

# On the Free-Radical Microemulsion Polymerization of Butyl Acrylate in the Presence of Poly(Oxyethylene) Macromonomer

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The o/w microemulsion polymerizations and copolymerization of butyl acrylate (BA) with methacryloyl-terminated poly(oxyethylene) macromonomer (POE-MA) initiated by both water-soluble (ammonium peroxodisulfate (APS)) and oil-soluble (AIBN) initiators were investigated. The maximum rate of microemulsion polymerization of butyl acrylate was found to increase with increasing APS and AIBN concentration and the increase was more pronounced in runs with APS. The dependence of the rate *vs.* conversion is described by a curve with a maximum at *ca.* 20–40 % conversion. The maximum rate of polymerization was found to increase with increasing APS concentration and the increase was proportional to the molecular mass of POE macromonomer. The high radical activity of AIBN was attributed to hopping events. The particle size in the microemulsion polymerization of BA slightly increases with conversion. However, the addition of POE macromonomer influences by a complex way the particle size. The addition of POE changes the electrostatic stabilization mechanism to the electro-steric stabilization mechanism. POE macromonomer or its graft copolymer promotes organized agglomeration and the formation of large number of particles at medium conversion. At low and high conversion larger particles are formed. The rearrangement of reactants and polymer molecules at the beginning and the end of polymerization and the interaction of hydrophilic BA-graft-POE copolymer molecules with polymer particles are assumed to be responsible for the dramatic variations in particle size.

A microemulsion is being defined as an optically transparent, isotropic, and thermodynamically stable microdispersion consisting of water, oil (monomer), and amphiphile(s) (emulsifier, coemulsifier, *etc.*). These transparent oil-in-water microdispersions are described as small spherical droplets dispersed in water. The interfacial layer of these droplets is formed by emulsifier and coemulsifier. The picture of the microemulsion structure as discrete droplets is realistic at a low volume fraction of the dispersed phase (monomer). In fact, this type of microemulsion resembles a swollen micellar solution. As the volume fraction of oil increases, the microemulsion may be converted to miniemulsion. This change depends on the partitioning of the monomer and coemulsifier between the three phases (water, interface, and the micelle oil core) and the formed interface layer. Coemulsifier is needed to neutralize the excessive hydrophilic character or a charge of the ionic emulsifier and to associate with emulsifier, water, and monomer molecules to form a condensed surface film of the microdroplet. The penetration of coemulsifier into the interfacial region of the microemulsion droplets increases the surface area, the number of microdroplets, and the fluidity of condensed surface phase. The high number of microdroplets favours the micellar model and the increase in the particle number during the polymerization [1].

The aggregates formed by association of amphiphilic POE oligomers of polymers in the aqueous solution have attracted widespread interest in recent years [2]. Block and graft copolymers of POE tend to aggregate in the aqueous phase in a similar way as nonionic emulsifiers. The complex formation of anionic emulsifier and POE macromonomer is known to affect the colloidal parameters of micellar system. The driving force which leads to such a complex formation is, however, still poorly understood, owing to the highly system-dependent nature of interactions [3]. The incorporation of a small amount of the nonionic emulsifier to the ionic micelles results in a large decrease in the critical micellar concentration (CMC) of the mixed emulsifiers. The synergistic lowering of the CMC on mixing emulsifiers arises from favourable (attractive) interactions on mixing of the nonionic and ionic head groups. The presence of the nonionic head group among the anionic head groups (sulfate) introduces sufficient separation between the sulfate head groups so that any changes in ionic strength have effect on the electrostatic interaction. The nature and extent of the interactions between reactants and reaction product will also by a complex way influence the size of polymer particles and the rate of polymerization.

Up to now there is very little information about the coemulsifier properties of amphiphilic poly(oxyethyl-

ene) macromonomers, the formation of mixed micelles of SDS and POE macromonomer, the nucleation or polymerization activity of macromonomer molecules and mixed micelles, and the effect of homogeneous nucleation on the microemulsion process. This is a reason why we intend to follow the effect of POE macromonomer on the kinetics of microemulsion polymerization of hydrophobic butyl acrylate. It is expected that the water phase polymerization of POE macromonomer as a coemulsifier will increase both the critical chain length of precipitated oligomeric radicals and the homogeneous nucleation. This behaviour is expected to be a function of the molecular mass and concentration of macromonomer and the partitioning of macromonomer between the aqueous phase and the micelles or particles. The partitioning of macromonomer between the particle surface and its interior is a further parameter which influences the colloidal and kinetic parameters, as well.

