

Effect of hydroquinone on the kinetics of emulsion polymerization of butyl acrylate

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The mechanism of free radical emulsion polymerization of butyl acrylate initiated by ammonium peroxodisulfate at 70°C in the presence of a small amount of hydroquinone has been studied. Over the stationary state the rate of polymerization decreases with increasing the hydroquinone concentration. The rate of polymerization is proportional to the emulsifier concentration (without hydroquinone) but in the presence of hydroquinone it decreases with increasing emulsifier concentration and the number of particles is proportional to the first power of the emulsifier concentration.

The inhibition efficiency decreases with increasing hydroquinone concentration. Hydroquinone and products from its interaction with initiator, oxygen and quinone to some extent participate also in complex way in some other reactions which may lead to both partial regeneration and deactivation of inhibitor.

The radical scavenger was found to decrease the average particle size. This was discussed in terms of the suppression of polymerization within the large emulsified monomer droplets.

Изучен механизм свободно-радикальной эмульсионной полимеризации бутилакрилата, инициируемой пероксодисульфатом аммония, при 70°C в присутствии небольшого количества гидрохинона. В стационарной фазе скорость полимеризации снижается при возрастании концентрации гидрохинона. Скорость полимеризации пропорциональна содержанию эмульгатора (в отсутствие гидрохинона), однако в присутствии гидрохинона она снижается при повышении концентрации эмульгатора, и число частиц пропорционально первому порядку концентрации эмульгатора.

Эффективность ингибирования уменьшается при увеличении концентрации гидрохинона. Гидрохинон и продукты его взаимодействия с инициатором, кислород и хинон в некоторой степени, сложным путем принимают участие в прочих реакциях, могущих привести как к частичной регенерации, так и к дезактивации ингибитора.

Обнаружено, что ловушка радикалов приводит к уменьшению среднего размера частиц. Это явление обсуждается в терминах подавления полимеризации внутри объемных эмульгированных капель мономера.

The radical scavenger is known to significantly influence the homogeneous bulk or solution free radical polymerization. In the early stage the polymerization proceeds very slowly or the inhibition time is observed. Then the rate increases to the maximum, which is mostly the same as that in the absence of the inhibitor. If the substance reduces both the relative molecular mass and the polymerization rate, it is called retarder [1].

The effect of the radical scavenger agents on the kinetics of the emulsion polymerization is not so well defined. In the emulsion polymerization of tetrafluoroethylene *Watanabe et al.* [2] found that hydroquinone and *p*-benzoquinone effectively deactivated primary radicals in the aqueous phase but not the growing radicals within the polymer particles.

Bartoň and Juraničová [3] reported on the mechanism of inhibition of emulsion polymerization of methyl methacrylate and acrylonitrile in the presence of *p*-benzoquinone, diphenylpicrylhydrazyl (DPPH) and a few derivatives of 2,2,6,6-tetramethylpiperidin-1-oxyl stable radicals. Most of these compounds were found to be very effective in deactivation of primary or oligomer radicals only in the aqueous phase.

In our earlier papers [4, 5] the effect of *p*-benzoquinone and hydroquinone on the kinetics of the free radical emulsion copolymerization of acrylonitrile and butyl acrylate was studied. Experimental data show that the presence of a small amount of hydroquinone or *p*-benzoquinone suppresses the formation of copolymer enriched with acrylonitrile and decreases the rate of polymerization but not the relative molecular mass and the size of polymer particles. The aim of this work is to kinetically evaluate the effect of hydroquinone on the emulsion polymerization of butyl acrylate.

Experimental

Materials

Commercially available butyl acrylate monomer was purified as described previously [4]. Ammonium peroxodisulfate as the initiator and hydroquinone as the inhibitor, both of extra-pure grade, were used as supplied. The emulsifier used was reagent-grade sodium dodecylphenoxybenzenedisulfonate (Dowfax 2A1) as a 45% aqueous solution. Twice distilled water (under nitrogen atmosphere) was used as a polymerization medium.

