

Emulsion polymerization of butyl acrylate in the presence of hydrophilic seed polymer particles

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The emulsion polymerization of butyl acrylate, initiated by ammonium peroxodisulfate in the presence of crosslinked poly(ethyl acrylate) seed particles, was kinetically investigated at 60°C by conventional gravimetric and dilatometric methods. Two polymer latexes, based on an incompatible pair of polymers, were prepared by a two-stage emulsion polymerization. In the presence of poly(ethyl acrylate-co-hexamethylene diacrylate) particles, the rate of polymerization was found to be proportional to the 0.55, 0.56, and 0.65 order with respect to the initiator concentration for the systems with 1.16, 2.32, and 3.47 mol dm⁻³ butyl acrylate. Here the number of polymer particles was found to be proportional to the 0.12, 0.10, and 0.22 order with respect to the initiator concentration and to the 0.2, 0.31, and 0.25 order with respect to the emulsifier concentration, for the same systems of butyl acrylate.

In the presence of poly(ethyl acrylate-co-divinylbenzene) particles the rate of polymerization was proportional to the 0.56 order with respect to the initiator concentration. The number of final polymer particles was proportional to the 0.07 and 0.51 order with respect to the initiator and emulsifier concentration, respectively. The rate of polymerization increases slightly with the increasing concentration of butyl acrylate. Deviation from the emulsion polymerization predictions is discussed in terms of the phase separation in seed particles, the reverse diffusion of monomer and the different polymerization activity in the monomer-swollen emulsifier micelles and the monomer-swollen seed polymer particles.

The free-radical crosslinking polymerizations and copolymerizations of bi-unsaturated monomers have been followed in [1–4]. It has been established that a vinyl–divinyl copolymerization leads to gelation of the systems. Here, due to the presence of cross-links, the polymers formed are insoluble in all solvents but are still able to swell in adequate diluents.

Since then, the polymerizations and copolymerizations of bi-unsaturated monomers have been performed also in the aqueous dispersion systems [5–7]. Here, the gell point does not lead to gelation of the dispersion systems. The coagulum formation and the polymer particle size in the emulsion polymerization of tetrafunctional monomers is a function of the monomer and water mass

ratio, the mass ratio of unsaturated and bi-unsaturated monomer and concentration of reactants.

The area of emulsion polymerization and copolymerization of multifunctional monomers has been the subject of many studies [5—9]. On the other hand, a small amount of work has been devoted to kinetic study of emulsion polymerization and copolymerization of multifunctional monomers. Crosslinked polymers are an important class of synthetic materials. Their main distinction from other classes of organic polymers lies in their crosslinked molecular structure, *i.e.* an “infinite” molecular mass. This special molecular structure leads to superior properties: a high glass transition temperature, high modulus of expansion and fracture strength and generally good performance at elevated temperature. In order to obtain this class of synthetic materials by the emulsion polymerization, we should know the mechanism of emulsion polymerization and copolymerization of multifunctional monomers, *i.e.* the dependence of the rate of polymerization, the polymer particle size, and the number of polymer particles on reaction conditions and the reactant concentrations.

Latex interpenetrating polymer networks (LIPN) are a unique type of polymer blend prepared by two-stage polymerization methods [8, 9]. The preparation involves making a seed latex of a crosslinked polymer (polymer 1) and then introducing into the reaction vessel the monomer 2 together with its crosslinking agent (monomer 1). Monomer 2 is then polymerized.

The mechanism of domain formation upon phase separation is not well understood because of the effect of numerous parameters [10—12], *e.g.* the compactibility, the composition of the reaction mixture, the degree of crosslinking, the monomer and polymer concentration, the polymerization temperature, the interfacial tension and the method of preparation, and the limitation of the experimental techniques. The paper [13] showed that the use of crosslinked polystyrene seed particles in the seeded emulsion polymerization of styrene with or without divinylbenzene, resulted in phase separation in the final latex particles, *i.e.* the formation of uniform nonspherical particles. These nonspherical particles comprised two identical polystyrenes, at least one of which was in the form of a crosslinked network.

Up to now, no kinetic studies were reported with these systems, for which the mechanism of polymerization was unknown. We, therefore, tried to clarify the effect of the simple and crosslinked seed polymer particles on the polymerization of hydrophobic butyl acrylate (monomer 2). This polymerization appears to be a very complex reaction system for studying reaction kinetics due to the large differences in hydrophobicity of polymers 1 (seeded) and 2 (formed).

The aim of this paper is to evaluate the effect of the water-soluble initiator and emulsifier concentrations, the domain formation and the reverse monomer diffusion on the kinetics and mechanism of emulsion polymerization of hydro-

phobic butyl acrylate in the presence of crosslinked hydrophilic poly(ethyl acrylate) particles and to compare the obtained results with the course of emulsion batch polymerization of butyl acrylate. In addition, variations of the particle size, the number of polymer particles and the rate of polymerization with two different seed polymer particles are described.

