]$ represents the average radical concentration within the polymer particle or the polymerization locus.

For the emulsion polymerization of butyl acrylate the chain transfer to initiator [9] and soap [10] is unlikely and transfer to polymer does not affect the number-average relative molecular mass of the polymer.

The number-average degree of polymerization \bar{X}_n can be expressed as

$$\bar{X}_n = \frac{R_p}{(R_i/n) + R_{tr}} \quad (2)$$

and consequently the rate of initiation R_i can be expressed as

$$R_i = nR_p((1/\bar{X}_n) - C_M) \quad (3)$$

where n is 2 when termination occurs, as in butyl acrylate polymerization [11], by coupling and 1 when termination occurs by disproportionation and C_M is the monomer transfer constant (for butyl acrylate Ref. [12] gives $C_M = 0.4 \times 10^{-4}$).

For the emulsion polymerization of vinyl monomer the rate of polymerization is

$$R_p = k_p[A \cdot][A] = (k_p/N_A)[A]_{eq}N\bar{Q} \quad (4)$$

where N_A stands for Avogadro's constant, $[A]_{eq}$ is the equilibrium monomer (A) concentration in the monomer swollen particle, N and \bar{Q} are the number of particles in a volume unit and average number of radicals per particle, respectively.

Thus

$$[A \cdot] = (N/N_A)\bar{Q} \quad (5)$$

Equation for fractional rate R_{pf} is

$$R_{pf} = \frac{R_p}{[A]_{eq}} = \frac{k_p}{N_A} N\bar{Q} \quad (6)$$

According to the Smith—Ewart [8] models, the final number of particles N per 1 cm^3 of water in an emulsion polymerization is given by

$$N = 0.208 S^{0.6} (R/K)^{0.4} \quad (7)$$

where S is the mass concentration of surfactant, R is the rate of radical production, and K is the rate of volume growth of particle during stage II of polymerization.

The value of S is given by [4, 8]

$$S = N_A a_s [S] \quad (8)$$

where a_s is the area occupied by a soap molecule, it is reported to be $4.9 \times 10^{-15} \text{ cm}^2$ for Dowfax 2A1 [13] and $[S]$ is the surfactant concentration (mol/(cm^3 water)).

The value of K for homopolymerization is given by [4, 8, 14] the equation

$$K = \frac{3}{4\pi} \frac{\rho_m}{\rho_p} \frac{\Phi_m}{(1 - \Phi_m)} \frac{k_p}{N_A} \quad (9)$$

where ρ_m and ρ_p stand for the monomer and polymer densities, and Φ_m is the monomer volume fraction in the particle.

The last parameter R (expressed as number of radicals produced in 1 cm^3 of water per second) is given by eqn (10)

$$R = 2fk_d[I]N_A = R_iN_A \quad (10)$$

where f stands for the initiator efficiency, k_d is the decomposition rate constant of initiator and $[I]$ is the concentration of initiator (mol cm^{-3}) in water.

The root-mean-cube average radius r is related to N by [8]

$$r = \left(\frac{3\rho_w m_m}{4\pi\rho_p m_w N} \right)^{1/3} \quad (11)$$

where m_m/m_w is the mass ratio of monomer and water and ρ_w is density of water.

The conversion-time relationship for heterogeneous emulsion polymerization is described by the following equation with adequate accuracy

$$V_p = At^2 + Bt \quad (12)$$

where V_p is the volume of polymer formed at time t , A and B are constants (here B is the Smith—Ewart rate). The values of the constants A and B can be estimated from the curve-fitting experiments.

From the experimental A , B , N , R , and Φ_m data the ratio of the rate constants for termination and propagation k_t/k_p can be calculated by the following equation

$$k_t/k_p = 0.158(RB/AN)^{1.062} \Phi_m / (1 - \Phi_m) \quad (13)$$

The equilibrium monomer concentration $[A]_{eq}$ in a monomer-swollen particle can be expressed by eqn (14)

$$[A]_{eq} = (\rho_m \Phi_m / M_0) \times 10^3 \text{ mol dm}^{-3} \quad (14)$$

where M_0 is the molecular mass of the monomer. Φ_m can be expressed as [15]

$$\Phi_m = \omega_{m/p} \cdot \rho_p / (\rho_m + \omega_{m/p} \cdot \rho_p) \quad (15)$$

where $\omega_{m/p}$ is the ratio of masses of monomer and polymer in the particle.

Experimental

Materials

Butyl acrylate was freed from inhibitor by washing with aqueous NaOH and then with water to neutral reaction, dried with anhydrous calcium chloride, and distilled before use under reduced pressure.

Anal. grade ammonium persulfate and Dowfax 2A1 (sodium dodecylbenzenesulfonate, abbr. DW, Dow Chemicals) were used as supplied.