## EXPERIMENTAL

Commercially available butyl acrylate (BA) was purified by the conventional method and then distilled under vacuum before use (see for example [1, 4]). The initiators ammonium peroxodisulfate (APS) and 2,2'-azobisisobutyronitrile (AIBN), and a reagent-grade sodium dodecyl sulfate (SDS) were used as supplied (Fluka). Methacryloyl-terminated poly(oxyethylene) macromonomers (POE-MA, NOF Corp.) with  $\{M_m\} = 1000$  (POE-MA<sub>1000</sub>), 1740 (POE-MA<sub>1740</sub>), and 4250 (POE-MA<sub>4250</sub>) were used. Twice distilled water was used as a polymerization medium.

The batch polymerizations were run at 60°C. In all runs recipe comprises 100 g water, 20 g SDS, and 0.025 g NaHCO<sub>3</sub>. Concentrations of APS varied from  $1.6 \times 10^{-3}$  mol dm<sup>-3</sup> to  $9.6 \times 10^{-3}$  mol dm<sup>-3</sup>, [BA] from 0.61 mol dm<sup>-3</sup> to 1.22 mol dm<sup>-3</sup>, and [POE-MA] from 0.003 mol dm<sup>-3</sup> to 0.015 mol dm<sup>-3</sup> [AIBN] was 0.005 mol dm<sup>-3</sup>. The polymerization technique, the measurements of viscosity and conductivity, conversion determination (dilatometric and gravimetric techniques), and particle size measurements were the same as described earlier [5–7].

## RESULTS AND DISCUSSION

### Polymerization Rate

Variations of the copolymerization rate of BA and POE-MA with the (macro)monomer concentration and conversion are expressed in Fig. 1. The rate *vs.* conversion dependence shows two distinct nonstationary regions. The position of the maximum rate for different POE-MA macromonomers is located in the conversion range 20–40%. The appearance of a maximum rate at medium conversions is a result of two opposite contributions [1, 8]; 1. The depletion

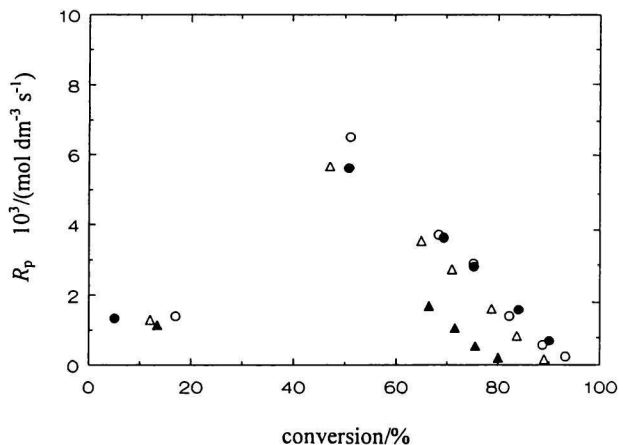


Fig. 1. Variation of the polymerization rate of the microemulsion polymerization of butyl acrylate in the presence of POE-MA macromonomers initiated by APS with conversion. Recipe: 100 g water, 10 g BA, 20 g SDS, 0.025 g NaHCO<sub>3</sub>, temperature 60°C. [APS] = 0.0016 mol dm<sup>-3</sup>,  $\{M_{m,POE-MA}\} = 1081$ , [POE-MA] = 0.0029 mol dm<sup>-3</sup> (●), [APS] = 0.0049 mol dm<sup>-3</sup>,  $\{M_{m,POE-MA}\} = 1081$ , [POE-MA] = 0.0029 mol dm<sup>-3</sup> (△), [APS] = 0.0049 mol dm<sup>-3</sup>,  $\{M_{m,POE-MA}\} \leq 1740$ , [POE-MA] = 0.0018 mol dm<sup>-3</sup> (●), [APS] = 0.0049 mol dm<sup>-3</sup>,  $\{M_{m,POE-MA}\} = 1740$ , [POE-MA] = 0.0022 mol dm<sup>-3</sup> (○).

of monomer droplets (beyond *ca.* 20–40% conversion) leads to the decrease of monomer concentration at reaction loci. This is a reason why the microemulsion polymerization proceeds under monomer-starved conditions already at medium conversion. However, the maximum rate in the microemulsion polymerization of BA is shifted to lower conversion (*ca.* 10–20%) [7–9]. In the miniemulsion polymerization the monomer-starved conditions are operative beyond *ca.* 40% conversion and in the classical emulsion polymerization beyond *ca.* 60% conversion, respectively. 2. The nucleation of particles proceeds throughout the polymerization which pronounces more the decrease of monomer concentration at reaction loci. This is not the case of emulsion polymerization where the nucleation period is suppressed to very low conversion interval, *ca.* up to 5% conversion. The initial increase in the rate with conversion is ascribed to the increase of the particle number and the decrease in the rate is mainly attributed to the decrease of monomer concentration at the reaction loci.