Experimental

Butyl acrylate (BA), ethyl acrylate (EA), divinylbenzene (DVB), and hexamethylene diacrylate (HMDA) monomers (Merck, Darmstadt) were shaken with 5 mass % aqueous sodium hydroxide solution, washed with water, dried over anhydrous calcium chloride, and finally distilled under reduced pressure. Purity was checked by gas chromatography. The reagent grade anionic emulsifier sodium dodecyl sulfate (SDS; Fluka, Switzerland) and the anal. grade ammonium peroxodisulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$ (Lachema, Brno) were used as supplied. Double-distilled water was used as the polymerization medium.

Preparation of seed polymer particles

Radical emulsion copolymerizations of ethyl acrylate (monomer 1) and divinylbenzene or hexamethylene diacrylate in a 0.5 dm³ three-necked separable glass flask fitted with a glass stirrer, a thermometer and a reflux condenser were carried out. The contents were 150 g water, 2 g SDS, 0.2 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 0.038 g NaHCO_3 , 88 g EA, and 4.8 g HMDA ($c = 0.022 \text{ mol dm}^{-3}$) (the system 1), or 4.6 g DVB ($c = 0.0352 \text{ mol dm}^{-3}$) (the system 2). Copolymerizations were run for 3 h at 60°C with stirring at the revolutions 400 min⁻¹ under nitrogen atmosphere in batch conditions. The recipe ingredients were charged into the reactor under the strict exclusion of oxygen. Then the reaction mixture was stirred for about 15 min at constant agitation speed at 60°C. At last the aqueous solution of ammonium peroxodisulfate was added with a syringe. Starting with this moment the reaction time was measured. Aliquots of 10 cm³ from the polymerization mixture were withdrawn for characterization of the polymer and determination of the conversion. An aqueous solution of hydroquinone was used to quench the polymerization at certain time intervals. The polymer was then precipitated with a fivefold volume of acidified methanol. After decantation, the pure polymer was dried *in vacuo* to constant mass at 20°C at maximum. Copolymerizations were led to conversion above 95%. The gravimetric method has been already described in [14]. The polymer samples prepared using 5.2 mass % HMDA or 5 mass % DVB were insoluble in toluene or acetone and gave turbid dispersions.

The poly(ethyl acrylate-co-hexamethylene diacrylate) (P(EA-co-HMDA), system 1) or poly(ethyl acrylate-co-divinylbenzene) (P(EA-co-DVB), system 2) latex was dialyzed against water with a cellophane Visking tubes (No. 36, Serva). Dialysis was performed by daily replacement of distilled water until the dialyzate attained a constant conduc-

tance of less than 50 μS . The cleaning by dialysis removes from the system the unreacted monomer, initiator, free emulsifier, and other low-molecular side products. The cleaning process requires at least two weeks. The latex treated in this way was filtered through a nylon filter cloth and used as seeded particles.

Seeded copolymerization

The seeded emulsion copolymerizations were done at 60°C with stirring at the revolutions 400 min^{-1} under the same conditions as described previously. The aliquots of the seeded polymer latex were mixed with the known amounts of BA and emulsifier ($[\text{SDS}] = 10^{-2} \text{ mol dm}^{-3}$) in a reactor. The monomer-swollen polymer particles were obtained by stirring the reactants for 48 h at constant agitation speed (revolutions *ca.* 60 min^{-1}) at 20°C. Then the emulsifier (the second fraction) and the aqueous solution of ammonium peroxodisulfate were added into reactor. In runs using gravimetric method a recipe containing 40 g water, 100 g of P(EA-co-DVB) or P(EA-co-HMDA) (with 20 mass % of polymer 1) and 0.03 g NaHCO_3 was used. A recipe for a dilatometry contains 20 g water, 50 g of seed latex, and 0.015 g NaHCO_3 . The amounts of SDS, ammonium peroxodisulfate and BA varied as shown later. The dilatometric method was used for determining the polymerization rates. The polymerization mixture for the dilatometric measurement was prepared in a similar way as described above for the gravimetric measurement. Monomer conversion was determined by measuring the volume contraction of the polymerization mixture during the reaction time. The volume contraction was converted to conversion by calibration using the gravimetric method for every run with different monomer concentration. The polymerization rate was determined as the mean rate within the range of 20–50 % conversion and equals the maximum rate. The relative error of measurement of the rate of polymerization by the dilatometry was below 3 %. The dilatometric method has been already described in [15, 16].

Particle size measurements were done by light scattering using commercially available instrument laser submicron particle analyzer Model 4 (Coulter Electronics, Hialeah, USA). Latexes diluted by distilled water to about 0.01–0.1 mass % were used in these measurements. Some latexes prepared in the presence of high emulsifier concentration were dialyzed to remove a large amount of free emulsifier. Results are quoted as the average particle diameter \bar{d} . The relative error of measurement of the particle diameter was found to be below 3 %.

The surface tension was determined by the stalagmometric method [17]. A glass-jacketed stalagmometer with a watch glass was used. Constant temperature (30°C) was maintained by connection of the jacketed stalagmometer to an adjustable water-bath pump.

The conductance of polymer latex in nitrogen atmosphere was measured using a conductometer OK 102/1 (Radelkis, Budapest), according to the method described in [18]. A 100 cm^3 jacketed glass beaker covered with a watch glass was used. Constant temperature (30°C) was maintained by connection of the jacketed beaker to an adjustable temperature water-bath pump. The electrode (type OK 902, Radelkis, Budapest) was used.