Water — aqueous phase of the emulsion polymerizations — was distilled and then deaerated by boiling and bubbling with nitrogen.

Solvents as acetone, methanol, etc. used for intrinsic viscosity measurements and precipitation experiments, were purified by distillation.

Polymerization

Emulsion polymerizations of butyl acrylate were carried out at 70°C. In all cases the recipe comprised 145 g of water and 95.6 g of butyl acrylate.

The concentrations of ammonium persulfate and Dowfax 2A1 were changed and used as shown in Results and discussion.

The conventional batch technique (bottle polymerization) was used to prepare polymer latexes. All ingredients except the initiator were charged into the reaction vessel. The reaction mixture was purged with nitrogen and thermostated to the temperature of polymerization. After that the initiator was charged and the polymerization started.

Monomer conversions were determined by withdrawing aliquots (≈ 1 g) from the reaction mixture in the appropriate intervals and by pipeting them into aluminium dishes and weighing. The water—methanol (volume ratio = 1 : 1) solution of hydroquinone ($c \approx 10^{-2}$ mol dm $^{-3}$) was used to quench the polymerization. Unconverted monomer, methanol, and water were driven off by drying to constant mass in vacuum oven at 50 °C. The aluminium dishes were then reweighed to obtain percent of solids and these values were converted to conversion (%) according to eqn (16)

$$\text{conv.} = \frac{\text{RW/AW} - \text{WS}}{\text{WMF}} \times 100 \quad (16)$$

where RW/AW is the ratio of the mass residue to the aliquot mass, WS is the mass fraction of nonpolymeric solids (soap and initiator) in the feed, and WMF is the mass fraction of monomer in the feed.

Polymer for characterization was obtained from latex by the procedure as follows. Emulsions were coagulated with methanol, then filtered, and the residual polymer was washed again with methanol. The product was dried and polymer was isolated by dissolution in acetone, followed by precipitation with methanol.

Molecular mass measurements

Limiting viscosity numbers were measured in acetone at 25 °C. The viscosity-average relative molecular mass, $\bar{M}_{r,v}$, of poly(butyl acrylate) was calculated according to the relation [16]

$$\{[\eta]\} = 6.85 \times 10^{-5} \cdot \bar{M}_{r,v}^{0.75} \quad (17)$$

Particle size measurements

The particle size of the latexes was determined by the light scattering measurements. All measurements were run at a wavelength of 400 nm using Specord UV VIS Spectrophotometer, according to the method described in [17]. Latexes diluted by distilled water to about 0.01—0.1 mass % were used in all the light scattering measurements.

Equilibrium monomer concentration measurements

Values of the mass ratio of monomer and polymer $\omega_{m,p}$ in latex particles were determined from the equilibrium swelling of nonpolymerizing latex samples by their monomers. Thus, the aliquots of the polymer latex were mixed with the known amounts of monomer in calibrated centrifuge tubes which contained the hydroquinone. The contents of the tubes

were intensively shaken and spun in the centrifuge to separate the monomer droplets from the aqueous phase. The volume of the monomer layer (nonswelling or residue monomer) was deducted from the calibrated centrifuge tube and converted into mass of nonswelling monomer. From these data and conversion figures the values of $\omega_{m,p}$ were calculated [10].

Results and discussion

Equilibrium monomer concentration

Monomer concentration parameters, monomer/polymer mass ratio, $\omega_{m,p}$, the volume fraction of monomer in the latex particle, Φ_m , and corresponding values of equilibrium monomer concentration $[BA]_{eq}$ during interval II of emulsion polymerization of butyl acrylate are presented in Table 1.

The values Φ_m or $[BA]_{eq}$ for the polymerization of butyl acrylate were only slightly influenced by soap concentration. The experimental values of $\Phi_m = 0.68$ correspond very well with that reported in literature ($\Phi_m = 0.65$) [18, 19]. The values of Φ_m are known to depend on particle size and soap concentration. It is accepted that the high soap concentration brings down the value of the particle/water interfacial tension and favours the formation of small particles. The decrease in the interfacial tension results in the increase of Φ_m values [20]. The decrease of the particle size at a given interfacial tension causes the reduction in Φ_m . The small changes in the experimental values of Φ_m indicate that the both effects of soap at polymerization upon Φ_m are partially selfcompensating.

