

Emulsifier and Initiator Effects on the Emulsion Copolymerization of Styrene with Butyl Acrylate

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The emulsion copolymerization of styrene with butyl acrylate in the presence of anionic and non-ionic emulsifier, initiated by potassium peroxodisulfate with or without activator was kinetically investigated. The reaction order with respect to initiator $K_2S_2O_8$ and to the initiator with $Na_2S_2O_4 \cdot 2H_2O$ activator was 0.47 and 0.71, respectively. Examination of the influence of anionic Mersol H and nonionic Slovasol 2430 emulsifier on the course of copolymerization showed that the nonionic emulsifier influences the rate of copolymerization in higher degree. Reaction order of the copolymerization rate in terms of Mersol H and Slovasol 2430 concentration was 0.83 and 1.17, respectively. The effect of nonionic emulsifier in the concentration region over its critical micellar concentration on the decomposition rate constant of $K_2S_2O_8$ at 60°C was studied. It was shown that the nonionic emulsifier at the used concentration (from 0.22×10^{-2} to 5.80×10^{-2} mol dm⁻³) accelerates the decomposition of peroxide. The change of the decomposition rate constant of initiator is higher up to the concentration of emulsifier 1.45×10^{-2} mol dm⁻³ than in the range from 1.45×10^{-2} to 5.80×10^{-2} mol dm⁻³, what is the concentration region of Slovasol 2430 in the investigated copolymerization system.

Dispersions of styrene—butyl acrylate copolymers are extensively used in paint and adhesive technology. Because of its practical significance many researchers have been interested in the emulsion copolymerization of styrene (S) with butyl acrylate (BA). The kinetics of this copolymerization and the properties of produced dispersion were studied in several papers [1—3]. The influence of surfactants on the course of copolymerization was explored [4]. The role of the nonionic surfactant octylphenoxypolyethoxyethanol in emulsion polymerization of styrene, butyl acrylate as well as their copolymerization was investigated [5—7] using the calorimetry as the main tool for the kinetics analysis. Dissociation initiators $K_2S_2O_8$ and $(NH_4)_2S_2O_8$ or redox systems $K_2S_2O_8/Na_2S_2O_4$ are most often used in emulsion polymerization system [8]. Also different aromatic aldehyde—sodium bisulfite adducts as redox pairs for $K_2S_2O_8$ initiator in the system at emulsion polymerization of S and its copolymerization with BA were investigated [9].

In our previous papers [10, 11] the influence of a conventional initiator ($K_2S_2O_8$) and of an untraditional heterogeneous type of initiator – oxidized isotactic polypropylene powder with an amine activator on the course of emulsion copolymerization of S with BA, on the latex particles size, and on the molecular mass characteristics of copolymer was investigated. It was found besides other that the use of the heterogeneous initiator type in the emulsion polymerization

system led to an extremely high value of molecular mass of copolymer P(S)/P(BA).

The present work deals with the effect of two types of emulsifier – ionic Mersol H and nonionic Slovasol 2430 as well as the effect of potassium persulfate initiator with or without $Na_2S_2O_4$ activator on the rate of emulsion copolymerization of S and BA. In the emulsion system with the nonionic emulsifier its possible effect on the initiator decomposition was also investigated.

EXPERIMENTAL

Styrene (Kaučuk, Kralupy) was purified by washing with NaOH and with water, dried and twice vacuum distilled in argon atmosphere. Butyl acrylate (Chemical Works Sokolov) was twice vacuum distilled under argon atmosphere. Potassium peroxodisulfate (Lachema, Brno), anal. grade, was used as an aqueous solution with a concentration of 9.2×10^{-2} mol dm⁻³ and kept in an inert atmosphere. Sodium dithionite dihydrate (Lachema, Brno), anal. grade, was used as aqueous solution ($c = 11.4 \times 10^{-2}$ mol dm⁻³) kept in argon atmosphere. Methanol, acetone, and 1,4-dioxane (Lachema, Brno) were of anal. grade.

Mersol H, an ionic type emulsifier of the composition $CH_3[CH_2]_{14}SO_3Na$ (Leunawerke, Merseburg), was used as an aqueous solution with a concentration of 0.14 mol dm⁻³. Oxygen was removed from

the solution before use by boiling in an inert atmosphere for 1 h. Slovasol 2430, a nonionic emulsifier of the composition $\text{CH}_3[\text{CH}_2]_{23}\text{O}[\text{C}_2\text{H}_4\text{O}]_{29}\text{C}_2\text{H}_4\text{OH}$ used as an aqueous solution with the concentration 0.14 mol dm^{-3} , was boiled before use for 1 h in argon atmosphere.

