

## Emulsion Polymerization of Butyl Acrylate IV.<sup>†</sup> Effects of Initiator Type and Concentration

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**ABSTRACT:** The free radical emulsion polymerizations of butyl acrylate initiated by a water-soluble (ammonium peroxydisulfate, AP) and an oil-soluble (2,2'-azobisisobutyronitrile, AIBN) initiator in the presence of an anionic emulsifier at 60°C were kinetically investigated. Polymerization with AP is faster than that with AIBN. The effect of the initiator type, blend and concentration on the kinetic and colloidal parameters was investigated. The rate of polymerization was found to be proportional to 0.46th or 0.5th power of AP or AIBN concentration at  $[\text{initiator}] \leq 1 \times 10^{-4} \text{ mol dm}^{-3}$  and 0.33rd or 0.16th power of AP or AIBN concentration at  $[\text{initiator}] \geq 5 \times 10^{-3} \text{ mol dm}^{-3}$ . The polymerization proceeded quantitatively with AP whereas with AIBN reached limiting conversion. The rate of polymerization with an initiator blend (AP and AIBN) was smaller than the sum of appropriate individual rates. AIBN saturated monomer/polymer particle acts as a radical trapper.

**KEY WORDS** Emulsion Polymerization / Micellar Model / Polymer Particle / Micelle / Butyl Acrylate / Water- and Oil-Soluble Initiator / Termination / Cage Effect /

In published studies on the emulsion polymerization the main interest has been devoted to the effect of the water-soluble initiator on the polymerization kinetics.<sup>1-4</sup> It has been reported that the initial rate of polymerization is approximately proportional to the 0.5th power of the initiator concentration. With the progress of reaction, the reaction order gradually decreases to 0.4 (the interval 2) and further to 0.3 (the interval 3). Very little experimental information is available on the kinetics of the emulsion polymerization of unsaturated monomers carried out at very low and high initiator concentrations.

Much less is known about the effect of the oil-soluble initiator type and concentration on the emulsion polymerization process and/or an initiator blend, although they are of industrial importance. Here (with an oil-soluble initiator)

there are two different mechanisms for the production of radicals: 1) in monomer-swollen polymer particles formed radicals desorb to the continuous phase and 2) in continuous phase formed radicals are generated from the fraction of the oil-soluble initiator dissolved in water.<sup>5,6</sup> The efficiency of the radical was quite limited (4%) compared to the normal ~50% in bulk polymerization because of cage effects.

More recently, Nomura *et al.*<sup>7</sup> suggest that radicals formed in the monomer swollen micelles or emulsified monomer droplets start particle growth and polymerization proceeds according to suspension polymerization kinetics.

In our earlier paper<sup>8</sup> we concluded that growth events are more favored by radicals formed in the continuous phase than in the monomer phase. The initiator located in the

<sup>†</sup> For Part III, see ref 9.

polymer particles supports termination. Deactivation of growing radicals was suggested to proceed *via* the cage effect mechanism, *i.e.*, the oil-soluble initiator molecules react with growing radicals in a volume in which the cage effect is operative.

We also reported<sup>9</sup> that the emulsion polymerization of butyl acrylate initiated by an oil-soluble initiator or an initiator blend of water- and oil-soluble initiators in the presence of a mixed emulsifier system reached limiting (80–90%) conversion. The rate of polymerization with the initiator blend was much smaller than the sum of individual rates of water- and oil-soluble initiators. The decrease in rate was ascribed to deactivation of growing radicals by reaction with mobile oil-soluble radicals. The effects of partitioning of the non-ionic emulsifier between water and monomer and coalescence of polymer particles were also examined.

The present paper deals with the kinetics of butyl acrylate polymerization initiated with a water- and/or oil-soluble initiator. To get more information on the history of radicals derived from the oil-soluble initiator we followed the effects of initiator charge, distribution of initiator or radicals between continuous and monomer phases, very low and high initiator concentration and initiator blend composition on polymerization.

## THEORY

According to the micellar theory<sup>10</sup> and homogeneous nucleation model,<sup>11</sup> the relation between the rate of polymerization for interval 2 (the 10–50% conversion range) and initiator concentration  $[I]$  is expressed as

$$R_p \propto [I]^x \quad \text{or} \quad R_{pp} \propto [I]^{x'} \quad (1)$$

where  $x=0.4$  and  $x'=0$ , respectively.

Exponents  $x$  or  $x'$  give some information about the termination mode of radicals. growing radicals can be deactivated 1) in a bimolecular process between themselves,  $x$  (or

$a)=0.5$ , 2) by reaction with primary radicals or monomeric radicals (formed in chain transfer reactions to monomer),  $x$  (or  $b) \leq 0.5$  and 3) in the first-radical loss process,  $x(c) > 0.5$ , respectively. The overall reaction order  $x$ , thus, is the sum of individual exponents, *i.e.*,  $x = a + b + c$ .