Similarly, the equilibrium concentration of monomer in a latex particle $[M]_{eq}$ is established because the free energy of mixing is balanced by the increase in surface energy due to the volume expansion of the particle. The value of $[M]_{eq}$ is also a function of water solubility of monomer and polymer solubility in monomer [21]. Monomer dissolved in water causes the reduction of the interfacial tension between

Table 1

Monomer concentration parameters in latex particles for interval II

The initial monomer concentration in the feed $[BA]_0 = 3.493 \text{ mol/dm}^3 = 6.24 \times 10^{-3} \text{ mol/(cm}^3 \text{ water)}$

$\frac{[DW] \times 10^5}{\text{mol/(cm}^3 \text{ water)}}$	$\frac{[BA]_{eq} \times 10^3}{\text{mol/(cm}^3 \text{ water)}}$	$\frac{[BA]_{eq}}{\text{mol/dm}^3}$	$\omega_{m/p}$	Φ_m
7.325	7.94	4.44	1.57	0.670
2.876	7.99	4.47	1.60	0.674
1.178	8.03	4.49	1.65	0.677
0.633	8.14	4.55	1.70	0.687

the oil and aqueous phases [19]. It is reasonable to suppose that the water solubility of monomer influences also the interfacial tension between polymer and water phases.

Thus, in the case of monomers as styrene, butyl acrylate, methyl methacrylate, *etc.* that are good solvents for their homopolymers, the different values of $[M]_{eq}$ may be related to monomer—water solubility. It is possible to set the order of monomers according to their increasing mass fraction ($w/\%$) dissolved in water: 0.036 (styrene) < 0.08 (butyl acrylate) < 1.5 (methyl methacrylate) [22]. The values of $[M]_{eq}$ increase in the following order: $[BA]_{eq} \approx 4.5 < [St]_{eq} = 5.0$ [23] $< [MMA]_{eq} = 7.0$ [8]. It may be deduced that the monomer—water solubility is an important factor in regulating the nature of polymerization loci. Lower value of $[BA]_{eq}$ than expected (on the basis of the higher water solubility of BA monomer in comparison with St monomer) can be attributed to different monomer surfactant solubility, polymerization temperature, absorption of monomer on surface polymer particles, polymer solubility in water, *etc.* Diffusion of monomer into polymer particles is extremely fast, the amount of monomer in the particle corresponds to a thermodynamic equilibrium. Thus the concentration of monomer in the growing particles should be constant and independent of conversion under the equilibrium conditions (in the presence of monomer droplets).

The data presented here indicate the complexity of the investigated emulsion polymerization system and it is taken into account in further discussion.

Rate of polymerization

The course of the free radical emulsion polymerization of butyl acrylate carried out at $70\text{ }^{\circ}\text{C}$ is presented in Figs. 1 and 2. The small induction periods observed are caused by the settlement of reaction conditions and most probably by the presence of small quantities of oxygen in the reaction system. In separate experiments it was found that oxygen exhibited a very strong inhibitory effect in emulsion polymerization of butyl acrylate. Carrying out polymerizations of butyl acrylate under an air atmosphere, long induction periods were observed or the polymerization did not start at all.

In the range of very low conversion (about 5 %) only small increase of the polymerization rate is observed. Even at high initiator concentration (Fig. 1*b*) used, the increase of the polymerization rate is not proportional to soap concentration. This effect may be explained in terms of retardation of polymerization process by Dowfax 2A1 itself [24]. At the beginning of polymerization the high concentration of the free emulsifier, dissolved in water, is present in the system. The interaction of the dissolved free radical with soap molecule may lead to desactivation of an active radical centre. Thus, interactions in the water phase occur

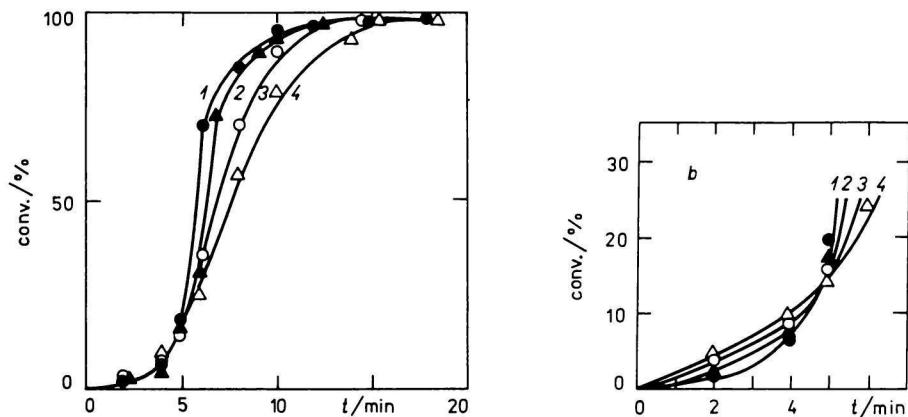


Fig. 1. Variation of the monomer conversion in the emulsion polymerization of butyl acrylate with reaction time and the concentration of soap.