The kinetics of thermal decomposition of aqueous solution of $\text{K}_2\text{S}_2\text{O}_8$ without and at the presence of nonionic emulsifier Slovasol 2430 was examined at 40°C and/or 60°C . The concentration of the peroxide was determined by iodometry [12].

The viscometric measurements were done in 1,4-dioxane at 25°C . The limiting viscosity number $[\eta]$ was obtained from the extrapolation of the dependence (1) to the zero concentration.

$$\frac{\eta - \eta_0}{\eta_0 \rho} = [\eta] + k_H [\eta]^2 \rho \quad (1)$$

where η , η_0 are the respective viscosities of solution and solvent, which are proportional to the flow time of the liquids through a capillary of viscometer, ρ is the concentration of solution in g cm^{-3} , and k_H is the Huggins constant.

Copolymerization of Monomers

The batch emulsion copolymerization of S with BA was performed in a 250 cm^3 glass reactor equipped with a mechanical stirrer, argon inlet and exit, and a rubber septum closed sampling neck.

The polymerization ingredients were charged into the reactor under argon in the following order: water, aqueous solution of emulsifier, monomers. The mixture was then stirred for 15 min at constant agitation speed at 40°C . The stirring was effected by paddle-type stirrer, rotating at 300 min^{-1} . At last, the aqueous solution of initiator and activator was added. The total volume of the emulsion was 80 cm^3 . The general composition of polymerization system is given in Table 1. The changes of molar concentration of initiator and emulsifiers in the polymerization system are stated in legends of the figures.

The course of copolymerization was followed at certain time intervals by taking a small amount of the emulsion. The styrene/butyl acrylate copolymer (P(S)/P(BA)) was precipitated from the samples obtained in an excess of methanol, filtered on a sintered glass funnel, washed with water, methanol and then dried. The conversion of monomers was estimated from the known mass of comonomers in the mixture (in mass %) according to the equation published in our previous paper [11].

RESULTS AND DISCUSSION

Conversion—time curves of the emulsion copolymerization of S with BA initiated by potassium persulfate in the presence or in the absence of sodium

Table 1. General Composition of the System for Copolymerization

Components	Volume	Concentration
	cm^3	mol dm^{-3}
Water phase:		
Initiator ($\text{K}_2\text{S}_2\text{O}_8$)	12	1.37×10^{-2}
Activator ($\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)	4	1.99×10^{-3}
Emulsifiers: Slovasol 2430	16	2.90×10^{-2}
Mersol H	16	2.90×10^{-2}
Organic phase:		
Monomers: Styrene ^a	16	
Butyl acrylate	16	

a) The mole fraction of styrene in the monomer feed was $f_{St} = 0.553$.