The polymerization is found to be relatively fast. Besides, the conversion *vs.* time data indicated that the conversion *ca.* 100% is reached during 10–15 min. In all cases the colloidal stable polymer latexes were formed.

The relationship  $R_{p,max}$  *vs.* [APS]<sup>*x*</sup> is used to discuss the termination and nucleation mechanisms. The reaction order *x* on [APS] was found to vary as follows (Table 1)

**Table 1.** Variation of Kinetic and Colloidal Parameters in the Microemulsion Polymerization of Butyl Acrylate in the Presence of POE-MA<sub>1081</sub> Macromonomer with APS Concentration

[APS] · 10 <sup>3</sup> mol dm <sup>-3</sup>	$R_{p,max} \cdot 10^3$ mol dm <sup>-3</sup> s <sup>-1</sup>	$D$		$N \cdot 10^{-18}$	
		nm		dm <sup>-3</sup>	
		a	b	a	b
1.6 <sup>1</sup>	4.6	45 (35)	42	0.67 (35)	2.0
3.0 <sup>1</sup>	5.3	44 (40)	42	1.09 (40)	2.1
4.9 <sup>1</sup>	6.1	39 (49)	42	1.4 (49)	2.2
9.6 <sup>1</sup>	8.0	38 (65)	41	2.06 (65)	2.5
1.6 <sup>2</sup>	4.0	44 (34)	41	0.7 (34)	2.2
3.0 <sup>2</sup>	5.0	44 (25)	41	0.63 (25)	2.25
4.9 <sup>2</sup>	6.3	43 (20)	41	0.44 (20)	2.35
9.6 <sup>2</sup>	8.3	42 (40)	40	0.94 (40)	2.4

a) The value in brackets is conversion/%, [BA] = 0.6 mol dm<sup>-3</sup>; b) 90–97 % conversion. 1. [POE-MA]<sub>1081</sub> = 0.0029 mol dm<sup>-3</sup>, 2. [POE-MA]<sub>1081</sub> = 0.0087 mol dm<sup>-3</sup>.

$$\begin{aligned}
 &0.46 \text{ (without POE-MA [9])} > \\
 &> 0.42 \text{ ([POE-MA] = 0.0087 mol dm}^{-3}\text{)} > \quad (1) \\
 &> 0.3 \text{ ([POE-MA] = 0.0029 mol dm}^{-3}\text{)}
 \end{aligned}$$

For the instantaneous termination of growing radicals by entered primary or oligomer (mobile) radicals the reaction order  $x = 0.4$  was suggested [10]. This is the case of emulsion polymerization where the radical capture efficiency of large polymer particles is high. In the stationary rate interval 2 the one half of particles is active and the other half is inactive. In the case of polymerization or copolymerization of hydrophilic monomer(s) the water phase termination may increase the reaction order to 0.5 (the bimolecular termination of growing radicals in water). In the microemulsion polymerization the radical rate coefficient for entry into polymer particles is by several orders smaller than that for the entry into the classical – emulsion type polymer particles. This indicates the initiating radicals are predominantly captured by the microemulsion droplets. This results from much larger surface area of micelles (by several orders) compared to that of the polymer particles. We have reported that the molecular masses of polyBA generated in the microemulsion polymerization were very large and nearly independent of initiator (APS) concentration which was different from  $-0.6$  power dependence on the water-soluble initiator concentration [10]. The chain transfer to monomer or emulsifier was suggested to terminate the chain growth within the polymer particles. This finding supports the previously reported slight dependence of the  $M_m$  on potassium persulfate (KPS) concentration reported by Guo *et al.* [11]. The chain transfer events regulate the molecular mass of polymer. The transferred radicals re-initiate the chain growth or desorb from the polymer particles. The presence of several polymer chains in microparticle results from the re-initiation activity of the transferred monomeric radicals.

It is well known that monomer radicals generated

by chain transfer tend to diffuse out of the polymer particles. It was shown [12] that the exit rate of mobile radicals increases with decreasing latex particle size. Therefore, the radical desorption from the poly(butyl acrylate) (PBA) microparticles is fast. These radicals predominantly re-enter the monomer microdroplets. The participation of monomer transferred radicals in the instantaneous termination in particle or water phase is very low. The existence and importance of desorption/re-entry events in the microemulsion polymerization were proofed in the post-polymerization of the photoinitiated microemulsion polymerization [13]. The dominant role of chain transfer/exit events, the large number of monomer-swollen micelles, and the small radical flux to each particle are responsible for the very low value of the number of radicals per particle, much less than 0.5 [1, 8]. This might be the case with POE graft copolymer where (degradative) chain transfer to POE units is operative.