The dependence of particle concentration initiator concentration is used to infer a nucleation mechanism. According to the emulsion polymerization theories<sup>10,11</sup> the relationship between the rate of polymerization and particle concentration is expressed as

$$R_p \propto N^{1.0} \quad \text{or} \quad N \propto [I]^{0.4} \quad (2)$$

The classical emulsion polymerization of acrylic monomers proceeds under the conditions of 40–50% conversion<sup>4</sup> in which high molecular weight polymers ( $M_n$ , *ca.*  $10^6$ – $10^7$ ) are formed. The very high viscosity of particle interior and very high molecular weight of polymer chains disfavor the translational motion of growing radicals so that bimolecular termination decreases. Under such conditions, growing radicals are trapped (entangled) in the polymer matrix.<sup>12</sup>

Stabile radicals formed by trapping, occlusion or degradative chain transfer favor increase in the reaction order with respect to  $[I]$  ( $R_p \propto [I]^x$ ). The primary radical termination, chain transfer to monomer and desorption of monomeric radicals to the aqueous phase decrease the reaction order.

Generally, reactions between entangled or occluded radicals in polymer particles are strongly suppressed. However, it has been suggested that radical loci can still wander and terminate by propagation (reaction diffusion<sup>13</sup>). The concentration of trapped (entangled) or occluded radicals was reported to be very low up to 75% conversion.<sup>14</sup> The highest concentration of occluded radicals reached at 95–98% conversion. Thus, the maximum concentration of occluded radicals is reached at a point where only a small percentage of unsaturated monomer remains.

Thus, it was postulated that radical (occluded)–radical (occluded) termination can only be achieved with a small amount of residual monomer enabling propagation to accommodate termination. The primary radicals are still being generated by thermal decomposition of the initiator. The number of new radicals achieving critical size is rapidly declining at this stage.<sup>14</sup> Under such conditions, mobile radicals would not take part in termination. However, this is open to experimental verification.

The low concentration of trapped radicals below 75% conversion may also be ascribed to the reaction of occluded radicals with mobile radicals (initiator fragments, oligomeric radicals, monomeric radicals, re-entered radicals). At very high conversion, at which the mobility of these “small” radicals is depressed, the life time of occluded radicals increases.

The aim of this work was to clarify the history of trapped and mobile radicals from the kinetic, molecular weight, and colloidal parameters of emulsion polymerization.

## EXPERIMENTAL

### *Materials*

Commercially available butyl acrylate (BA) monomer and initiators ammonium peroxodisulfate (the water-soluble initiator, AP) and 2,2'-azobisisobutyronitrile (the oil-soluble initiator, AIBN), both of extra-pure (from Fluka), were used as supplied. The emulsifier was reagent-grade sodium dodecylsulfate (SDS, from Fluka). Twice-distilled water was used as a polymerization medium.

### *Polymerization Procedure*

Batch emulsion polymerizations of butyl acrylate monomer were carried out at 60°C. In all runs the recipe contained 30 g water, 5 g butyl acrylate, 0.0076 g NaHCO<sub>3</sub>, and 0.065 g SDS. The amounts of AP and AIBN varied. The polymerization technique used has been already described in detail elsewhere.<sup>15</sup> Rates are in mol per dm<sup>-3</sup> of water per second and

concentrations of initiator, emulsifier and particles in mol per dm<sup>3</sup> of water.

### *Polymer and Latex Characterization*

The polymer latexes were made free of monomer, initiator, emulsifier and low molecular weight by-products by dialysis according to a method described previously.<sup>16</sup> Conversion of monomer was determined by dilatometric measurement. The (maximum) polymerization rate was determined by non-linear least squares regression analysis. Particle size ( $D$ , diameter) measurements were done by the light scattering method. The number of particles ( $N$ ) was calculated as described previously.<sup>8</sup> Limiting viscosity number  $[\eta]$  were measured in acetone at 25°C and used to estimate viscosity–average molecular weights.<sup>9</sup>

### *Spectral Measurements*

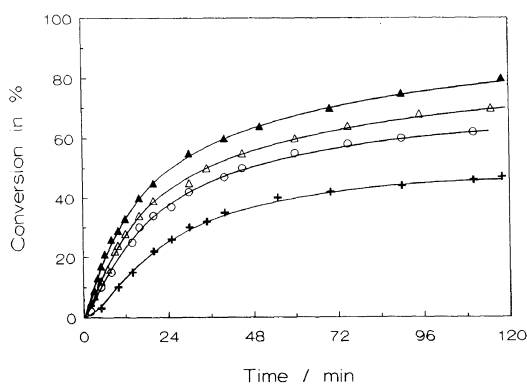
To determine the solubility of AIBN in the aqueous phase in the presence of butyl acrylate and/or sodium dodecylsulfate, the absorbance of the oil and aqueous phases saturated with AIBN was measured at room temperature.