Polymerizations

The batch polymerizations were run at constant temperature 70°C. In all cases the recipe comprises 140 g of water, 95.6 g of butyl acrylate, and 0.772 g of ammonium peroxodisulfate. Concentrations of emulsifier and inhibitor varied as given later.

Emulsion polymerizations were performed in a 500 cm³ three-necked flask, equipped with a stirrer (frequency of revolutions *ca.* 400 min⁻¹), a bulb condenser, a nitrogen inlet and a device for sample collection. Components of the reaction mixture were charged into the reaction vessel under nitrogen in the order: 1. Aqueous solution of emulsifier (Dowfax 2A1); 2. aqueous solution of hydroquinone; 3. monomer. The mixture was then stirred for about 30 min at constant agitation speed at (70 ± 0.1)°C. After this stage the aqueous solution of ammonium peroxodisulfate was dosed with a syringe. From this moment the reaction time was measured. The samples of the polymerization mixture, taken at certain intervals, were coagulated in acidified ethanol. After decantation, the precipitated polymer was dried at room temperature and later under vacuum. Other conditions of the polymerization procedure and techniques used have been described in detail elsewhere [4].

Measurements

The particle size of latexes was determined by the light scattering method [6]. The number of particles *N* was estimated from the experimental value of the average particle radius according to the method described [7].

Results and discussion

The conversion—time curves of the emulsion polymerization of butyl acrylate (BA) initiated by ammonium peroxodisulfate (APS) in the presence of Dowfax 2A1 (DW) as anionic emulsifier and of hydroquinone (QH₂) as inhibitor are presented in Fig. 1. After the inhibition, the rate of polymerization

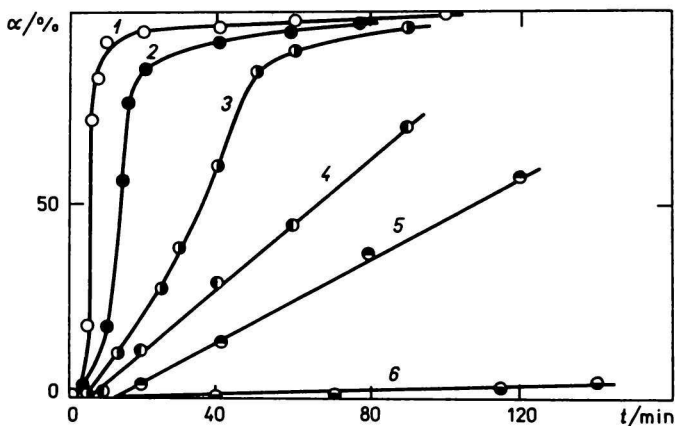


Fig. 1. Variation of the monomer conversion α in the emulsion polymerization of butyl acrylate with the reaction time and the concentration of hydroquinone. $[DW] = 7.3 \times 10^{-2}$ mol dm⁻³ (referred to water), $[APS] = 2.28 \times 10^{-2}$ mol dm⁻³, $[QH_2] \cdot 10^4 / (\text{mol dm}^{-3})$: 1. 0; 2. 0.35; 3. 1.74; 4. 3.48; 5. 17.4; 6. 87.0.

gradually increases (in systems with inhibitor concentration lower than $3.48 \times 10^{-4} \text{ mol dm}^{-3}$), reaching approximately a constant value of the rate of polymer formation within 30—70 % conversion. Using inhibitor concentration higher or equal to $3.48 \times 10^{-4} \text{ mol dm}^{-3}$, conversion increases linearly with time even up to high conversion. Values of the rate determined within 30—70 % conversion are expressed as a function of the inhibitor concentration in Table 1