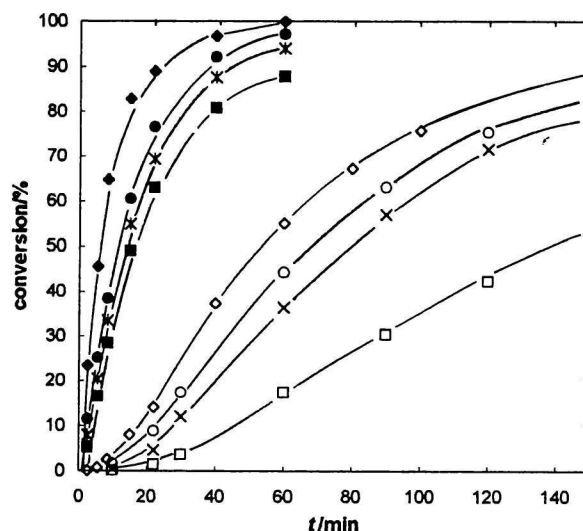


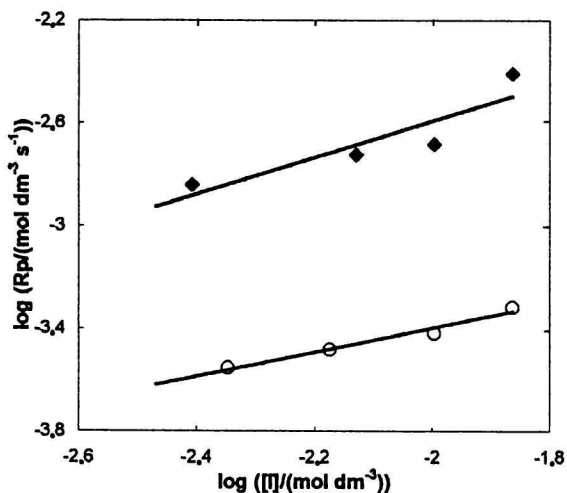
Fig. 1. Conversion—time curves of the emulsion copolymerization of S with BA at 40°C with activator for $[\text{K}_2\text{S}_2\text{O}_8] \cdot 10^2 / (\text{mol dm}^{-3})$: 0.39 (■), 0.74 (*), 1.00 (●), 1.37 (◆) and without activator for $[\text{K}_2\text{S}_2\text{O}_8] \cdot 10^2 / (\text{mol dm}^{-3})$: 0.45 (□), 0.67 (×), 1.00 (○), 1.37 (◇).

dithionite activator are illustrated in Fig. 1. The rate of copolymerization was determined from the second part of conversion curves (in the range of conversion from 20 to 40 %) for a consideration of the relation $((\text{conv.}/\%) / t) = f(t)$. The rates of polymerization thus obtained (Table 2) have significantly higher value in the polymerization system in the presence of activator compared with the system without activator.

Lower value of the rate of S—BA emulsion copolymerization initiated only with $\text{K}_2\text{S}_2\text{O}_8$ may be connected with the low dissociation rate constant of this initiator at 40°C . Our study of the kinetics of decomposition of $\text{K}_2\text{S}_2\text{O}_8$ in aqueous solution at 40°C showed that k_d is equal to $0.16 \times 10^{-2} \text{ h}^{-1}$ which is comparable with $k_d = 0.12 \times 10^{-2} \text{ h}^{-1}$ determined in [12]. According to the results in paper [13] the rate constant of decomposition of $\text{K}_2\text{S}_2\text{O}_8$ rapidly grows

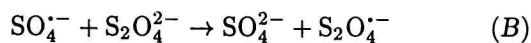
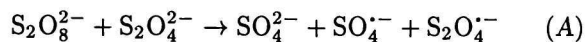
Table 2. Variation of the Rate of Copolymerization R_p and Limiting Viscosity Number of Copolymers with Initiator Concentration in the Emulsion Copolymerization of S and BA

Parameter	$K_2S_2O_8 \cdot 10^2 / (\text{mol dm}^{-3})$							
	with activator				without activator			
	0.39	0.74	1.00	1.37	0.45	0.67	1.00	1.37
$R_p \cdot 10^3$ $\text{mol dm}^{-3} \text{ s}^{-1}$	1.83	1.89	2.08	3.90	0.28	0.33	0.38	0.48
$[\eta] \cdot 10^2$ $\text{cm}^3 \text{ g}^{-1}$	2.8	2.6	1.6	0.9	8.1	7.0	5.2	4.8

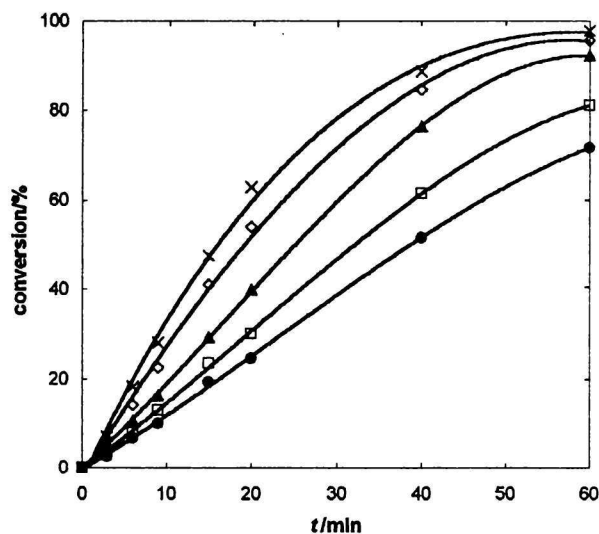
**Fig. 2.** Log—log plot of the rate of emulsion copolymerization of S with BA at 40°C vs. $K_2S_2O_8$ concentration in the system with activator (◆) and without activator (○).

with temperature. At 60°C they determined $k_d = 2.52 \times 10^{-2} \text{ h}^{-1}$ and according to our results at 60°C $k_d = 3.10 \times 10^{-2} \text{ h}^{-1}$. It is well known that the increase of the temperature is one of the possibilities to positively influence the rate of polymerization. Another opportunity is to use a suitable redox initiation system in which the free radicals are formed at low temperature.