## RESULTS AND DISCUSSION

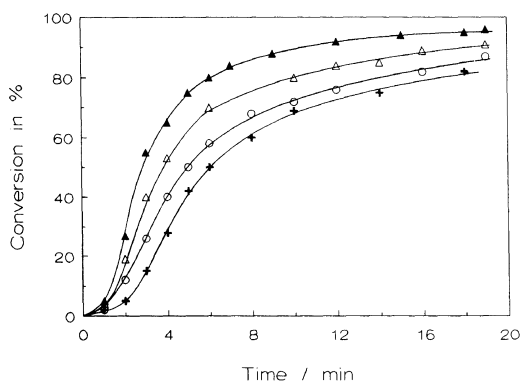
### *Rate of Polymerization*

Conversion–time data for the radical polymerization of butyl acrylate initiated by ammonium peroxodisulfate (AP) (a low (L-AP) or high (H-AP) concentration range) are shown in Figures 1 and 2. Conversion curves for the H-AP systems differ from those for the L-AP systems. In H-AP runs the conversion curves showed a sigmoidal shape typical of conventional emulsion polymerization with a rate maximum at medium conversions (the interval 2). The conversion curves for the L-AP runs were more similar to those for the solution and/or dead-end polymerization, and the rate maximum appeared at low (0–20%) conversion.

The maximum rates of polymerization ( $R_p$ ) estimated (within the 5–20% and 10–50%



**Figure 1.** Variation of monomer conversion in the emulsion polymerization of butyl acrylate (BA) with reaction time and initiator concentration (L-AP). Recipe, 30 g of water; 5 g of BA, 0.065 g of SDS, 0.0076 g of  $\text{NaHCO}_3$ ; temp,  $60^\circ\text{C}$ .  $[\text{AP}]/\text{mol dm}^{-3}$  of water: (+),  $1.0 \times 10^{-5}$ ; (O),  $2.0 \times 10^{-5}$ ; ( $\Delta$ ),  $5.0 \times 10^{-5}$ ; ( $\blacktriangle$ ),  $10.0 \times 10^{-5}$ .



**Figure 2.** Variation of monomer conversion in the emulsion polymerization of butyl acrylate (BA) with reaction time and initiator concentration (H-AP).  $[\text{AP}]/\text{mol dm}^{-3}$ : (+),  $0.5 \times 10^{-2}$ ; (O),  $1.0 \times 10^{-2}$ ; ( $\Delta$ ),  $2.0 \times 10^{-2}$ ; ( $\blacktriangle$ ),  $5.0 \times 10^{-2}$ . For other conditions, see the legend to Figure 1.

conversion range for L-AP and H-AP runs, respectively) are summarized in Table I and Figures 3 and 4. These data show that the rate of polymerization increases with  $[\text{AP}]$  and increase is more pronounced in the L-AP runs.

The reaction orders  $x$  and  $x'$  obtained from the log-log plots ( $R_p \propto [\text{AP}]^x$  or  $R_{pp} \propto [\text{AP}]^{x'}$ —Figure 3 or 4, where  $R_{pp}$  is the rate per particle) are summarized as functions of the initiator type in Table II. The reaction order ( $x$ ) with respect to  $[\text{AP}]$  was found to decrease with

increasing initiator concentration as follows

$$\begin{aligned} &0.46([\text{AP}] \leq 1.0 \times 10^{-4} \text{ mol dm}^{-3}, \text{L-AP}) \\ &> 0.43([\text{AP}] \leq 5.0 \times 10^{-3} \text{ mol dm}^{-3}) \\ &> 0.33([\text{AP}] \geq 5.0 \times 10^{-3} \text{ mol dm}^{-3}, \text{H-AP}) \\ &> 0.25([\text{AP}] \geq 5.0 \times 10^{-3} \text{ mol dm}^{-3} \\ &\quad + [\text{AIBN}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}) \\ &= 0.25([\text{AP}] \leq 5.0 \times 10^{-3} \text{ mol dm}^{-3} \\ &\quad + [\text{AIBN}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}) \quad (3) \end{aligned}$$

The reaction order ( $x$ ) with respect to  $[\text{AP}]$  for the L-AP system is somewhat larger than that predicted by the micellar model. This can be explained in terms of the low viscosity of the reaction medium and/or the bimolecular termination between growing radicals themselves because low-conversion rates were considered.

At high concentration of initiator, the primary radical termination becomes operative. Indeed the reaction order  $x=0.33$  was observed in the H-AP system. To evaluate primary radical termination, polymerization initiated with the initiator blend (AP and AIBN) was investigated.

The presence of AIBN in the monomer-swollen particles is expected to keep the concentration of mobile radicals on a level similar to that for the solution polymerization. If this is true, the deactivation of growing radicals should increase. A decrease in the rate of polymerization was observed. Here the reaction order  $x$  was 0.25.