Table 1

Polymerization kinetic data^a

$[\text{QH}_2] \cdot 10^4$ mol dm	$\frac{R_p}{10^3} \cdot 10^3$ ^b mol dm ⁻³ s ⁻¹	t_{inh} min	μ	$([\text{QH}_2]/[\text{APS}]) \cdot 10^2$
0	53.0	1		
0.35	9.0	2	2.1	0.15
1.74	2.5	4.5	0.96	0.76
3.48	0.8	8	0.85	1.52
17.4	0.5	13	0.28	7.63
87.0	0.1	25	0.11	38.15

a) $[\text{DW}] = 7.32 \times 10^{-2} \text{ mol dm}^{-3}$ $[\text{APS}] = 2.28 \times 10^{-2} \text{ mol dm}^{-3}$ (referred to water). b) Maximum rate of polymerization in the interval $[\text{QH}_2]$.

together with the kinetic parameters characterizing the inhibitor efficiency. Table 1 shows the variation of the inhibition time t_{inh} with the stoichiometric mole number and with QH_2 concentration. The stoichiometric mole number μ is in the relation with the inhibition time t_{inh} according to eqn (1)

$$t_{\text{inh}} = \frac{\mu[\text{QH}_2]}{R_i} \quad (1)$$

where R_i is the rate of initiation. For the polymerization temperature of 70 °C the rate constant $k_d = 2.7 \times 10^{-5} \text{ s}^{-1}$ obtained for the decomposition of potassium peroxydisulfate (PKS) [8], $f = 0.5$ for peroxydisulfate [9] and $[\text{APS}] = 2.28 \times 10^{-2} \text{ mol dm}^{-3}$ were used for calculating the rate of initiation according to the term $R_i = 2k_d f [\text{APS}]$. The value of $R_i = 6.16 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$ thus obtained was used to calculate μ at the given QH_2 concentration.

The inhibitor efficiency apparently decreases with increasing QH_2 concentration. This fact might support the assumption that in a series of reactions part of inhibitor is deactivated. Hydroquinone interacts not only with primary radicals (formed in the aqueous phase *via* peroxydisulfate decomposition) but also with growing radicals which can produce some radical intermediates, such as semiquinone (QH^\bullet) or quinones [10] with different activity to initiating and growing radicals.

Hydroquinone is presumed to exert its inhibition action through first being oxidized by the peroxydisulfate to *p*-benzoquinone which then inhibits polymerization by a copolymerization mechanism [11]. An abrupt halt of propagation stage may also be brought by contribution of a transfer reaction to hydroquinone with production of a relatively unreactive free radical.

The concentration of the most active inhibitor form *p*-benzoquinone is regulated by the present amount of peroxydisulfate and oxygen dissolved in water, indicated by the inhibition time in the system without inhibitor. Some portion of oxygen is also generated during the polymerization by the decomposition of peroxydisulfate [12].

It is supposed that only certain amount of *p*-benzoquinone may be produced in the system, which is only slightly influenced by the concentration of hydroquinone. With the increasing concentration of QH₂ the concentration of complex formed between hydroquinone and quinone increases, which negatively influences the active concentration of both components in the inhibition, especially of quinone.

Partition coefficient of QH₂ between butyl acrylate (100 cm³) and water (140 cm³) at 25°C is 1.222 and shows that the radicals should be deactivated in both phases depending on the concentration of radicals in the particular phases.

It was found that the relationship between t_{inh} and the initial concentration ratio [QH₂]/[APS] is not linear. The deviation from linearity was probably caused by side reactions mentioned above. One can say that the inhibition effect of QH₂ is very complex and is a function of reaction conditions.