140 g water, 95.62 g BA, $[(\text{NH}_4)_2\text{S}_2\text{O}_8] = 2.287 \times 10^{-5} \text{ mol}/(\text{cm}^3 \text{ water})$, temperature 70°C .

1. $[\text{DW}] = 7.325 \times 10^{-5} \text{ mol}/(\text{cm}^3 \text{ water})$; 2. $[\text{DW}] = 2.876 \times 10^{-5} \text{ mol}/(\text{cm}^3 \text{ water})$;

3. $[\text{DW}] = 1.178 \times 10^{-5} \text{ mol}/(\text{cm}^3 \text{ water})$; 4. $[\text{DW}] = 0.633 \times 10^{-5} \text{ mol}/(\text{cm}^3 \text{ water})$.

a) The whole conversion curve; b) conversion curve up to 20% conversion.

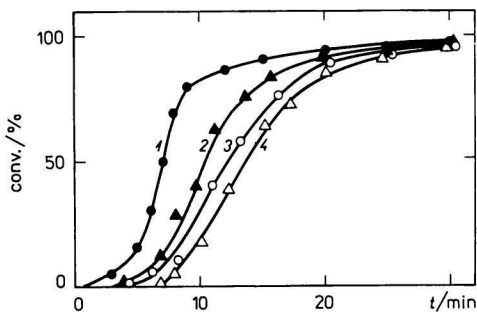


Fig. 2. The same as in Fig. 1, but $[(\text{NH}_4)_2\text{S}_2\text{O}_8] = 2.287 \times 10^{-6} \text{ mol}/(\text{cm}^3 \text{ water})$.

and continue effectively until the emulsifier is depleted and polymerization is not more significantly influenced. The recent results obtained in the polymerization of acrylic acid in water support this assumption [25]. It was found that Dowfax 2A1 exhibited a strong retarding effect on polymerization rate of acrylic acid.

Beyond the conversion 5–10% the polymerization rate increases abruptly and its increase is proportional to soap concentration. The measured rates of polymerization and initiation are in medium range of conversion listed in Table 2. It is evident that the rates of both polymerization and initiation are strongly influenced by the amount of the emulsifier in the feed.

Table 2

$\frac{[DW] \times 10^5}{\text{mol}/(\text{cm}^3 \text{ water})}$	Kinetic data parameters	
	polymerization $R_p \times 10^{5a}$	Rate of initiation
		$R_i \times 10^{9b}$
	mol/ $(\text{cm}^3 \text{ aqueous phase})\text{s}$	mol/ $(\text{cm}^3 \text{ aqueous phase})\text{s}$
7.325	1.74	5.76
2.876	1.05	3.47
1.178	0.73	1.65
0.633	0.55	1.15

a) Rate of polymerization obtained up to 20 % conversion (data taken from Fig. 1); b) rate of initiation calculated from eqn (3) using experimental polymerization rate (a) and the number-average degree of polymerization, \bar{P}_n (Table 7).

Conversion vs. time data (Figs. 1 and 2) were graphically differentiated to yield the fractional rate of polymerization $(dx/dt)/(1-x)$, shown in Figs. 3 and 4. The value x was calculated from the relation

$$x = 1 - n_t/n_0 \quad (18)$$

where n_0 and n_t represent the total amount of substance of the monomer (mol) in feed at time zero and t of the polymerization. The dependence of the fractional rate on the conversion is in all systems described by the curve with a maximum

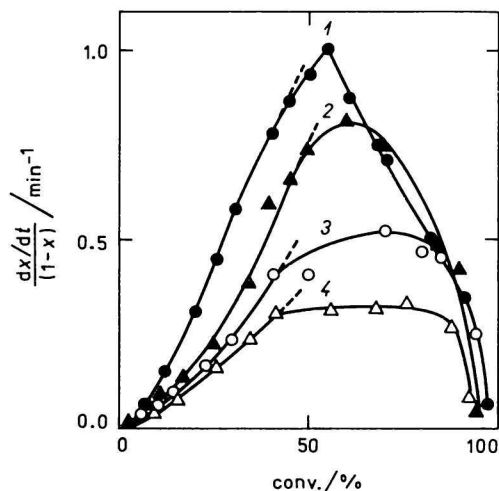


Fig. 3. Variation of the fractional rate of polymerization $(dx/dt)/(1-x)$ of butyl acrylate with soap concentration and conversion. Other conditions as given in the legend to Fig. 1.