The number of polymer particles N was estimated from the polymer concentration in the latex and the radius r of polymer particles using the equation [19]

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

where m_m/m_w is the mass ratio between monomer and water, ρ_w and ρ_p are the densities of water and polymer, respectively.

Results and discussion

Fig. 1 shows a plot of the conversion *vs.* time for the radical emulsion polymerization of butyl acrylate (monomer 2) initiated by ammonium peroxydisulfate in the presence of P(EA-co-HMDA) seed particles (polymer 1). Initially, the rate of polymerization is high and equals nearly the maximum rate. The curves for all runs are practically linear up to 50% conversion, then they level off and approach complete conversion asymptotically.

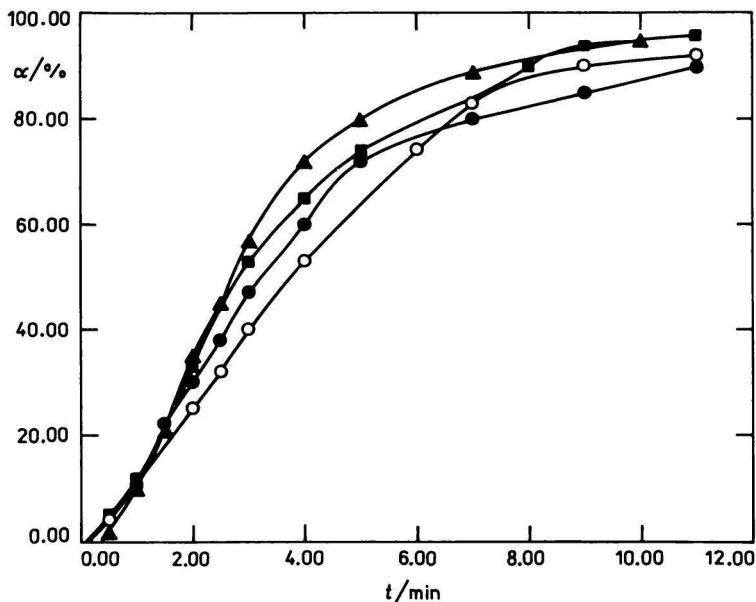


Fig. 1. Variation of the monomer conversion in the radical emulsion polymerization of BA in the presence of seed latex particles with the reaction time and with the ammonium peroxydisulfate concentration at $[\text{SDS}] = 5.76 \times 10^{-2} \text{ mol dm}^{-3}$

The system 1: 20 g water, 50 g P(EA-co-HMDA) latex, 10 g BA, 0.03 g NaHCO_3 ; 60°C; $c((\text{NH}_4)_2\text{S}_2\text{O}_8) \cdot 10^3 / (\text{mol dm}^{-3})$: ○ 1.46, ● 2.19, ■ 2.92, ▲ 3.65.

The conversion curves in the emulsion polymerization of BA (without seed polymer particles) have a few separate regions [14, 20]. Initially, the polymerization is very slow even if a relatively high concentration of ammonium peroxodisulfate was used ($2.28 \times 10^{-2} \text{ mol dm}^{-3}$). As polymerization proceeds, the rate of polymerization gradually increases, reaching approximately the constant rate of polymerization within a long conversion region. At last, the polymerization rate falls as the monomer droplets disappear. In this system the first interval is located within the conversion region of 0–20 %, the second interval within 25–75 % and the last one above 75 % conversion.

Table 1

The kinetic parameters of emulsion polymerization of BA in the presence of seed polymer particles ($\bar{d}_s = 140 \text{ nm}$, $N_s = 1.3 \times 10^{13} \text{ cm}^{-3}$) at $[\text{SDS}] = 5.76 \times 10^{-2} \text{ mol dm}^{-3}$
50 cm^3 P(EA-co-HMDA) latex, 20 cm^3 water, 10 cm^3 BA; 60 °C

$[(\text{NH}_4)_2\text{S}_2\text{O}_8] \cdot 10^3$	$R_p \cdot 10^3$	\bar{d}_r	$N_r \cdot 10^{-14b}$	N_r/N_s	Surface tension γ	Conductance κ
mol dm^{-3}	$\text{mol dm}^{-3} \text{ s}^{-1}$	nm	cm^{-3}		mNm^{-1}	mS
1.46	2.8	157	1.76	1.36	43	2.3
2.19	3.5	153	1.90	1.46	43	2.4
2.92	4.2	152	1.92	1.48	44	2.4
3.65	4.6	151	1.96	1.51	44	2.6

a) \bar{d}_r — the average diameter of final polymer particles; b) N_r — the number of final polymer particles.