Variations of the average particle diameter \bar{D} , the number of particles N , and the average number of radicals per particle \bar{n} with the QH₂ concentration are summarized in Table 2. With increasing QH₂ concentration the particle size decreases unexpectedly and the number of particles increases, even if the DW concentration is constant. It is clear that QH₂ can influence only the radical

Table 2

Polymerization kinetic data

$\frac{[\text{QH}_2] \cdot 10^4}{\text{mol dm}^{-3}}$	\bar{D} nm	$\frac{N \cdot 10^{-18}}{\text{dm}^3}$	\bar{n}	$\frac{k_t \cdot 10^2}{\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$
0	68	4.1	(3.8)	3.92
0.35	66	4.4	0.6	7.2
1.74	60	5.5	0.13	11.6
3.48	57	6.0	0.04	15.1
17.4	52	8.4	0.018	22.8

k_t termination rate constant calculated using eqn (3).

concentration in both phases, *i.e.* in the polymer particle and the aqueous phases. The contribution of the polymerization within the emulsified monomer droplets due to their large size and low radical capture efficiency can be neglected. Therefore, final particles with lower average size may be formed. The large portion of radicals are present within the aqueous phase and micelles, where after deactivation of the radical scavenger by entered radicals polymerization takes place. The measure of retardation are values of the average number of radicals per particle \bar{n} , which was calculated using the following equation

$$\bar{n} = \frac{R_p \cdot N_A}{k_p \cdot [\text{BA}]_{\text{eq}} \cdot N} \quad (2)$$

where $[\text{BA}]_{\text{eq}}$ is the equilibrium butyl acrylate monomer concentration ($c = 4.5 \text{ mol dm}^{-3}$, [13]), N_A is the Avogadro's constant and k_p is the propagation rate constant ($k_p = 450 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, [14]). These data indicate the strong influence of the QH_2 amount upon the \bar{n} values. This may be caused by the deactivation of radicals in both the aqueous and the polymer particle phases. The deactivation of radicals in the aqueous phase leads to the lower initiating concentration and lower entry rate of radicals to polymer particles. Deactivation of radicals within the polymer particles by the chain-transfer to QH_2 or by copolymerization with quinone decreases the number of radicals in particles. These reactions generate stable radicals and therefore may be very active in desorption processes [15].

It was observed that with the increasing emulsifier concentration in the presence of QH_2 the rate of polymerization decreases even if the number of polymer particles increases. The rate of polymerization is referred to the emulsifier concentration with the relationship $R_p \approx [\text{DW}]^{-0.64}$ and the relationship between the number of particles and the emulsifier concentration can be expressed as $N \approx [\text{DW}]^{1.05}$. The exponents of $[\text{DW}]$ deviate from those proposed by micellar and homogeneous nucleation theories [16, 17]. This observation should be explained by retardation effect of QH_2 , which increases with increasing emulsifier concentration, as indicated by the values of the average number of radicals per particle. At higher $[\text{DW}]$, more QH_2 molecules are emulsified within monomer swollen emulsifier micelles proposed as polymerization loci. The same trend was also observed in the emulsion copolymerization of acrylonitrile and styrene in the presence of seed polybutadiene latex and of the chain-transfer agent *tert*-dodecylthiol [18]. The decrease of the rate was explained by the increase of desorption rate of radicals from the polymer particle. In the present system the desorption of semiquinone radicals formed by transfer can also contribute to the decrease of radicals within latex particles. The ratio of the rates in the absence and the presence of QH_2 increases with increasing emulsifier concentration. This indicates that the inhibitor is sensitized by emulsification.

Here in micelles or primary particles the inhibitor terminates effectively the free radicals. Due to the short life-time of these radicals the growth rate of polymer particles is low, which can favour the formation of larger portion of smaller polymer particles.