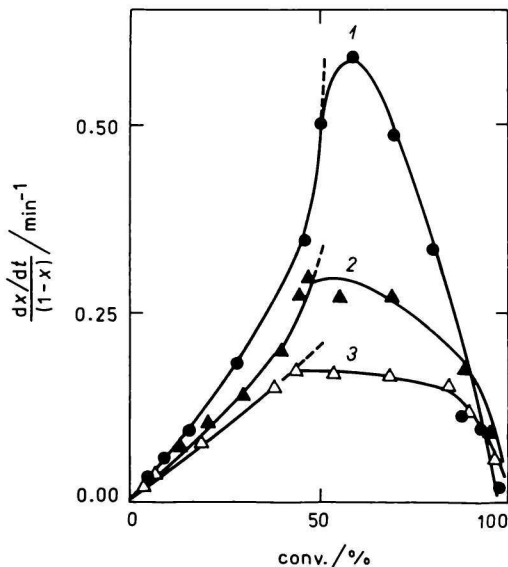


Fig. 4. Variation of the fractional rate of polymerization $(dx/dt)/(1-x)$ of butyl acrylate with soap concentration and conversion.

1. $[DW] = 7.325 \times 10^{-5}$ mol/(cm³ water);

2. $[DW] = 2.876 \times 10^{-5}$ mol/(cm³ water);

3. $[DW] = 0.633 \times 10^{-5}$ mol/(cm³ water).

Other conditions as given in the legend to Fig. 2.

corresponding to a certain conversion. The fractional rate of polymerization increases with the soap concentration and reaches the maximum. The position and the shape of the curve in the maximum with respect to conversion is different for each soap concentration.

In the system with higher initiator concentration (Fig. 3), the maximum is shifted to lower conversions with the increase of soap concentrations. On the contrary, using lower concentrations of initiator, the maximum is shifted to higher conversions (Fig. 4).

The kinetic data show that there is an approximately constant fractional rate up to conversion of monomer approaching about 40%. Beyond this conversion deviation from linearity is observed and it is indicated by a broken line.

It is reasonable to suppose that the deviation from linearity is the result of monomer droplets depletion. The depletion of butyl acrylate droplets during polymerization was observed in the range of 40–50% conversion [26]. In this interval the reaction proceeds far enough so that monomer droplets disappear, and the reaction mixture becomes a two-phase system of swollen particles and aqueous phase. Thus, unconverted (nonpolymerized) monomer is present only in latex particles and in water.

Transition between intervals II and III was used to determine the value of the ratio of the masses of monomer and polymer ($\omega_{m/p}$) in the particles from the fractional rate—conversion relationship. The values $\omega_{m/p}$ were taken in the range of deviation from linearity of the fractional rate—conversion dependence (Figs. 3 and 4) and are listed in Tables 3. The values of $\omega_{m/p}$ in dependence on soap

Table 3

Values of the ratio of the monomer and polymer masses in the particles, $w_{m/p}$

$\frac{[DW] \times 10^5}{\text{mol (cm}^3 \text{ water)}}$	$\frac{\text{conv.}^a}{\%}$		$\frac{\text{conv.}^b}{\%}$	
7.325	~40	1.5	~50	1.5
2.870	~45	1.3	~45	1.2
1.178	~40	1.5	—	—
0.633	~42	1.4	~42	1.4

a) Data taken from Figs. 1 and 3; b) data taken from Figs. 2 and 4.

concentration listed in Table 3 are in good agreement with those obtained in separate experiments (Table 1) and Ref. [26].

The polymerization rate acceleration observed at low and medium conversion is known to be attributed to the accumulation of growing radicals as a result of radical recombination depression. The decrease in the rate of polymerization at higher conversion is explained by reduction of monomer concentration around reaction loci.

Estimated concentrations of particles and radicals

In this work eqns (3—11) were used to estimate rates of volume growth of particles, mean particle radius, number of particles, concentration of growing radicals, and the ratio of the constants for termination and propagation. The results of these calculations are listed in Tables 4—6.

Table 4

Calculated rate of particle volume growth, particle radius, and number of particles

$\frac{[DW] \times 10^5}{\text{mol/(cm}^3 \text{ water)}}$	Rate of volume growth $K \cdot 10^{18}/(\text{cm}^3 \text{ s}^{-1})$	Particle radius r_c/nm	Number of particles in 1 cm^3 of aqueous phase $N \cdot 10^{-15}/\text{cm}^{-3}$
7.325	1.24	28	6.96
2.876	1.27	34	3.65
1.178	1.29	45	1.59
0.633	1.15	54	0.92

 r_c — Radius calculated.

Table 5

Calculated and experimental particle radii

$\frac{[DW] \times 10^5}{\text{mol}/(\text{cm}^3 \text{ water})}$	Particle radius r_c/nm	Particle radius r_{exp}/nm	Ratio of r_{exp}/r_c
7.325	28	33	1.18
2.876	34	41	1.21
1.178	45	55	1.22
0.633	54	75	1.39

 r_{exp} — Radius experimentally obtained.