Table 2

The kinetic parameters of emulsion polymerization of BA in the presence of seed polymer particles at $[\text{SDS}] = 5.76 \times 10^{-2} \text{ mol dm}^{-3}$
50 cm^3 P(EA-co-HMDA) latex, 20 cm^3 water, 20 cm^3 BA; 60 °C

$[(\text{NH}_4)_2\text{S}_2\text{O}_8] \cdot 10^3$	$R_p \cdot 10^3$	\bar{d}_r	$N_r \cdot 10^{-14}$	N_r/N_s	γ	κ
mol dm^{-3}	$\text{mol dm}^{-3} \text{ s}^{-1}$	nm	cm^{-3}		mNm^{-1}	mS
1.46	2.8	176	1.83	1.41	45	2.1
2.19	3.4	177	1.81	1.39	46	2.2
2.92	4.0	174	1.90	1.46	46	2.7
3.65	4.7	170	2.00	1.56	48	2.5
5.84	6.4	165	2.10	1.60	—	—
7.30	7.8	164	2.10	1.60	—	—

The rates of polymerization R_p are calculated from linear portions of the conversion curves (Fig. 1). They are summarized in Table 1 together with other kinetic parameters as a function of the initiator concentration. In Tables 2 and 3 are also shown the same kinetic parameters using, however, higher monomer concentrations in the monomer feed. The reaction orders (Table 4) with respect to the initiator concentration $[I]$ were obtained from the polymerization rate variations. The polymerization data follow the relationship

$$R_p \sim [I]^{0.55 \text{ } 0.65} \quad (2)$$

which deviates from the model proposed by *Smith and Ewart* [21] and *Fitch and Tsai* [22].

Table 3

The kinetic parameters of emulsion polymerization of BA in the presence of seed polymer particles at $[\text{SDS}] = 5.76 \times 10^{-2} \text{ mol dm}^{-3}$
50 cm³ P(EA-co-HMDA) latex, 20 cm³ water, 30 cm³ BA; 60 °C

$[(\text{NH}_4)_2\text{S}_2\text{O}_8] \cdot 10^3$ mol dm ⁻³	$R_p \cdot 10^3$ mol dm ⁻³ s ⁻¹	\bar{d}_r nm	$N_r \cdot 10^{-14}$ cm ⁻³	N_r/N_s	γ mN m ⁻¹	κ mS
1.46	2.8	192	1.88	1.45	48	1.5
2.19	3.4	191	1.91	1.47	44	2.2
2.92	4.2	188	2.00	1.54	43	2.1
3.65	5.1	188	2.00	1.54	43	2.5
5.84	7.5	186	2.10	1.62	—	—
7.30	8.6	185	2.10	1.62	—	—

Table 4

The reaction orders with respect to the initiator and emulsifier concentration

[BA] mol dm ⁻³	Exponent x , y or z from					
	$R_p \sim [I]^x$		$N \sim [I]^y$		$N \sim [E]^z$	
	a	b	a	b	a	b
1.16	0.55	—	0.12	—	0.20	—
2.32	0.56	0.56	0.10	0.07	0.31	0.51
3.47	0.65	—	0.22	—	0.25	—

a) The system 1 (see Tables 1—3, 8 and 9).

b) The system 2 (see Tables 10 and 11).

According to Smith—Ewart's and Fitch—Tsai's model, the rate of polymerization is related to the equilibrium monomer concentration $[M]_{\text{eq}}$, the propagation rate constant k_p , the number of polymer particles N , the average number of radicals per particle \bar{n} , and Avogadro's constant N_A

$$R_p = k_p [M]_{\text{eq}} \bar{n} N N_A \quad (3)$$

and the number of polymer particles is related to the initiator $[I]$ and emulsifier $[E]$ concentration

$$N \sim [I]^{0.4} [E]^{0.6} \quad (4)$$

which shows that the rate of polymerization is proportional to the 0.4 and 0.6 order with respect to the initiator and emulsifier concentration (Table 4).

The reaction order with respect to the initiator concentration is connected with the termination mechanism of radicals. Radicals entered into the seed PBA particles activate or deactivate the growth of particles. If the deactivation of particles proceeds by the bimolecular reaction process then the reaction order with respect to the initiator concentration is 0.4. Our data show that the reaction order is unexpectedly very high for the emulsion polymerization. In the range of low conversion the rate of emulsion copolymerization of hydrophilic monomers ethyl acrylate and methyl methacrylate was found to be proportional to the 0.5 power of the initiator concentration [23]. The reaction order of 0.5 was ascribed to the bimolecular termination of macroradicals in the aqueous phase. This is not the case here, since BA is hydrophobic monomer and its polymerization in the aqueous phase is suppressed. Radicals generated in the aqueous phase are also trapped by the monomer-swollen emulsifier micelles, which makes the reaction system more complex. The entry of radicals into micelles initiates the growth of polymer chains and transforms the micelles to primary polymer particles. The crosslinked seed polymer particles favour the formation of fixed radicals where the growth of macroradicals is somewhat hindered. The reaction locus becomes surrounded by a glassy polymer matrix through which no further monomer can diffuse. The radicals fixed within the polymer particles are not procurable to bimolecular termination reactions, but they are deactivated most probably in the monomolecular termination mechanism. It seems that the formation of trapped radicals in polymer networks favours the increase of the reaction order with respect to the initiator concentration above 0.4. In favour of this assumption is the work of authors [24] which show that the reaction order above 0.5 is a result of hindered termination.