The value of the termination rate constant k_t for butyl acrylate without inhibitor (Table 2) at the volume fraction of polymer ($\varphi_p = 0.33$, corresponding to the mass fraction $w_p = 0.36$) obtained by *Soh—Sundberg* theory [19—21] is $3.92 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This is few orders of magnitude less than the typical values at zero conversion. The theory of *Soh* and *Sundberg* is able to describe the experimental behaviour for conditions where “residual termination” is the main contribution of the overall termination. Residual termination occurs at mass fractions of polymer so high that the chain entanglements severely hinder the macroradical translation diffusion. Here bimolecular termination between macroradicals may occur only as a consequence of propagation. The values of k_t at different emulsifier and hydroquinone concentrations studied are summarized in Tables 2 and 3. They were calculated from the following *Soh—Sundberg* equations

$$k_t = f_t \pi \sigma^2 a_{\text{RMS}} N k_p [\text{BA}]_{\text{eq}} / J_c^{0.5} \quad (3)$$

$$\sigma = r^{-1} (\ln(r^3 V_s / \bar{n} \pi^{1.5}))^{0.5}, \quad r^2 = 3 / (2 J_c a_{\text{RMS}}^2) \quad (4)$$

where a_{RMS} is the root mean-square end-to-end distance per square root of the number of monomer units (reported as 0.64 nm for butyl methacrylate [22] and adopted here for BA), $J_c = P_{\text{cr}} / 2 \varphi_p$, P_{cr} being the critical degree of polymerization for entanglement of pure polymer (reported in [22] as $P_{\text{cr}} = 200$ for this monomer), f_t being an efficiency factor (reported as 0.2 for methyl methacrylate [14] and adopted here for BA), and V_s is the swollen volume of the latex particle.

Applying the *Soh—Sundberg* theory, *Maxwell et al.* [14] obtained the value of $k_t = 7 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is five orders of magnitude higher than in this study. Their experimental value of k_t was one order lower than that calculated from eqn (2). The polymerization of butyl acrylate was followed at the mass fraction of polymer $w_p = 0.58$, temperature 50°C and the range of initiator concentration 10^{-5} — $1.5 \times 10^{-3} \text{ mol dm}^{-3}$.

The difference between the literature [14] and our value of k_t can be assigned to the experimental conditions. The high polymerization temperature (70°C) and high initiator concentration favour the assumption that the termination occurs between primary radicals (or oligomer radicals) and macroradicals and the residual termination is only a slight contributor to k_t . The high temperature and monomer portion within polymer particles decrease the inner polymer particle viscosity and increase the normal bimolecular radical termination (Tables 2 and 3).

Table 3

Polymerization kinetic data^a

$\frac{[DW] \cdot 10^2}{\text{mol dm}^{-3}}$	$\frac{R_p \cdot 10^4}{\text{mol dm}^{-3} \text{ s}^{-1}}$	\bar{D} nm	$\frac{N \cdot 10^{-18}}{\text{dm}^3}$		R_{p0}/R_p^b	\bar{D}_0/\bar{D}^c	$\frac{k_t}{\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$
0.63	24.5	123	0.64	1.12	2.24*	1.22*	1.54
0.8	20.0	100	1.18	0.51	3.25	1.30	2.93
1.18	13.0	95	1.38	0.29	5.6*	1.16*	3.02
2.88	7.5	65	4.32	0.051	14.0*	1.26*	12.4
4.0	6.3	60	5.5	0.033	20.6	1.23	16.5
5.76	5.5	58	6.1	0.027	28.7	1.17	18.4
7.32	5.0	50	9.5	0.0155	34.8*	1.32*	28.7

a) $[QH_2] = 1.74 \times 10^{-3} \text{ mol dm}^{-3}$, $[APS] = 2.82 \times 10^{-2} \text{ mol dm}^{-3}$ b) The ratio of the rates of polymerization without (R_{p0}) and with QH_2 (R_p); * R_{p0} taken from [13]. c) The ratio of the final average particle diameters obtained without (\bar{D}_0) and with QH_2 (\bar{D}); * \bar{D}_0 taken from [13].

In the presence of hydroquinone the value of k_t (residual) increases with increasing emulsifier concentration, which can be explained by smaller interradi- cal distances in small particles. The higher values of k_t at higher QH_2 concentra- tion point out that the macroradical may also be partially deactivated by the reaction with inhibitor.

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