The reaction order  $x$  is supposed to be a complex function of the lifetime of growing and desorbed radicals and the (continuous) particle nucleation. For example, the rapid desorption and the efficient water-phase termination should model the bimolecular termination (a short lifetime) with the reaction order close to 0.5. The re-entry of transferred radicals prolongs the growth events with the termination mode close to the first-order radical loss process. Furthermore, the accumulation of active polymer particles increases the rate of polymerization and the reaction order as well. Thus, the accumulation of surface-active graft copolymer increases the total emulsifier concentration and so the reaction order.

The contribution of the water-phase termination was modelled by the microemulsion copolymerization of hydrophobic BA and amphiphilic POE macromonomer. It is expected that the increasing POE-MA concentration increases the extent of water-phase polymerization and the contribution of bimolecular termination. This behaviour should lead to the

value of reaction order close to 0.5. The experimental results show that the reverse is true, *i.e.* the reaction order decreases with increasing extent of the water-phase polymerization. This disfavors the dominant role of the water-phase termination in determining the reaction order. The presence of high amount of polymer in the continuous (water/ethanol) phase of the dispersion copolymerization of styrene and POE-MA macromonomer favours the importance of water-phase termination [14]. In the microemulsion system the formation of graft copolymer in the water phase is assumed to be much lower while the amphiphilic PBA-graft-POE oligomeric radicals are efficiently absorbed by microdroplets. Under such conditions the homogeneous nucleation is somewhat suppressed while the precipitation of long-chain growing radicals from the aqueous phase is suppressed. The radical capture efficiency of microemulsion droplets and the exit/re-entry process govern the formation of reaction loci (particles). Thus the reaction order  $x$  is a complex function of graft copolymer formed (it increases the number of particles and so the value of  $x$ ), the degradative chain transfer to POE chains (it increases the termination and so decreases the value of  $x$ ) and the exit and re-entry of transferred radicals.

Variation of the rate of polymerization with the concentration and the molecular mass of POE-MA ( $R_{p,max} \propto [\text{POE-MA}]^y$ ) and the BA ( $R_{p,max} \propto [\text{BA}]^z$ ) concentration is as follows (Tables 2–4)

$$y/\{M_{m,POE-MA}\}: 0.05/1081 < 0.13/1740 < 0.29/4250 \quad (2)$$

and

$$z/\{M_{m,POE-MA}\}: 1.0/(\text{without POE-MA}) \gg -0.3/1081 > -0.6/4259 > -0.7/1740 \quad (3)$$

The rate of polymerization increases with increasing macromonomer concentration and the increase is proportional to the molecular mass and concentration of POE macromonomer. Thus, the most pronounced increase in  $R_p$  was observed in runs with the POE-MA<sub>4250</sub>. This is attributed to the formation of surface-active graft copolymer (acts as emulsifier) and also polymer particles. Furthermore, the partitioning of POE-MA macromonomer between the aqueous phase and the polymer particles is also very important. The more hydrophobic POE-MA<sub>1081</sub> prefers the interior of the micelle or particle while the more hydrophilic POE-MA<sub>4250</sub> the aqueous phase or the interface. Thus, a certain fraction of POE-MA is consumed in the particles due to which the rate of polymerization decreases (POE-MA is buried in particles). On the contrary, the copolymerization of POE-MA in the aqueous phase or within the particle interface preferentially generates the surface-active graft copolymers which promote the formation of larger number of particles. The growth events are disfavoured by the high segment density around the propagating chain ends

**Table 2.** Variation of Kinetic and Colloidal Parameters in the Microemulsion Polymerization of Butyl Acrylate with POE-MA<sub>1081</sub> Concentration<sup>a</sup>

[POE-MA] · 10 <sup>3</sup> mol dm <sup>-3</sup>	$R_{p,max} \cdot 10^3$ mol dm <sup>-3</sup> s <sup>-1</sup>	$D$ nm	$N \cdot 10^{-18}$ dm <sup>-3</sup>
0	7.5	44	1.1
2.89	6.1	42	2.2
5.78	6.2	42	2.2
8.67	6.3	41	2.4
14.45	6.5	41	2.3

a) [APS] = 4.9 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [BA] = 0.6 mol dm<sup>-3</sup>, conversion<sub>final</sub> = 90–94 %.

**Table 3.** Variation of Kinetic and Colloidal Parameters in the Microemulsion Polymerization of Butyl Acrylate with POE-MA Molecular Mass and Concentration<sup>a</sup>

{M <sub>m</sub> }	[POE-MA] · 10 <sup>3</sup> mol dm <sup>-3</sup>	$R_{p,max} \cdot 10^3$ mol dm <sup>-3</sup> s <sup>-1</sup>	$D$ nm	$N \cdot 10^{-18}$ dm <sup>-3</sup>
1081	2.89	6.1	42	2.2
1081	8.67	6.3	41	2.35
1740	1.8	6.6	42	2.3
1740	5.4	7.6	41	2.4
4250	0.74	6.4	42	2.2
4250	2.2	8.8	41	2.4

a) [APS] = 4.9 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [BA] = 0.6 mol dm<sup>-3</sup>, conversion<sub>final</sub> = 90–94 %.