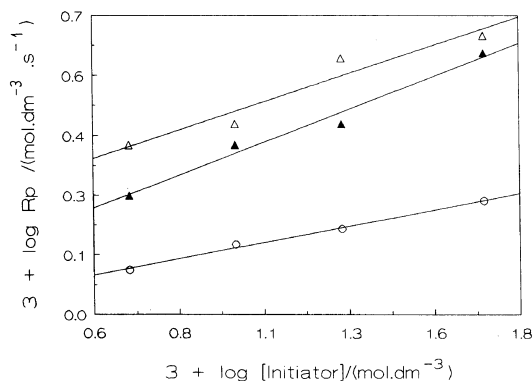
The reaction order ( $x'$ ) with respect to  $[\text{AP}]$  ( $R_{pp} \propto [\text{AP}]^{x'}$ , see Table II) as a function of the emulsifier and initiator type and concentration varies as follows

$$\begin{aligned} &0.5([\text{AP}] \leq 5.0 \times 10^{-3} \text{ mol dm}^{-3}) \\ &> 0.25([\text{AP}] \leq 5.0 \times 10^{-3} \text{ mol dm}^{-3} \\ &\quad + [\text{AIBN}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}) \\ &> 0.18([\text{AP}] \leq 1.0 \times 10^{-4} \text{ mol dm}^{-3}, \text{L-AP}) \\ &> 0.0([\text{AP}] \geq 5.0 \times 10^{-3} \text{ mol dm}^{-3}, \text{H-AP}) \\ &= 0.0([\text{AP}] \geq 5.0 \times 10^{-3} \text{ mol dm}^{-3} \\ &\quad + [\text{AIBN}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}) \quad (4) \end{aligned}$$

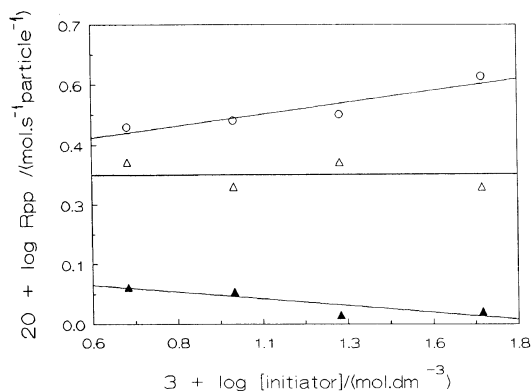
**Table I.** Variation of kinetics and particle size in the emulsion polymerization of butyl acrylate with initiator type and concentration<sup>a</sup>

[Initiator] $\times 10^4$ $\text{mol dm}^{-3}$	$R_p \times 10^4$		$R_{pp} \times 10^{20}$		$D$		$N$	
	$\text{mol dm}^{-3} \text{s}^{-1}$		$\text{mol s}^{-1} \text{particle}^{-1}$		$\text{nm}$		$\times 10^{-16} \text{dm}^3$	
	b	c	b	c	b	c	b	c
0.1		3.0		1.0		200		3.0
0.2		4.55		1.02		175		4.4
0.25	1.3		0.52		230		2.5	
0.5	1.9	5.66	0.59	1.1	195	167	3.2	5.1
1.0	2.5	8.0	0.71	1.33	189	158	3.5	6.0
2.0	3.5		0.95		186		3.7	
100	15.0		3.0		170		4.0	

<sup>a</sup> Recipe *cf.* Experimental part. <sup>b</sup> With AIBN, <sup>c</sup> With AP.



**Figure 3.** Variation of the rate of polymerization in the emulsion polymerization of butyl acrylate (BA) with initiator type and concentration. (○), H-AIBN, (▲), H-AP, and (△), H-AP/AIBN ([AIBN] =  $1 \times 10^2 \text{ mol dm}^{-3}$  of water). For other conditions, see legends to Figures 2, 6, and 7.



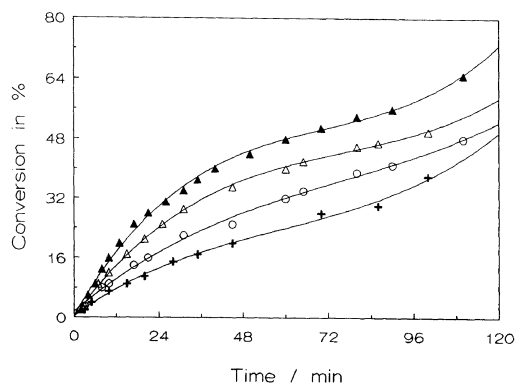
**Figure 4.** Variation of particle rate in the emulsion polymerization of butyl acrylate (BA) with initiator type and concentration. (▲) H-AP, (△) H-AP/AIBN ([AIBN] =  $1 \times 10^2 \text{ mol dm}^{-3}$ ), and (○) H-AIBN. For other conditions, see legends to Figures 2, 6, and 7.