The relationship between the rate of polymerization and the BA monomer concentration is given in Table 5. From these results follows the relationship

$$R_p \sim [BA]^{0.1} \quad (5)$$

Table 5

Variation of the kinetic parameters of emulsion polymerization of BA in the presence of seed polymer particles at $[(\text{NH}_4)_2\text{S}_2\text{O}_8] = 3.65 \times 10^{-2} \text{ mol dm}^{-3}$ and $[\text{SDS}] = 5.76 \times 10^{-2} \text{ mol dm}^{-3}$ with the BA concentration

[BA]	$R_p \cdot 10^3$	\bar{d}_r	$N_r \cdot 10^{-13}$	N_r/N_s
mol dm^{-3}	$\text{mol dm}^{-3} \text{ s}^{-1}$	nm	cm^{-3}	
1.16	4.6	151	2.0	1.54
1.74	4.7	160	2.0	1.54
2.32	4.7	170	2.0	1.54
2.90	4.9	180	2.0	1.54
3.47	5.1	188	2.0	1.54

which indicates that the polymerization is only slightly influenced by the monomer concentration. The dependence given by eqn (3) shows that the rate of polymerization is proportional to $[\text{M}]_{\text{eq}}$. The equilibrium monomer concentration $[\text{M}]_{\text{eq}}$ is for a given monomer/polymer system constant. The dependence given by eqn (5) indicates that the monomer concentration in reaction loci is not influenced by the increase of the total monomer concentration.

The formation of the heterogeneous morphology in P(EA-co-BA) particles [25] favours the idea that the monomer-swollen seed polymer particles contain the monomer domains. This process seems to be connected with the phase separation in polymer particles, the polymerization in monomer domains and the reverse diffusion of monomer, *i.e.* the flow of monomer from monomer domains to the emulsifier micelles or new formed particles. If the polymerization proceeds in monomer domains of seed particles then the sensitivity of the rate of polymerization to the monomer concentration decreases while the polymerization in monomer domains is governed by the kinetics of block polymerization.

The swelling monomers contained no HMDA and so the resulting latex was a semi-IPN. The size of these latex particles before and after swelling and during polymerization was measured (Table 6). It was observed that the size of monomer-swollen seed particles did not increase further after swelling for 48 h (at 20 °C). The mixture of monomer-swollen seed particles and emulsifier was then stirred for 10 min at constant agitation rate at 60 °C. After this "pre-emulsification" stage the aqueous solution of ammonium peroxodisulfate was added. After starting polymerization, the size of polymer particles has increased beyond that of the original monomer-swollen seed particles (*ca.* about 20 vol. %). On

Table 6

Component concentration parameters in the polymerization systems 1 and 2

System	$\frac{[\text{BA}] \cdot 10^3}{\text{mol dm}^{-3}}$	$\frac{[\text{SDS}]_{\text{sat}} \cdot 10^3}{\text{mol dm}^{-3}}$ ^a	$\frac{[\text{SDS}]_{\text{sat, BA}} \cdot 10^3}{\text{mol dm}^{-3}}$ ^b		$\frac{[\text{SDS}]}{[\text{SDS}]_{\text{sat, BA}}}$		$\bar{d}_{s, \text{sw}}$ ^d nm	$\frac{m_{\text{m}}}{m_{\text{p}}}$
			PEA	PBA	PEA	PBA		
			layer	layer	layer	layer		
1 ^f	0	1.5	—	—	—	—	—	—
2 ^g	0	3.0	—	—	—	—	—	—
1	1.16	—	2.4	3.6	24.0	16.0	180	0.9
1	1.74	—	2.7	4.1	21.3	14.2	190	1.3
1	2.32	—	3.1	4.7	18.6	12.4	200	1.8
1	2.90	—	3.4	5.1	17.0	11.3	212	2.3
1	3.47	—	3.8	5.7	15.0	10.0	223	2.7
2	2.32	—	6.3	9.5	9.1	6.0	175	2.7

a) The concentration of SDS used to saturate the surface of the seed polymer particles (without monomer). b) The concentration of SDS used to saturate the surface of the monomer-swollen seed polymer particles. c) $[\text{SDS}] = 5.76 \times 10^{-2} \text{ mol dm}^{-3}$ d) The diameter of the monomer-swollen seed polymer particles. e) The ratio of masses of monomer and polymer in the monomer-swollen seed polymer particles. f) $\bar{d}_s = 140 \text{ nm}$, $N_s = 1.3 \times 10^{13} \text{ cm}^{-3}$ g) $\bar{d}_s = 120 \text{ nm}$, $N_s = 1.3 \times 10^{13} \text{ cm}^{-3}$.

Table 7

Variation of the kinetic parameters of emulsion polymerization of BA in the presence of seed polymer particles with the SDS concentration at $[(\text{NH}_4)_2\text{S}_2\text{O}_8] = 1.46 \times 10^{-3} \text{ mol dm}^{-3}$
 $50 \text{ cm}^3 \text{ P(EA-co-HMDA) latex, } 20 \text{ cm}^3 \text{ water, } 10 \text{ cm}^3 \text{ BA; } 60^\circ \text{C}$

$[\text{SDS}] \cdot 10^2$ mol dm^{-3}	$R_p \cdot 10^3$ $\text{mol dm}^{-3} \text{ s}^{-1}$	\bar{d}_r nm	$N_r \cdot 10^{-13}$ cm^{-3}	N_r/N_s
3.5	2.9	157	1.76	1.36
5.76	2.8	157	1.76	1.36
7.5	2.7	151	1.96	1.51
9.2	2.4	149	2.03	1.57
10.9	2.6	143	2.23	1.72