**Table 4.** Variation of Kinetic and Colloidal Parameters in the Microemulsion Polymerization of Butyl Acrylate with BA and POE-MA Molecular Mass and Concentration<sup>a</sup>

[BA]	[POE-MA] · 10 <sup>3</sup> mol dm <sup>-3</sup>	{M <sub>m</sub> }	$R_{p,max} \cdot 10^3$ mol dm <sup>-3</sup> s <sup>-1</sup>	$D$ nm	$N \cdot 10^{-18}$ dm <sup>-3</sup>
0.6	8.67	1081	6.3	41	2.4
0.9	8.67	1081	5.5	43	2.1
1.2	8.67	1081	5.7	45	1.9
0.6	5.4	1740	7.6	41	2.5
0.9	5.4	1740	6.3	43	2.1
1.2	5.4	1740	4.7	45	1.8
0.6	2.2	4250	8.8	41	2.5
0.9	2.2	4250	7.4	44	2
1.2	2.2	4250	5.9	47	1.6

a) [APS] = 4.9 × 10<sup>-3</sup> mol dm<sup>-3</sup>, conversion<sub>final</sub> = 90–94 %.

and the bulky macromonomer which hinder the incorporation of macromonomer molecules into polymer chains.

The rate of microemulsion polymerization was found to increase strongly with increasing BA concentration ( $R_p \propto [\text{BA}]^{1.0}$ ) [15]. The strong increase



in  $R_p$  with increasing BA concentration is attributed to the contribution of the kinetics of classical emulsion polymerization where the polymerization proceeds under the monomer-saturated conditions. This is not the case with POE macromonomer where POE graft copolymer stabilizes the microemulsion droplets even at very high BA concentration. Furthermore, this also results from the participation of less reactive macromonomer in the propagation events. Here, the macromonomer also participates on the formation of surface-active graft copolymer and latex particles. However, the addition of POE-MA leads to the negative reaction order  $z$ , *i.e.* the rate of polymerization decreases with increasing BA concentration and the decrease is proportional to the molecular mass of POE macromonomer. These data may be discussed in terms of partitioning of POE macromonomer between the aqueous phase and the monomer phase and the stabilization of monomer droplets *via* accumulation of hydrophobe in the monomer phase (the monomer droplet degradation is suppressed). For example, BA serves as an extraction agent for POE macromonomer because the amphiphilic POE-MA macromonomer is miscible with BA. With increasing BA concentration increases the fraction of POE macromonomer in the monomer droplets or buried POE segments within the polymer particles. The presence of POE macromonomer or its graft copolymer in the monomer droplet decreases the transfer of monomer from monomer droplets to reaction loci and so the polymerization rate.

Furthermore, the mixing of SDS and POE graft copolymer leads to the increased aggregation number of these mixed micelles due to which increases density of the interfacial layer [16]. This results from favourable (attractive) interactions between the sulfate head groups and the oxyethylene (hydroxyl) group of the nonionic (POE graft copolymer) emulsifier. POE graft molecules penetrate into the SDS micellar palisade layer which screens negative charges of micelle and so promotes formation of the close-packed interfacial layer. A close-packed particle surface layer is known to act as a barrier to entering radicals and slow down the rate of polymerization.

The rate of polymerization of BA and POE macromonomer initiated by a water-soluble APS was found to be much larger than that initiated by an oil-soluble initiator (AIBN, DBP, ...) [8, 9]. Similar behaviour was observed in the present microemulsion polymerization of BA with POE-MA initiated by APS or AIBN (Tables 1 and 5). Initiation of microemulsion polymerization by APS is a two-step process. It starts in the aqueous phase by primary radicals derived from APS. The second step occurs by the entry of oligomer radicals or re-entry of desorbed radicals into the monomer microdroplets. In the case of the oil-soluble initiator (AIBN) the initiating radicals are formed in two phases: 1. in the monomer-swollen micelles or particles, formed radicals desorb into the

**Table 5.** Variation of Kinetic and Colloidal Parameters in the Microemulsion Polymerization of Butyl Acrylate Initiated by AIBN with POE-MA Molecular Mass and Concentration<sup>a</sup>

$\{M_m\}$	$[\text{POE-MA}] \cdot 10^3$	$R_{p,\max} \cdot 10^3$	$D$	$N \cdot 10^{-18}$
	$\text{mol dm}^{-3}$	$\text{mol dm}^{-3} \text{ s}^{-1}$	nm	$\text{dm}^{-3}$
1081	8.67	1.73	40	2.2
1740	5.4	1.88	40	2.1
4520	2.2	2.16	41	2.1

<sup>a</sup>)  $[\text{AIBN}] = 0.005 \text{ mol dm}^{-3}$ ,  $[\text{BA}] = 0.6 \text{ mol dm}^{-3}$ , conversion<sub>final</sub> = 75–85 %.

aqueous phase and 2. in the continuous phase, formed radicals are generated from the fraction of AIBN dissolved in water.