Table 6

Kinetic data of butyl acrylate emulsion polymerization

$\frac{[DW] \times 10^5}{\text{mol}/(\text{cm}^3 \text{ water})}$	$\frac{(dx/dt)}{(1-x)} \times 10^{2a}$ s^{-1}	k_t/k_p^b	$\frac{\text{BA radical} \times 10^9}{\text{mol}/(\text{cm}^3 \text{ water})}$	Number of radicals per particle ^b \bar{Q}
7.325	0.80	20	6.58	0.57
2.876	0.65	60	5.40	0.89
1.176	0.40	70	3.30	1.25
0.633	0.30	120	2.50	1.64

a) Fractional rate of polymerization taken at about 40 % conversion (at broken lines of Fig. 3);
b) values for interval II.

It can be seen (Table 4) that the rate of particle growth K is not influenced by the concentration of soap in the feed. Particle growth is known to be dependent on homopropagation rate. One can suppose that emulsifier does not influence the homopropagation rate constant and monomer concentration near the reaction loci. The particle radius and number of particles are assumed to be affected by the soap concentration, respectively.

Good agreement has been attained between the calculated and observed particle sizes (Table 5). It is observed that the experimental particle radii were larger and with the rise in the surfactant concentration the ratio r_{exp}/r_c decreases. Thus, the values of the observed particle radius decrease more markedly with the emulsifier concentration in comparison with those calculated on the basis of the kinetic model valid in interval II. It appears that the effects of the anionic surfactant on the size and the type of association of surfactant micelles should be taken into account. The

results given in paper [27] support this idea. They indicate that the electrolyte concentration significantly influences the size of the surfactant micelles. The change of the size and the type of association of micelles may influence the growth and size of polymer particles. This probably reflects the discrepancies between the model used and the real systems. It is reasonable to suppose that the observed difference between experimental and calculated radius is mainly due to the foregoing factor.

BA radical concentration is a function of the rate of initiation, termination, and conversion. It is estimated that it increased with increasing the surfactant content in the feed. This is to be expected, of course, from the nature of the emulsion polymerization.

Application of the Gardon's equations to the experimental data indicates that the ratio of the rate constants for termination and propagation (k_t/k_p) is of 10—100 order, by several orders of magnitude lower than in homogeneous polymerization at low conversion. As *North* and coworkers have shown [28, 29], the rate of termination process is governed by segmental diffusion at low conversion. Growing radicals are brought together by translation diffusion, whereupon the radical ends reorient by segmental diffusion to facilitate termination reaction.

It was reported [30] that the ratio k_t/k_p decreased with conversion. (The value of k_t decreased more rapidly than k_p with conversion in homogeneous polymerization.) Thus, the high conversion model seems to fit better than the low conversion one for the heterogeneous emulsion polymerization. Unfortunately, little work has been done in this area (high conversion stage) where the kinetics are very complex.

In emulsion polymerization the particles contain 50—70 % monomer and polymer of relative molecular mass 10^6 — 10^7 . The viscosity in the particles is therefore very high and polymerization may be treated as certain "high conversion type of polymerization". In the emulsion polymerization (except of the initial stage) the rate-controlling process seems to be the translation diffusion to the segmental diffusion of the active polymer chains within the polymer particles. Similarly as for the gel-effect of mass polymerization the abrupt increase of the segmental motion is due to the changed thermodynamic character of solvent within the polymer particles. It appears that the quality of solvent within the polymer particles is decreased.

The translation motion, however, must decrease because of the formation of high molecular masses. Thus, the higher relative molecular mass, the higher chain entanglement and the lower rate of translation motion are observed.

As the reaction advances, the polymer formation increasingly inhibits the diffusion of polymer radicals or other reactive species to the side (or the end) of polymer which bears chain-propagating free radical. Thus, radicals become fixed in the polymer particles and they can no longer freely diffuse together to affect the

termination. Crosstermination between the large chains is therefore not much probable, because the active polymer chains can be regarded as strongly entangled and thus, they are of restricted mobility. This fact results in a decrease of k_t , i.e. the rate constant for termination.

However, the small active chains (primary and oligomer radicals) are regarded as having the same mobility as in more diluted solution and can crossterminate the large propagating radicals.

It is assumed that the first step of initiation started in the aqueous phase by formation of the primary free radicals from the water-soluble initiator. The second step of initiation occurs in the monomer-loaded micelles by entering of the water-soluble or water-insoluble radicals (primary, oligomer or macro-).