Table 8

Variation of the kinetic parameters of emulsion polymerization of BA in the presence of seed polymer particles with the SDS concentration at $[(\text{NH}_4)_2\text{S}_2\text{O}_8] = 1.46 \times 10^{-3} \text{ mol dm}^{-3}$
 $50 \text{ cm}^3 \text{ P(EA-co-HMDA) latex, } 20 \text{ cm}^3 \text{ water, } 20 \text{ cm}^3 \text{ BA; } 60^\circ \text{C}$

$[\text{SDS}] \cdot 10^2$ mol dm^{-3}	$R_p \cdot 10^3$ $\text{mol dm}^{-3} \text{ s}^{-1}$	\bar{d}_r nm	$N_r \cdot 10^{-13}$ cm^{-3}	N_r/N_s
5.76	2.8	176	1.83	1.41
7.5	1.8	173	1.93	1.50
9.2	1.8	168	2.10	1.63
10.9	1.4	163	2.30	1.78
14.4	1.6	160	2.42	1.87

the contrary, the size of final particles has decreased below that of the original monomer-swollen polymer particles (Tables 5, 7—9). It was clear that the growth of polymer particles in the range of low conversions did not proceed by the association of particles. It was proposed by authors [26] that at the polymerization temperature 70°C a phase separation takes place, which transforms the spherical to nonspherical particles. The measurements of these nonspherical particles by the light scattering procedure led to the higher size due to the nonspherical shape of monomer-swollen seed particles.

From Table 6 it can be seen that the swelling of seed particles produces monomer-swollen seed particles with the monomer content below and above the equilibrium monomer concentration. The equilibrium monomer concentration in the monomer-swollen PBA particles or monomer-swollen PEA particles is in the range from 4.5 to 6.0 mol dm^{-3} which corresponds to m_m/m_p in the range from 1.5 to 2.0 [14, 19, 23]. These results indicate that in the range of high

Table 9

Variation of the kinetic parameters of emulsion polymerization of BA in the presence of seed polymer particles with the SDS concentration at $[(\text{NH}_4)_2\text{S}_2\text{O}_8] = 1.46 \times 10^{-3} \text{ mol dm}^{-3}$
 $50 \text{ cm}^3 \text{ P(EA-co-HMDA) latex, } 20 \text{ cm}^3 \text{ water, } 30 \text{ cm}^3 \text{ BA; } 60 \text{ }^\circ\text{C}$

$[\text{SDS}] \cdot 10^2$ mol dm^{-3}	$R_p \cdot 10^3$ $\text{mol dm}^{-3} \text{ s}^{-1}$	\bar{d}_r nm	$N_f \cdot 10^{-13}$ cm^{-3}	N_f/N_s
5.76	2.8	192	1.88	1.45
7.50	1.8	190	1.96	1.51
9.20	1.5	180	2.26	1.74
10.90	0.44	180	2.26	1.74
14.40	0.62	175	2.41	1.85

monomer concentration (above the equilibrium monomer concentration) the phase separation or the formation of micro- or macromonomer domains probably takes place.

The effect of the anionic emulsifier SDS on the rate of the emulsion polymerization of BA in the presence of P(EA-co-HMDA) particles is summarized in Tables 7–9. In this series, the overall concentration of initiator has been kept constant and those of emulsifier and monomer have been varied. In both systems the rate of polymerization for all polymerizations unexpectedly decreases with the increasing concentration of emulsifier. Besides, the decrease of the rate of polymerization is more pronounced in the systems with high monomer concentration. The similar trend was also observed in [27]. Here the authors reported that at very high concentration of anionic emulsifier (*i.e.* above $0.0035 \text{ mol dm}^{-3}$) the rate of emulsion polymerization of methyl acrylate was found to decrease with the increasing emulsifier concentration. The excess of emulsifier acted as an electrolyte which caused the decrease of the number of polymer particles. In the emulsion polymerization, the number of latex particles N increases with the increasing colloidal stability of the latex particles and becomes maximum when the colloidal stability reaches a maximum. Tables 7–9 show that the number of polymer particles slightly increases with the increasing concentration of emulsifier. Thus, the efficiency of emulsifier in the formation of new particles is very low. The low reaction orders with respect to $[\text{E}]$ and ratios N_f/N_s point out the low activity of emulsifier. The reaction order z (taken from the dependence $N = f([\text{E}]^z)$) was found to be 0.2, 0.31, and 0.25 for the systems with 1.16, 2.32, and 3.47 mol dm^{-3} of BA. These data are not consistent with the emulsion polymerization predictions [21, 22] as given by eqn (4). The reaction order z lower than 0.6 was found also in the systems with acrolein, acrylonitrile [28, 29], and vinyl acetate [30]. The value of z in the system with acrylonitrile

ranged between 0.2 and 0.3. On the contrary, in the bath emulsion of hydrophobic BA in the absence of seed polymer particles using the anionic emulsifier (disodium dodecylphenoxybenzenedisulfate) z was found to be 0.64 [16]. From these data it follows that the reaction order depends also on the nature of interactions of polymer molecules or their segments with emulsifier molecules. If the emulsifier molecules are strongly adsorbed by the polymer molecules (hydrophobic) on the particles surface, the reaction order z was found to be close to 0.6. If the polymers have partial polarity, as in the case of polyacrylates, the order would be less than 0.6 possibly because of poor interactions between the emulsifier and the polymer molecules, as confirmed experimentally in [31]. Thus, the hydrophobic interaction is the driving force of complex formation. The hydrophilic PEA seed particles do not interact strongly with emulsifier molecules and therefore the reaction orders with respect to $[E]$ are found to be below 0.6.