In our case the sodium dithionite activator together with potassium peroxydisulfate forms a convenient redox system. We suppose that in this system the formation of primary radicals responsible for the initiation of monomers proceeds according to the following equation



During the application of this redox initiator in the emulsion copolymerization of S with BA we realized that already a low concentration of activator significantly increases the rate of copolymerization (Ta-

**Fig. 3.** Variation of monomer conversion in the emulsion copolymerization of S and BA with reaction time and concentration of Mersol H emulsifier. $[Mersol] \cdot 10^2 / (\text{mol dm}^{-3})$: 1.45 (●), 2.17 (□), 2.90 (▲), 3.62 (◇), 4.35 (×).

ble 2). The differences between the emulsion copolymerization of S with BA in the system with and/or without activator are expressed in the values of the reaction order of the copolymerization rate in terms of initiator concentration (Fig. 2).

$$R_p \propto \{[KPS]\}^{0.47} \text{ for the copolymerization with } K_2S_2O_8$$

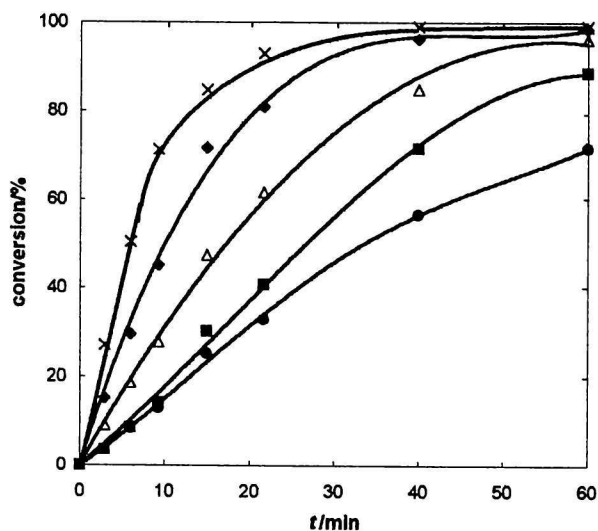
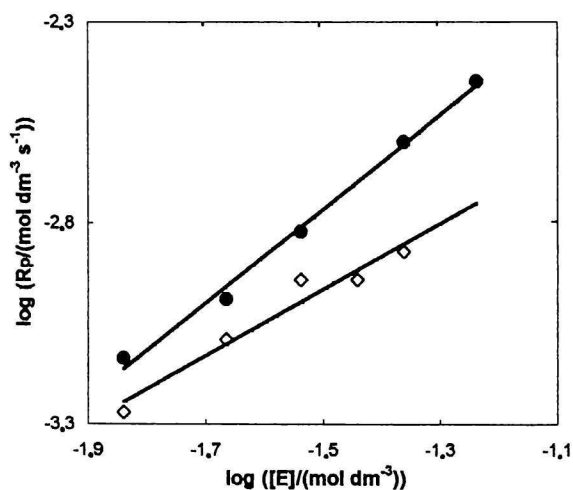
$$R_p \propto \{[KPS]\}^{0.71} \text{ for the copolymerization with } K_2S_2O_8/Na_2S_2O_4$$

The investigation of influence of the initiator concentration on limiting viscosity number $[\eta]$ of prepared copolymers showed the decrease of their values with the increase of initiator concentration (Table 2), which is usual at common radical emulsion polymerization.

Another factor of the emulsion polymerization system, which can influence the rate of copolymerization

Table 3. Variation of the Rate of Copolymerization and Limiting Viscosity Numbers of Copolymers with Emulsifier Concentration in the Emulsion Copolymerization of S and BA

Parameter	[Slovasol] · 10 ² /(mol dm ⁻³)					[Mersol] · 10 ² /(mol dm ⁻³)				
	1.45	2.17	2.90	4.35	5.80	1.45	2.17	2.90	3.62	4.35
R _p · 10 ³ mol dm ⁻³ s ⁻¹	0.73	1.02	1.50	2.52	3.55	0.54	0.81	1.14	1.16	1.34
[η] · 10 ² cm ³ g ⁻¹	0.8	0.8	1.0	1.1	1.2	1.0	1.0	1.2	1.1	1.2

**Fig. 4.** Variation of monomer conversion in the emulsion copolymerization of S and BA with reaction time and concentration of Slovasol 2430 emulsifier. [Slovasol] · 10²/(mol dm⁻³): 1.45 (●), 2.17 (■), 2.90 (Δ), 4.35 (◆), 5.80 (×).**Fig. 5.** Log—log plot of the rate of emulsion copolymerization of S and BA vs. emulsifier concentration in the system with Mersol H (◇) and Slovasol 2430 (●).