Such assumptions indicate the presence of the electrostatic repulsion between the negatively charged polymer particles and negatively charged primary ion-radicals such as SO_4 , etc. [31]. In other words, with increasing concentration of Dowfax 2A1 (negatively charged) will increase a repulsive energy barrier between the negatively charged polymer particles and the negatively charged free radicals, and so the polymer particles may not be able to capture effectively the active radicals. The oligomer radical can also project its active end to the particle, while the charged end will be directed away from the surface of the micelles or latex particles, so that the electrostatic repulsion will be lowered. This shows that the entry of the oligomer radicals into the primary radicals is not so strongly affected by the nature and concentration of surfactant, and so they will take part mostly in the propagation and termination process in the reaction loci. In favour of this idea is the work of authors [32] on the emulsion polymerization which shows that only one free radical in 2.6×10^3 of those produced in the aqueous phase actually enters the latex particles. This suggests that the rate of initiation in the aqueous phase should regulate the rate constant of termination, k_t . Besides, the reactions which trap the water-soluble radicals regulate the rate of entry of radicals into polymer particles and micelles. The trend of the values of the ratio of the rate constant for termination and propagation, k_t/k_p , favours the idea that the emulsifier (DW) traps the water-soluble radicals. This shows that the surfactant may contribute to the regulation either of the rate of entry of radicals into polymer particles, and/or of the termination rate within latex particles.

The chain termination which controls the lifetime of each growing chain, will be regulated mainly by the rate of entry of free radicals into particles. This suggests that the increase of Dowfax 2A1 concentration results in the decrease of k_t and of the concentration of the active radicals in polymer particles because of regulation of entry rate of free radicals (mainly primary) into polymer particles and micelles.

Smith and *Ewart* [4] previously reported that no two radicals can coexist in a particle. If the radical enters the growing particle, it will immediately terminate the growth of the chain. Thus, each particle contains one radical for half of time and

no radical for the other half of time ($Q = 0.5$). However, as it was shown in literature, this assumption holds only for latexes of very small particle sizes at low initiation rate and conversion.

In emulsion polymerization of butyl acrylate the small particles were generated and polymerizations proceeded at high initiation rate up to total monomer conversion. Due to these factors, the average number of radicals per particle did not hold the value 0.5, but was found at the lowest soap concentration to be as high as 1.6. It was reported [8] that in the case of the emulsion polymerization of methyl methacrylate, the average number of radicals per particle under high conversion and large particle sizes was found to be around 10.

Relative molecular mass investigation

It has been found that viscosity average relative molecular masses of poly(butyl acrylate) run parallelly with fractional rate (Fig. 3, curve 1), as shown in Fig. 5. In the region of low conversion (below 10 %) relative molecular mass of polymers depends on $[I]^{-0.5}$, which suggests the mutual macroradical termination, even though the polymerization is heterogeneous in character (from Fig. 6 the value of exponent on initiator concentration -0.444 can be found by least-squares method).

Similarly as in the work [31] it appears that the termination at low conversion proceeds in polymer particles by the interaction of two macroradicals. Also the increase in the relative molecular mass of polymer with conversion (here up to 40 %) is consistent with the slow termination of the growing radicals. Beyond 40 % conversion the relative molecular mass of polymer was being slightly lowered. The rise and fall of relative molecular masses of polymer were also noted by several research groups [31, 33–36].

Generally, the relative molecular mass of polymer is controlled by the ratio of k_p/k_t under given condition [37]. Similarly as in the heterogeneous polymerization

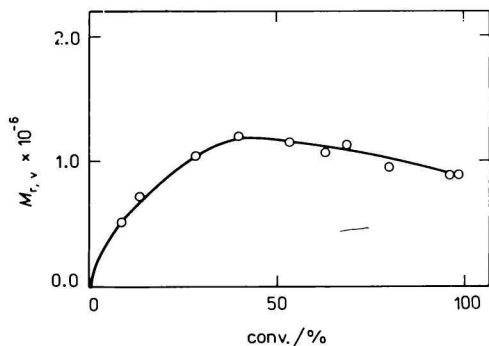
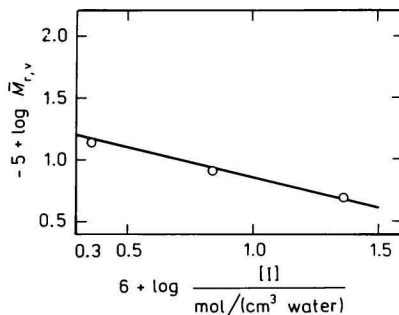


Fig. 5. The viscosity-average relative molecular mass as a function of conversion. $[DW] = 7.325 \times 10^{-5}$ mol/(cm³ water). Other conditions (recipe) as given in the legend to Fig. 1 (curve 1).