Based on the assumption that in the microemulsion polymerization the water phase termination is negligible, all radicals generated enter the monomer-swollen micelles (or microemulsion droplets) and the fraction of radicals which entered the monomer-swollen polymer particles is negligible, we can establish the following steady-state balance equation for each type of initiator

APS<sub>1</sub>:

$$d[\text{R}^*]_{1w}/dt = 0 = 2k_{d1} \cdot f_1 \cdot [\text{APS}]_w + k_{des} \cdot \phi_w \cdot N_{p1}^* / N_A - k_{e,R1} \cdot N_d \cdot [\text{R}^*]_{1w} \cdot \phi_w / N_A \quad (4)$$

AIBN<sub>2</sub>:

$$d[\text{R}^*]_{2w}/dt = 0 = 2k_{d2} \cdot f_2 \cdot [\text{AIBN}]_w + k_{des} \cdot \phi_w \cdot N_{p2}^* / N_A - k_{e,R2} \cdot N_d \cdot [\text{R}^*]_{2w} \cdot \phi_w / N_A + k_{des,AIBN} \cdot \phi_w \cdot N_d / N_A + k_{des,AIBN} \cdot \phi_w \cdot N_{p2}^* / N_A \quad (5)$$

where the left-hand side represents the variation of free radicals in the aqueous phase, which is equal to zero for the pseudo-steady state assumption. The first term of the right-hand side accounts for the generation of primary radicals ( $^{\bullet}\text{SO}_4^-$ ) by initiator (APS) decomposition, the second one for the desorption of transferred monomeric radicals from the polymer particles and the third for the capture of radicals by the microemulsion droplets. In the microemulsion polymerization initiated by AIBN the right-hand side contains two more terms; the fourth accounts for the desorption of primary radicals derived from AIBN from the microemulsion (the cage) droplets and the last term for the desorption of primary radicals derived from AIBN from the monomer-swollen polymer (the cage) particles. The number of microemulsion droplets ( $N_d$ ) is much larger than the number of polymer particles ( $N_p$ ) and therefore the last term for AIBN system can be neglected.  $k_d$  is the rate constant for thermal decomposition of the initiator,  $f$  is the initiator efficiency,

[APS] or [AIBN] is the initiator concentration,  $k_{\text{des}}$  is the rate coefficient for desorption of transferred radicals from polymer particles,  $k_{\text{des,AIBN}}$  is the rate coefficient for desorption of primary radicals derived from AIBN from micelles or polymer particles,  $\phi_w$  is the volume fraction of water in the aqueous system,  $N_p^*$  is the number of active particles (containing one or more growing radicals),  $[R^*]_w$  is the total concentration of radicals in the aqueous phase,  $N_A$  is Avogadro's constant,  $k_{e,R}$  is the radical rate coefficient for entry into the micelles (microemulsion droplets), the subscript 1 denotes APS and 2 AIBN, respectively.

Based on the experimental results, we can write

$$d[R^*]_{1w} > d[R^*]_{2w} \quad (6)$$

or

$$2k_{d1} f_1 [APS]_w - k_{e,R1} N_d [R^*]_{1w} \cdot \phi_w / N_A > 2k_{d2} f_2 [AIBN]_w - k_{e,R2} N_d [R^*]_{2w} \cdot \phi_w / N_A + k_{\text{des,AIBN}} \cdot \phi_w N_d / N_A \quad (7)$$

The initiating radicals are effectively absorbed by the microemulsion droplets and therefore the terms  $k_{e,R1} N_d \cdot [R^*]_{1w} \cdot \phi_w / N_A$  and  $k_{e,R2} \cdot N_d \cdot [R^*]_{2w} \cdot \phi_w / N_A$  do not much affect the radical concentration in water. We can neglect the contribution of terms  $k_{\text{des}} \cdot \phi_w \cdot N_p^* / N_A$  and  $k_{\text{des}} \cdot \phi_w \cdot N_p^* / N_A$  due to the fact that in both systems the same number of particles were generated [8, 9]. The term  $2k_{d1} f_1 [APS]_w \gg k_{d2} f_2 [AIBN]_w$  is modelled due to the very low water solubility of AIBN. However, the rates of polymerization for APS or AIBN do not parallel the difference in water solubility of APS and AIBN. The  $R_{p,\text{max},S}$  (APS) were only several times larger than the  $R_{p,\text{max},S}$  (AIBN), which indicates that the term  $k_{\text{des,AIBN}} \phi_w N_d / N_A$  dominates the formation of single radicals. The high initiation efficiency of AIBN is directly connected with the escape of AIBN-derived radicals from the microemulsion droplets. The hopping of hydrophobic fragments (single radicals) from the monomer droplet to other droplet within the droplet or particle clusters or the transfer of single radicals from one droplet to another droplet through interface (or channels opening) between droplets during collisions might occur [17]. Under such conditions the concentration of single radicals and/or the reaction loci is increased and so the rate of polymerization.