is a type and concentration of emulsifier. The conversion vs. time data for copolymerization of S with BA in the presence of redox initiator and ionic Mersol H and/or nonionic Slovasol 2430 emulsifier are given in Figs. 3 and 4. The rate of copolymerization is considerably higher in the case of application of nonionic Slovasol 2430 (Table 3), even if the molar concentration of both used emulsifiers in the system is on the same level (from 1.45×10^{-2} to 5.80×10^{-2} mol dm⁻³). In all cases the used concentration region of emulsifiers is much higher than their critical micellar concentrations (CMC), which have the values [11] for Mersol H CMC = 1.35×10^{-3} mol dm⁻³ and for Slovasol 2430 CMC = 1.35×10^{-4} mol dm⁻³.

From the plot of the rate of copolymerization as a function of emulsifier concentration (Fig. 5) the reaction orders with respect to the emulsifiers concentration were determined

$$R_p \propto \{[\text{Mersol}]\}^{0.83}$$

$$R_p \propto \{[\text{Slovasol}]\}^{1.17}$$

The observed reaction orders, especially in the case of nonionic Slovasol 2430 are found to be higher than those expected according to the Smith—Ewart theory [14].

Several authors [12, 15, 16] realized during the study of the influence of various types of emulsifiers on the course of emulsion polymerization that emulsifier can take part also in reaction of peroxides decomposition.

The influence of ionic emulsifier sodium dodecyl sulfate (SDS) on the rate of decomposition of K₂S₂O₈ initiator in aqueous solution was investigated [16, 17]. It was found that SDS molecules in the micellar state do not contribute to the acceleration of K₂S₂O₈ decomposition. Decomposition of K₂S₂O₈ in aqueous solution is accelerated by “free” molecules of emulsifier in monomolecular dispersed state.

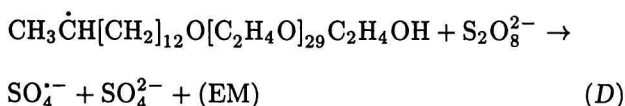
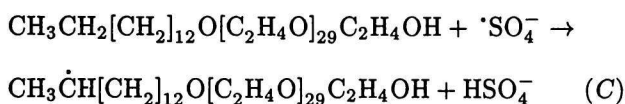
We investigated the influence of nonionic type of emulsifier Slovasol 2430 on the decomposition rate constant k'_d of K₂S₂O₈ initiator. Decomposition was examined at concentrations of emulsifier which were

Table 4. The Influence of [Slovasol] on the Decomposition Rate Constant of $K_2S_2O_8$ * at 60 °C

[Slovasol] · 10 ² mol dm ⁻³	0.22	0.53	0.80	1.45	2.90	4.35	5.80
k'_d dm ³ mol ⁻¹ h ⁻¹	0.28	0.59	0.75	1.12	1.34	1.49	1.57

*[$K_2S_2O_8$] was 1.4×10^{-2} mol dm⁻³. Rate constant of decomposition of $K_2S_2O_8$ without emulsifier is $k_d = 0.031$ h⁻¹.

higher than the CMC values and were near to the concentrations used in the real polymerization system. We supposed, similarly as in Refs. [16, 17], that the mechanism of acceleration of the $K_2S_2O_8$ decomposition by nonionic emulsifier could occur as follows



where (EM) is an intermediate product.

The decomposition rate constants of $K_2S_2O_8$ (k'_d), determined at 60 °C in an aqueous system with variable concentration of Slovasol 2430 from 0.22×10^{-2} to 5.80×10^{-2} mol dm⁻³ are given in Table 4. The obtained results show that the used nonionic emulsifier in the studied concentration region accelerates the decomposition of $K_2S_2O_8$. The change of the decomposition rate constant of initiator with emulsifier concentration is higher up to the concentration of emulsifier 1.45×10^{-2} mol dm⁻³ than in the range from 1.45×10^{-2} to 5.80×10^{-2} mol dm⁻³, what is the concentration region of Slovasol in our polymerization system. From these results it is evident that the positive effect of Slovasol 2430 on the rate of copolymerization of S with BA in complete polymerization system will be only to a small extent the consequence of its acceleration of $K_2S_2O_8$ decomposition. The main influence of Slovasol is probably related with its ability to influence colloidal characteristics of emulsion. In connection with this the chemical structure, the length of hydrophilic segments from $[C_2H_4O]$ and the end-groups of nonionic emulsifier molecule together with the character of other components of the polymerization system can play an important role.

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