Fig. 6. Variation of the viscosity-average relative molecular mass with the initiator concentrations at low conversion (below 10 %). [DW] = 7.325×10^{-5} mol/(cm³ water), 140 g water, 95.62 g BA, temperature 70 °C, [(NH₄)₂S₂O₈] varied.



with advance of reaction k_t decreases [33, 34], relative molecular mass increases. It is assumed [31] that at high conversion the concentration of monomer at the reaction loci is so small that the propagation rate would decrease, leading to the fall in the relative molecular mass. Literature data (and present) show that in the emulsion polymerization the average relative molecular masses become maximum at about 25–40 % conversion, while in the heterogeneous polymerization the maximum is held at about 70 % conversion.

It is difficult to believe that propagation rate constant and concentration of monomer around reaction loci themselves are being affected by the changes in diffusion characteristics of the reaction system within conversion 25–40 %.

It is possible that this phenomenon arises not only from what is known about the features of the heterogeneous polymerization but also from the specific nature of emulsifier and monomer utilized, polymers produced, and their influence on the course of the process itself.

Experimental results show that the viscosity average relative molecular mass depends nearly inversely on the soap concentration (Table 7), not as it was expected. Following from the *Stockmayer* [38] and *van der Hoff* [39] treatments, the relative molecular masses of polymers generated in small particles are higher than of those generated in big particles. The relative molecular masses of polymer obtained from emulsion polymerization should be closely related to the growing particle sizes.

It is speculated that except already discussed matters, the deviation appears also due to the participating following factors:

1. Solubility of Dowfax 2A1 in the oil phase. If the polymerization of butyl acrylate is carried out at a low emulsifier-concentration, a large portion of the emulsifier will be “stored” in the droplets. Consequently, the amount of emulsifier available for the formation of micelles or for the stabilization of polymer particles is drastically reduced. This leads to the rise of “microheterogeneous type” of polymerization which generates the high relative molecular mass fraction of

Table 7

Relative molecular mass parameters

$\frac{[DW] \times 10^5}{\text{mol}/(\text{cm}^3 \text{ water})}$	$\frac{[\eta]^a}{\text{cm}^3 \text{ g}^{-1}}$	$\bar{M}_{r,v} \times 10^{-6b}$	$\bar{M}_{r,N} \times 10^{-c}$	$\bar{P}_n \times 10^{-d}$
7.325	200	0.899	6.237	4.866
2.876	200	0.899	6.237	4.866
1.178	250	1.211	8.398	6.552
0.633	260 ^e	1.276 ^f	8.849 ^f	6.904 ^f

a) Limiting viscosity number of poly(butyl acrylate) in acetone at 25 °C; b) the viscosity-average relative molecular mass calculated according to eqn (17) using limiting viscosity number data; c) the number-average relative molecular mass calculated according to Ref. [41], using limiting viscosity number data; d) the number-average degree of polymerization; e) only 20 % of polymer was dissolved in acetone and the rest remained in the form of swollen crosslinked gel; f) the value of the soluble part of polymer.

polymers or even crosslinked gel. As for the polymerization with high concentration of emulsifier, enough emulsifier was available for the formation of micelles and for the stabilization of polymer particles, so that "normal" emulsion polymerization proceeded.

2. Retardation effect of Dowfax 2A1.

3. Change of the emulsifier volume fraction Φ_e [40] with component feed composition and the association [41] between polymer formed and emulsifier utilized. For low Φ_e , the system is heterogeneous — two bulk phases, or one phase dispersed in another. At higher values of Φ_e , oil and water "dissolve" in the emulsifier to produce a homogeneous equilibrium mixture.

Change in feed composition and in the association between polymer formed and emulsifier may influence the value of Φ_e which is responsible for the nature of the proceeding polymerization.

4. Presence of supermolecules, branched and/or crosslinked polymer chains in solution may reduce the limiting viscosity number of polymer in comparison with a dissolved linear polymer with the same relative molecular mass [42, 43]. Thus, the branched and crosslinked aggregates and/or microgels have smaller dimensions, and consequently, also the limiting viscosity number than linear polymer of the same relative molecular mass.

On the basis of the experimental values of the limiting viscosity numbers, it is possible to say that rather the branched and crosslinked polymers than the broad relative molecular mass distributions are the cause of a lower limiting viscosity number. However, without additional experimental evidence it is impossible to say whether the supermolecules, branching, or crosslinking only are responsible for a lower limiting viscosity number.

5. It was confirmed [44] that the rate of the thermal decomposition increased considerably in the presence of emulsifier, so that the higher concentration of free radicals may affect the initiation and termination of polymerization reaction in the aqueous phase, in the micelles, and in the polymer particles. Besides this fact interaction may lead to the formation of radicals derived from the emulsifier molecules with the same or lowered reactivity as that of primary radicals, which can influence the termination rate within the polymer particles and the molecular masses.

These observations reveal the complex character of the emulsion polymerization and the final conclusion about polymerization mechanism is still open to the theoretical and experimental verification.

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