### The Colloidal Parameters

In the microemulsion polymerization of BA the particle size ( $D$ ) was found to slightly increase with conversion nearly up to very high conversion. For example, in the emulsion polymerization of BA with the recipe  $[BA] = 0.6 \text{ mol dm}^{-3}$ ,  $[SDS] = 0.53 \text{ mol dm}^{-3}$ , and  $[APS] = 9.6 \times 10^{-3} \text{ mol dm}^{-3}$ , the particle diameter increased from 32 nm (10 % conversion) to 35 nm (60 % conversion), and then to 40 nm (at ca. 100 % conversion). However, the addition of

POE-MA macromonomer led to a more complex dependence of  $D$  on conversion. The dependence of  $D$  vs. conversion is described by a curve with a minimum at ca. 60 % conversion. For example, the addition of POE-MA<sub>1081</sub> ( $2.9 \times 10^{-3} \text{ mol dm}^{-3}$ ) led at the beginning of polymerization to the strong increase in turbidity and the formation of larger particles with  $D$  about 50–60 nm. As the polymerization advanced the particle size decreased and at ca. 60 % conversion  $D$  reached the value 37 nm. Beyond this critical conversion the particle diameter again increased and at ca. 100 % conversion  $D$  reached 40 nm. This behaviour can be discussed in terms of the continuous formation of graft copolymer and depressed monomer droplet degradation (the accumulation of hydrophobe in the monomer droplet) due to which the average size of polymer particles decreases. On the contrary, agglomeration events promote the increase in the average particle size. In the former case the accumulation of hydrophobe (macromonomer, polymer) within the monomer droplets depresses the monomer droplet degradation (or the formation of larger number of smaller monomer droplets) which promotes the nucleation of larger number of latex particles. However, as soon as the level of BA in the continuous phase (at higher conversion) decreases the graft copolymer rich in POE units appears. Under such conditions the less hydrophobic graft copolymer accumulates [14, 18]. The adsorption of more hydrophilic graft copolymers (or primary particles) strongly modifies the particle surface and the colloidal stability (initiate agglomeration events) of latex particles. Furthermore, the latex particles with very thick shell of POE chains make the emulsion polymerization mechanism very complicated. In this case, the colloidal stability of latex particles stabilized by poly(oxyethylene) (POE) type emulsifier is dependent on the interparticle interaction *via* the extended surface of POE chains (bridging flocculation mechanism) [19].

The formation of surface-active graft copolymers by the copolymerization of POE macromonomer and BA and their interaction with the monomer-swollen SDS micelles promotes rearranging of reactants due to which the electrostatic stabilization mechanism is changed to the electro-steric one. SDS provides latex particles with repulsive force between similarly charged electric double layers of two approaching particles (electrostatic stabilization) [20], whereas non-ionic emulsifier imparts steric stabilization to the interactive particles [21]. Furthermore, the steric stabilization effect provided by POE/styrene graft copolymer alone is not sufficient to prevent latex particles from flocculation during polymerization [2]. On the other hand, the electrosterically stabilized latex particles are stable due to the synergistic effect provided by SDS and PBA/POE graft copolymer. The strong interaction between graft copolymer and negatively charged microdroplets is a reason why the average par-

particle size increased after the start of polymerization. The accumulation of hydrophobe or polymer within the microdroplets, however, stabilizes the monomer droplets due to which the average particle size decreases. At very high conversion the depletion of more reactive BA leads to the formation of a POE-rich graft copolymer which promotes the particle agglomeration and formation of large-sized particles. Indeed the data in Table 1 show that the number of final particles varies only slightly with APS concentration at high conversion while the particle size is governed by agglomeration events. However, at medium conversion where the particle agglomeration is negligible (the graft copolymer molecules increase the colloidal stability of latex particles) the particle size or particle number varies strongly with increasing APS concentration.