This shows that the system with a mixed emulsifier system (a blend of anionic and non-ionic emulsifiers)<sup>9</sup> deviates from the classical emulsion model as well as from the present results (with an anionic emulsifier only). Solubility of the nonionic emulsifier in monomer and/or partitioning of the nonionic emulsifier between monomer and water, and formation of coagulum as well influence polymerization.

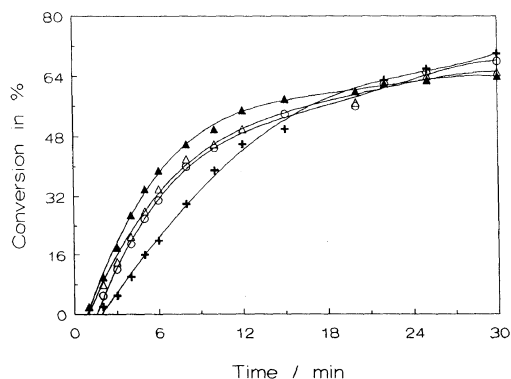
If the monomer polymerizes in water, the solution polymerization can increase the reaction order  $x'$  ( $x' > 0$ ). The sparingly water-soluble BA monomer, however, obeys

the micellar model. The water solubility of BA is 11 mM.<sup>17</sup> Thus, variation in the monomer concentration in polymer particles and surface-phase (an emulsifier zone of particles) polymerization with the number and/or size of particles may thus be responsible for this behavior.<sup>4</sup>

Conversion-time data for the radical polymerization of butyl acrylate initiated by AIBN (low and high concentration ranges, L- and H-AIBN) are shown in Figures 5 and 6. These conversion curves, especially for the L-AIBN systems, did not show sigmoidal shape typical



**Figure 5.** Variation of monomer conversion in the emulsion polymerization of butyl acrylate (BA) with reaction time and initiator (L-AIBN) concentration. Recipe, 30 g of water; 5 g of BA, 0.065 g of SDS, 0.0076 g of  $\text{NaHCO}_3$ ; temp,  $60^\circ\text{C}$ .  $[\text{AIBN}]/(\text{mol dm}^{-3}$  of water): (+),  $0.25 \times 10^4$ ; (O),  $0.5 \times 10^4$ ; ( $\Delta$ ),  $1.0 \times 10^4$ ; ( $\blacktriangle$ )  $2.0 \times 10^4$ .



**Figure 6.** Variation of monomer conversion in the emulsion polymerization of butyl acrylate (BA) with reaction time and initiator concentration (H-AIBN).  $[\text{AIBN}]/(\text{mol dm}^{-3})$ : (+),  $0.5 \times 10^2$ ; (O),  $1.0 \times 10^2$ ; ( $\Delta$ ),  $2.0 \times 10^2$ ; ( $\blacktriangle$ ),  $5.0 \times 10^2$ . For other conditions, see the legend to Figure 5.

of classical emulsion polymerization but a shape more similar to that for the solution polymerization. The polymerization reached 70–80% limiting conversion.

Limiting conversion would not be due to depletion of the initiator or monomer because the half lifetime of AIBN is above 10 h at  $60^\circ\text{C}$ <sup>18</sup> and there is enough monomer at 70 or 80% conversion. Limiting conversion ( $\text{conv.}_{\text{limit}}$ ) is nearly inversely proportional to AIBN concentration. Generally slow polym-

**Table II.** Variation of the reaction order with initiator type<sup>a</sup>

System	Initiator exponent $x$ or $x'$ from $R_p \propto [\text{I}]^x$ or $R_{pp} \propto [\text{I}]^{x'}$		Exponent $y$ or $z$ from $R_p \propto N^y$ or $N \propto [\text{I}]^z$	
	$x$	$x'$	$y$	$z$
L-AP	0.46	0.18	1.0	0.3
H-AP	0.33	-0.06	0.8	0.4
L-AIBN	0.5	0.35	1.5	0.18
H-AIBN	0.16	0.1	0.5	0.05
H-AP/AIBN	0.25	0.0	0.9	0.3

<sup>a</sup> Recipe *cf.* Experimental part.  $R_{pp}$ , at 30% conversion.

erization at high conversion is ascribed to low initiator efficiency.<sup>19,20</sup> Decrease of  $R_p$  with increasing  $[\text{AIBN}]$  at high conversion and the appearance of limiting conversion indicate that low initiator efficiency alone can not explain this behavior. Deactivation of radicals also varied.

The maximum rates of polymerization (within the 5–20% conversion range for the L-AIBN system and 5–40% conversion range for the H-AIBN system) are listed in Table I and Figures 3 and 4. The kinetic parameters  $x$  and  $x'$  are summarized in Table II.