From Table 6 it can be seen that the dodecylsulfate anion concentration (the saturated concentration of emulsifier, $[SDS]_{\text{sat, BA}}$) on the monomer-swollen seed particles is lower than the total SDS concentration. The ratio of $[SDS]/[SDS]_{\text{sat, BA}}$, which is the measure of partitioning of emulsifier molecules between the seed particles and emulsifier micelles shows that the largest part of emulsifier molecules concentrates in the form of micelles. The monomer-swollen seed particles were found to be stable in the range of SDS concentration above $10^{-2} \text{ mol dm}^{-3}$. In order to get stable particles all swelling experiments were performed at $[SDS] = 10^{-2} \text{ mol dm}^{-3}$. The saturated concentration of SDS (the amount of SDS used to saturate the surface of seed particles) was lower than that used to stabilize the swelling seed particles. The saturation concentration $[SDS]_{\text{sat, BA}}$ was calculated using the values of the area occupied by an emulsifier molecule ($A_{\text{SDS, PEA}} = 0.9 \text{ nm}^2$ and $A_{\text{SDS, PBA}} = 0.6 \text{ nm}^2$ [32]) and the total area of the surface of seed monomer-swollen particles. The values of $[SDS]_{\text{sat, BA}}$ for the seed particles with the PEA or PBA layer are listed in Table 6. As expected the values of $[SDS]_{\text{sat, BA}}$ for PBA particles (or particles with the PBA layer) are larger than those for PEA particles. The low value of the reaction order with respect to the SDS concentration indicates that the surface of particles consists of PEA molecules. The real value of $[SDS]_{\text{sat, BA}}$ seems to be situated between these two limit values but closer to PEA particles.

After addition of emulsifier and initiator the system contains the seed particles (with monomer domains) and emulsifier micelles poor in monomer. From the thermodynamic standpoint one would expect a thermodynamic equilibrium among the monomer-swollen seed particles, the aqueous phase and emulsifier micelles with respect to the distribution of monomer in these phases. As soon as polymerization starts in the aqueous phase, the molecules of monomer from the domains diffuse through the aqueous phase to the emulsifier micelles. This

assumption is supported by the ratio N_f/N_s , which is in all runs larger than 1. Diffusion of monomer from seed particles to emulsifier micelles and later primary particles makes the polymerization mechanism very complex, especially the initiation process. The initiation of emulsion polymerization seems to proceed in a few-step process. The primary initiation occurs in the aqueous phase by the decomposition of peroxydisulfate. Here the formation of primary and oligomer radicals takes place. The secondary step starts by the entry of radicals to the monomer-swollen seed particles and emulsifier micelles. This step includes also the association of precipitated macroradicals as precursors of new polymer particles and/or the association of primary with seed particles. The third step starts by diffusion of monomer and radicals to emulsifier micelles and the nucleation of monomer-swollen micelles. With the increasing emulsifier concentration the average monomer concentration in monomer-swollen emulsifier micelle decreases but the portion of radicals in micelles increases. Under such conditions, the deactivation rate of oligomer radicals may increase. The diffusion of monomer from seed particles favours the desorption of radicals and the entry of all radicals to micelles or new particles. It is clear that the largest part of monomer is situated in seed particles. On the other hand, the radicals are mostly captured by micelles or new particles. Thus, with increasing emulsifier concentration the deactivation of radicals in monomer-starved micelles increases. The deactivation of radicals in micelles together with the reverse diffusion of monomer and the low radical activity of seed particles are probably responsible for the observed polymerization course.

The hydrophilic PEA influences the polymerization of hydrophobic BA. The swelling of PEA by water was shown to be very good, even for higher poly(alkyl acrylates) water acts as a precipitant. PEA forms in water a honey-like mass which is very difficult to handle and characterize. This indicates that water together with other water-soluble components penetrates into PEA particles. Under such conditions, the chain transfer to these components becomes operative. Besides, the generation of radicals can proceed in microdomains of water where the mutual termination of radicals can be very effective [33].

The exit of radicals is further factor which influences the rate of polymerization. The exit rate of radicals was found to increase with the decreasing size of polymer particles [34]. With the increasing emulsifier concentration the size of new polymer particles which favours the exit of radicals from new particles decreases. The reverse diffusion of monomer increases the rate of desorption of mobile radicals to the aqueous phase. The exit of radicals from the seed particles decreases both the average number of radicals per particle and the rate of polymerization.

The kinetics and mechanism of the emulsion polymerization of BA were investigated also in the presence of P(EA-co-DVB) seed particles (the system 2).