Variations in the particle size or the particle number with initiator type and concentration, the macromonomer concentration and molecular mass, and conversion are summarized in Tables 1–5. According to the micellar theory [10], the relation between the number of particles and the emulsifier, initiator and monomer concentration, can be expressed as follows

$$N \propto [\text{emulsifier}]^y, [\text{initiator}]^z, \text{ and } [\text{monomer}]^s \quad (8)$$

where  $y = 0.6$ ,  $z = 0.4$ , and  $s$  is close to zero. The final particle size and number were found to vary slightly with APS concentration; *i.e.* the exponents  $m$  and  $z$  from the relationships  $D \propto [\text{APS}]^m$  and  $N \propto [\text{APS}]^z$  varied with POE-MA type and concentration as follows

$$m: 0.05 \text{ (without POE-MA [7–9])} > 0 \text{ ([POE-MA] = 0.0029 mol dm}^{-3}\text{)} = 0 \text{ ([POE-MA] = 0.0087 mol dm}^{-3}\text{)} \quad (9)$$

$$z: 0.17 \text{ (without POE-MA [7–9])} > 0.12 \text{ ([POE-MA] = 0.0029 mol dm}^{-3}\text{)} > 0.04 \text{ ([POE-MA] = 0.0087 mol dm}^{-3}\text{)} \quad (10)$$

The slight variation in the reaction order  $z$  results from the chain-transfer events and particle agglomeration (see above). Furthermore, the low radical entry rate is assumed to be operative. This is typical for the sterically stabilized (hairy) particles with the thick interfacial layer. However, the particle nucleation is quite strong at *ca.* 30–40 % conversion where the exponent  $z$  varies in the range 0.6–0.8 ([POE-MA] = 0.0029 mol dm<sup>-3</sup>). Here, the amphiphilic PBA-graft-POE copolymers increase the total amount of emulsifier or interfacial area. Besides, the amphiphilic radicals are efficiently absorbed by microdroplets. This increases the number of nucleated particles and the rate of polymerization.

The observed reaction order  $r$  from the dependence

of final number polymer particles  $N_p$  *vs.*  $[\text{BA}]^r$  varies as follows (Tables 3 and 4)

$$-0.44 \text{ (}\{M_m\} = 1081, [\text{POE-MA}] = 0.0087 \text{ mol dm}^{-3}\text{)} > -0.5 \text{ (}\{M_m\} = 1740, [\text{POE-MA}] = 0.0054 \text{ mol dm}^{-3}\text{)} > -0.7 \text{ (}\{M_m\} = 4250, [\text{POE-MA}] = 0.0022 \text{ mol dm}^{-3}\text{)} > -1.2 \text{ (without POE-MA [15])} \quad (11)$$

From these data it appears that the addition of POE macromonomer suppresses the negative effect of BA on the particle concentration. Thus, the colloidal stability (the number of particles) is proportional to the molecular mass or the concentration of macromonomer. However, the particle size for the POE-MA<sub>1081</sub> was nearly independent of BA concentration in the range of medium conversion where the particle diameter varied in the range from 40 nm to 43 nm. This was not the case in the microemulsion polymerization of BA where the particle size increased with increasing BA concentration [15]. These data support the idea that amphiphilic graft copolymer takes part in the particle nucleation and stabilization.

## CONCLUSION

The maximum rate of microemulsion copolymerization of butyl acrylate and POE macromonomer was found to increase with increasing APS and AIBN concentration and the increase was more pronounced in runs with APS. The dependence of the rate on the macromonomer concentration is described by a curve with a minimum at a very small amount of POE macromonomer. The maximum rate of polymerization and the number of particles increased with increasing macromonomer molecular mass and concentration. The rate of microemulsion polymerization of BA increases with increasing monomer concentration. The reverse is true in the runs with POE-MA macromonomer. The formation of surface-active POE graft copolymers and their penetration into the interfacial layer changes the electrostatic stabilization mechanism to the electro-steric. The penetration of POE graft copolymer molecules into the interfacial layer increases the density of the particle surface layer which disfavours the radical entry events. The accumulation of hydrophobe (graft copolymer) in the microdroplets decreases the monomer droplet degradation and so the rate of polymerization. The presence of large number of microemulsion droplets depresses the water-phase polymerization but favours the radical entry events. The PBA-graft-POE graft copolymer promotes the formation of large particles at low and high conversion.

The high concentration of SDS or the high mass ratio SDS/water ensures that the degree of dissociation of emulsifier is decreased. This favours the penetration of undissociated emulsifier into the microdroplet

monomer core. Under such conditions, the monomer concentration in the microdroplets decreases and the side reactions (chain transfer) increase. The decreased monomer concentration at the reaction loci and the increased desorption of transferred emulsifier radicals decrease the rate of polymerization. The nucleation of emulsifier-saturated microdroplets leads to the release of free emulsifier from particles into aqueous phase. The released emulsifier stabilizes polymer particles and/or forms new micelles (microdroplets) for the continuous particle nucleation.

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