The reaction order  $x$  *ca.* 0.5 ( $R_p \propto [\text{AIBN}]^x$ , where the rates were estimated at low conversions) was obtained for L-AIBN and L-AP runs. The bimolecular termination of growing radicals takes place. In other words, suspension polymerization kinetics are operative.<sup>7</sup> A small amount of AIBN in micelles or particles disfavors the primary radical termination. The latter should be dominant at high  $[\text{AIBN}]$ . The low reaction order  $x=0.12$  was observed in the H-AIBN system.

Table II shows that  $x$  are lower in AIBN systems. Primary radical termination is thus more pronounced in AIBN systems. AIBN radicals are formed in both phases but mainly in the monomer phase. AP radicals are formed in water only. AP derived oligomeric radicals (carrying  $\text{SO}_4^-$  group) enter the micelles where

they initiate growth. It is clear that (AP) oligomeric radicals can reach only the particle shell zone. The charged end group keeps the entered radicals at the particle surface. Here they propagate or by the chain transfer to monomer diffuse to the particle core or exit to water. AIBN initiating radicals enter the particle surface or diffuse into the particle core without electrostatic hindrance. This may be one reason why kinetic relationships for [AP] differ from those for AIBN.

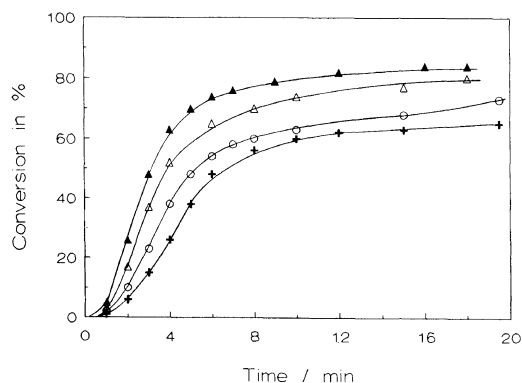
The reaction order  $x' = 0.35$  for L-AIBN system supports the hypothesis that solution or suspension polymerization is operative. In the H-AIBN system, the reaction exponent ( $x' = 0.1$ ) is very small (typical for the emulsion polymerization). At high [AIBN], the formation of radicals in the monomer-swollen particles is depressed due to the cage effect (small initiator efficiency). However, the increased amount of AIBN in water favors more water-phase polymerization (formation of oligomeric radicals) and particle formation as well, and so emulsion polymerization kinetics are operative.

It was shown that *ca.* 5–7 wt% of the initial AIBN concentration (in the range  $1 \times 10^{-3}$  mol dm<sup>-3</sup>– $1 \times 10^{-2}$  mol dm<sup>-3</sup> of AIBN) is transferred from the monomer phase into the aqueous phase. If we use the [AIBN] =  $5 \times 10^{-2}$  mol dm<sup>-3</sup>, the water-soluble fraction of AIBN is only 3–5 wt%. This indicates that there is a value of AIBN at a certain initiator concentration above which the concentration of AIBN in water is constant or only slightly increases with [AIBN].

If we use the total [AIBN] =  $1 \times 10^{-5}$  mol dm<sup>-3</sup> (L-AIBN system), the aqueous phase contains *ca.* [AIBN] =  $7.0 \times 10^{-7}$  mol dm<sup>-3</sup>. To evaluate initiation with such a small amount of AIBN in water we conducted the emulsion polymerization with [AP] =  $5 \times 10^{-7}$  mol dm<sup>-3</sup>. It was found that polymerization was very slow, or did not start at all. Polymerization carried out at very low [AIBN] (L-AIBN system), is thus independent of

water-phase polymerization or the soluble-fraction of AIBN in water. Here, initiator molecules in micelles and/or polymer particles control polymerization. In favor of his hypothesis is the high reproducibility of kinetic data and fast polymerization with [AIBN] =  $5 \times 10^{-5}$  mol dm<sup>-3</sup>.

The effects of the initiator blend (AP and AIBN) on emulsion polymerization of butyl acrylate are summarized in Figures 3, 4, and 7 and Table II (conversion curves, rates of polymerization and reaction orders  $x$  and  $x'$ ). The conversion curves in Figure 7 are more similar to those for the AIBN system in both shape and limiting conversion. The overall rate for the AP/AIBN blend was smaller than the sum of individual rates for AP and AIBN runs (see Figure 3). This behaviour may be explained in terms of the formation of radicals in water and monomer as well. It is clear that the addition of AIBN can only slightly increase radical concentration in the aqueous phase. The decrease in the rate ( $R_{p, AIBN/AP}$ ) can be ascribed to 1) increased water-phase termination caused by exited AIBN radical fragments and 2) increased termination in polymer particles. The low water-solubility of AIBN indicates that only a small fraction of AIBN radicals can desorb and take part in heterogeneous



**Figure 7.** Variation of monomer conversion in the emulsion polymerization of butyl acrylate (BA) with reaction time and initiator type and concentration. (AP/AIBN), [AIBN] =  $1 \times 10^2$  mol dm<sup>-3</sup>, [AP]/(mol dm<sup>-3</sup>): (+),  $0.5 \times 10^2$ ; (O),  $1.0 \times 10^2$ ; (Δ),  $2.0 \times 10^2$ ; (▲),  $5.0 \times 10^2$ . For other conditions, see the legend to Figure 1.