Table 10

Variation of the kinetic parameters of emulsion polymerization of BA in the presence of seed polymer particles ($\bar{d}_s = 120 \text{ nm}$, $N_s = 3.62 \times 10^{13} \text{ cm}^{-3}$) with the ammonium peroxodisulfate concentration at $[\text{SDS}] = 5.76 \times 10^{-2} \text{ mol dm}^{-3}$
 $50 \text{ cm}^3 \text{ P(EA-co-DVB) latex, } 20 \text{ cm}^3 \text{ water, } 20 \text{ cm}^3 \text{ BA; } 60^\circ \text{C}$

$\frac{[(\text{NH}_4)_2\text{S}_2\text{O}_8]}{\text{mol dm}^{-3}} \cdot 10^3$	$\frac{R_p}{\text{mol dm}^{-3} \text{ s}^{-1}} \cdot 10^3$	$\frac{\bar{d}_f}{\text{nm}}$	$\frac{N_f \cdot 10^{-13}}{\text{cm}^{-3}}$	N_f/N_s
1.46	1.00	142	3.41	0.94
2.19	1.14	140	3.58	1.00
2.92	1.46	140	3.58	1.00
3.65	1.64	139	3.65	1.00
5.84	2.40	137	3.80	1.05
7.30	2.60	137	3.80	1.05

Table 11

Variation of the kinetic parameters of emulsion polymerization of BA in the presence of seed polymer particles ($\bar{d}_s = 120 \text{ nm}$, $N_s = 3.62 \times 10^{13} \text{ cm}^{-3}$) with the SDS concentration at $[(\text{NH}_4)_2\text{S}_2\text{O}_8] = 1.46 \times 10^{-3} \text{ mol dm}^{-3}$
 $50 \text{ cm}^3 \text{ P(EA-co-DVB) latex, } 20 \text{ cm}^3 \text{ water, } 20 \text{ cm}^3 \text{ BA; } 60^\circ \text{C}$

$\frac{[\text{SDS}]}{\text{mol dm}^{-3}} \cdot 10^2$	$\frac{R_p}{\text{mol dm}^{-3} \text{ s}^{-1}} \cdot 10^3$	$\frac{\bar{d}_f}{\text{nm}}$	$\frac{N_f \cdot 10^{-13}}{\text{cm}^{-3}}$	N_f/N_s
3.5	1.1	144	3.20	0.90
5.76	1.0	142	3.41	0.94
7.5	0.9	138	3.80	1.05
9.2	0.9	137	3.81	1.05
10.9	0.9	130	4.45	1.23
14.4	0.9	122	5.39	1.49

The values of the rate of polymerization, the final average particle size, and the number of polymer particles obtained in the system 2 are listed in Tables 10 and 11. The reaction orders with respect to the initiator and emulsifier concentration (obtained from the data presented in Tables 10 and 11) are shown in Table 4. In the system 2 the rate of polymerization is found to be proportional to the 0.56 order with respect to the ammonium peroxodisulfate concentration. The number of particles is proportional to the 0.07 and 0.51 order with respect to the ammonium peroxodisulfate and SDS concentration, respectively. A good agreement between the reaction orders (obtained from the dependence of $R_p \sim [\text{I}]^x$ or

$N \sim [I]^n$) for both systems 1 and 2 is observed. On the other hand, the reaction order (0.51) (obtained from the dependence of $N \sim [E]^m$) for the system 2 is somewhat higher than that (0.31) for the system 1. The difference in the reaction orders results from the higher hydrophobicity of new particles of the system 2 compared to that of seed particles of the system 1. Tables 10 and 11 show that the rate of polymerization increases with the increasing initiator concentration and decreases with the increasing emulsifier concentration. The average particle size decreases and the number of particles increases with the increasing initiator and emulsifier concentration, respectively.

The dependences of the rate of polymerization, the average particle size, and the number of polymer particles on the initiator and emulsifier concentration are the same in both systems 1 and 2. Exception is the dependence of the ratio N_f/N_s on the initiator and emulsifier concentration. The ratio N_f/N_s is supposed to be a measure of particle nucleation and/or coalescence and seems to be influenced by the nature of seed polymer particles. The emulsion copolymerization of EA with HMDA produces the hydrophilic polymer particles with the homogeneous polymer networks (with statistical distribution of crosslinking joints). The formation of this network results from the low concentration of the crosslinking monomer used and from the same reactivity of both monomers [35]. The emulsion copolymerization of DVB (copolymerization parameter $r_{\text{styrene}} = 0.8$) and EA ($r_{\text{EA}} = 0.17$) [36] generates the more hydrophobic polymer particles. The difference in the monomer reactivity in this system indicates the formation of particles with core/shell structure. The stronger interaction between polymer particles surface and emulsifier molecules in the system 2 decreases both the A_{SDS} of emulsifier molecules and the amount of free micelle emulsifier in water.

On the basis of our results we conclude that the traditional concept of the emulsion polymerization, in which the rate of polymerization is proportional to the 0.4 and 0.6 order with respect to the initiator and emulsifier concentration, does not apply in the present polymerization systems. The large differences in the hydrophobicity of the seed and formed polymer, the formation of dispersed domains in the seed polymer particles, the reverse diffusion of monomer and the semi-IPN morphology are responsible for the deviation from the expected behaviour.

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