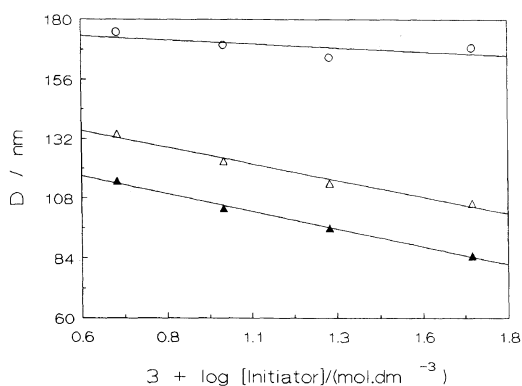
termination (AP with AIBN derived radicals) in the aqueous phase. A large amount of AIBN in the monomer swollen micelles or particles favors the idea that AIBN radical fragments somehow take part in termination. It is well known that the formation of radicals within the particle is limited due the strong cage effect.

Similar kinetic behavior in<sup>8</sup> can be explained by the reaction of the short-lived radicals with the growing radicals (the cage effect is operative). Limiting conversion supports this idea—increased termination of growing (entangled). Otherwise, the reactions of oligomer radicals (derived from AP and AIBN) formed in the aqueous phase would be governed by classical emulsion polymerization kinetics where polymerization proceeds to 100% conversion.

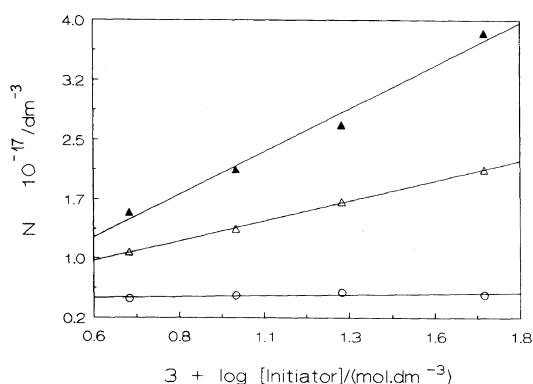
The rates of initiation estimated from the eq  $R_i = 2fk_d [I]$ , where  $f$  is the initiator efficiency and  $k_d$  the decomposition rate constant of initiator ( $I$ ), using  $f=0.7$  and  $0.6$  for peroxydisulfate<sup>21</sup> and AIBN,<sup>22</sup>  $k_d = 5.8 \times 10^{-6} \text{ s}^{-1}$  and  $1.6 \times 10^{-5} \text{ s}^{-1}$  for peroxydisulfate<sup>23</sup> and for AIBN<sup>22</sup> and the initiator (see Experimental part, AP, AIBN or AP/AIBN runs) concentrations are similar or slightly higher in AIBN systems. The polymerization rates should be similar in both AP and AIBN runs. The experimental results show the reverse is true, *i.e.*, polymerization is faster in the AP runs. It was mentioned above that partitioning of initiator between water and monomer, desorption of radicals and increased termination in the AIBN system are responsible for the observed behavior. Variation in colloidal parameters with the initiator type influences polymerization behavior, as discussed below.

#### Particle Parameters

Variation in particle size ( $D$ , diameter) and number ( $N$ ) with the initiator type (AIBN and AP) and concentration is illustrated in Table I and Figures 8 and 9. We observed that particle number was constant from 30% up to 100% conversion.



**Figure 8.** Variation of particle size in the emulsion polymerization of butyl acrylate (BA) with initiator type and concentration. ( $\blacktriangle$ ) H-AP, ( $\Delta$ ) H-AP/AIBN ( $[\text{AIBN}] = 1 \times 10^2 \text{ mol dm}^{-3}$ ), and ( $\circ$ ) H-AIBN. For other conditions, see legends to Figures 2, 6, and 7.



**Figure 9.** Variation of particle number in the emulsion polymerization of butyl acrylate (BA) with initiator type and concentration. ( $\circ$ ) H-AIBN, ( $\Delta$ ) H-AP/AIBN ( $[\text{AIBN}] = 1 \times 10^2 \text{ mol dm}^{-3}$ ), and ( $\blacktriangle$ ) H-AP. For other conditions, see legends to Figures 2, 6, and 7.

Generally, the size of a particle decreases and the number of particles increases with initiator concentration. These trends are found in all systems except of the H-AIBN run (see Table I and Figures 8 and 9).

In the H-AIBN runs, the size and number of particles are nearly independent of  $[\text{AIBN}]$ . The kinetic results of the L-AIBN system and H-AIBN one indicate that there is  $[\text{AIBN}]$  above which particle number is constant or varies slightly. In favor of the saturation value for  $[\text{AIBN}]$  are also measurements of a



water-solubility of AIBN (see above).

The most intensive increase in particle number with [initiator] was observed in the AP system. Thus, the two-step initiation process (for AP, formation of radicals in water and nucleation of particle) is more effective than the one-step initiation process (for AIBN). However, the addition of AIBN to the AP system (the AP/AIBN system) decreases particle concentration. This indicates that radical concentration in the whole system decreases by the addition of AIBN.

Table II shows that exponents  $y$  and  $z$  (from  $R_p \propto N^y$  and  $N \propto [I]^z$ ) for the AP runs agree very well with those predicted by the micellar model ( $y$  and  $z$  are close to 1.0 and 0.4, respectively).<sup>10,11</sup> AIBN systems strongly deviate from the micellar model, *i.e.*, the reaction order  $y$  varies from 1.5 to 0.5 and  $z$  from 0.18 to 0.05. The rate of polymerization ( $R_p$ ) in AP runs is *ca.* two-three times that in AIBN runs. The same is also found for the rates of polymerization per particle.

In both systems (with and without AIBN) polymers with very high molecular weights are formed ( $10^6$ – $10^7$ ). The solution of PBA in good solvents for poly(butyl acrylate) contained insoluble gels. The molecular weights  $M_v$  of polymer sols were in the range  $1.0 \times 10^6$ – $8 \times 10^6$  and did not vary with AP or AIBN concentration.

## CONCLUSIONS

The foregoing discussion shows that primary radical termination increases with initiator concentration and the increase is more pronounced in systems with AIBN.

The kinetics of suspension polymerization are assumed to govern polymerization at low conversion and low AIBN concentrations.

The presence of AIBN favors deactivation in the aqueous phase (a heterogeneous termination) and in monomer swollen polymer particles. AIBN molecules or their radical fragments should react with growing radicals

in high viscous medium in which the cage effect is operative.

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## REFERENCES

1. S. P. Chatterjee, M. Banerjee, and R. S. Konar, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 1517 (1978).
2. M. Banerjee and R. S. Konar, *Polymer*, **27**, 147 (1986).
3. I. Capek and L. Q. Tuan, *Makromol. Chem.*, **187**, 2063 (1986).
4. J. Barton and I. Capek, "Radical Polymerization in Disperse Systems," T. J. Kemp and J. P. Kennedy, Ed., Ellis Horwood, Chichester, 1994, pp 49–56, 104–118, and 123–167.
5. I. Capek, J. Bartoň, and A. Kárpátýová, *Makromol. Chem.*, **188**, 703 (1987).
6. J. M. Asua, V. S. Rodrigues, E. D. Sudol, and M. S. El. Aasser, *J. Polym. Sci., A, Polym. Chem.*, **27**, 3569 (1989).
7. M. Nomura, J. Ikoma, and K. Fujita, *J. Polym. Sci., A, Polym. Chem.*, **31**, 2103 (1993).
8. I. Capek, M. Riza, and M. Akashi, *Polym. J.*, **24**, 959 (1992).
9. I. Capek, *Makromol. Chem.*, **195**, 1137 (1994).
10. W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).
11. R. M. Fitch and C. H. Tsai, *J. Polym. Sci., Polym. Lett. Ed.*, **8**, 703 (1970).
12. K. F. O'Driscoll, *Pure Appl. Chem.*, **53**, 617 (1981).
13. G. W. Schulz, *Z. Phys. Chem.*, **8**, 290 (1956).
14. G. R. Cuttig and B. J. Tabner, *Macromolecules*, **26**, 951 (1993).
15. I. Capek, J. Bartoň, and E. Orolinová, *Chem. Zvesti*, **38**, 803 (1984).
16. I. Capek, J. Bartoň, L. Q. Tuan, V. Svoboda, and V. Novotný, *Makromol. Chem.*, **188**, 1723 (1987).
17. J. W. Vanderhoff, *J. Polym. Sci., Polym. Symp.*, **72**, 161 (1985).
18. J. Brandrup and E. H. Immergut, Ed., "Polymer Handbook," 3rd ed, John Wiley and Sons, Inc., New York, N.Y., 1989.
19. I. A. Maxwell, D. H. Napper, and R. G. Gilbert, *J. Chem. Soc., Faraday Trans. 1*, **83**, 1449 (1987).
20. S. T. Balke and A. E. Hamielec, *J. Appl. Polym. Sci.*, **17**, 905 (1973).
21. J. M. Goldwasser and A. Rudin, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 1993 (1982).
22. C. D. Berezhnoi, P. M. Khomikovskij, and S. S. Medvedev, *Vysokomol. Soedin. Ser. A*, **2**, 141 (1960).
23. E. Hakoila, *Ann. Univ. Turku., Ser. A*, **66**, 7 (1963).