Influence of the type of activator and emulsifier on heterogeneously initiated polymerization of styrene

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Dedicated to Professor Ing. A. Hrivík, CSc., in honour of his 60th birthday

In the emulsion polymerization of styrene initiated by hydrogen peroxide of the oxidized isotactic polypropylene at 30 °C the influence of the activator $FeSO_4$—disodium salt of ethylenediaminetetraacetic acid (EDTA) and of the ionic (Mersol H) as well as nonionic (Slovasol 2430) type of emulsifier on the course of polymerization was investigated. The method of planned experiment was used for determining the optimum concentration of activator ($c_{em} = 0.89 \times 10^{-3}$ mol dm^{-3}) and Slovasol 2430 ($c_{em} = 7.4 \times 10^{-2}$ mol dm^{-3}) in emulsion. For these concentrations the 90.7 % degree of conversion of styrene was obtained after 60 min polymerization. Provided the combination of the $FeSO_4$—EDTA activator with Mersol H was used, an increase in activator concentration had negative effect on the rate of styrene polymerization, which might be due to rapid consumption of available peroxides. It has been found that $FeSO_4$——EDTA also affects the pH value of medium because of acidification of the metallic component. Owing to its basic character, the nonionic emulsifier Slovasol 2430 is capable, to a certain extent, to restrain this influence of activator, which has not been observed with the ionic emulsifier Mersol H.

При эмульсионной полимеризации стирола, инициируемой гидроперекисью окисленного изотактического полипропилена при 30 °C было изучено влияние активатора $FeSO_4$—двунатриевая соль этилендиаминтетрауксусной кислоты (ЭДТА), а также ионного (Мерсол Н) или неионного (Словасол 2430) типа эмульгаторов на ход полимеризации. Методом планируемого эксперимента были определены оптимальные концентрации в эмульсии активатора ($c_{em} = 0{,}89 \cdot 10^{-3}$ моль дм$^{-3}$) и Словасола 2430 ($c_{em} = 7{,}4 \cdot 10^{-2}$ моль дм$^{-3}$), при которых после 60 минут протекания полимеризации была достигнута 90,7%-ная степень конверсии стирола. При использовании сочетания $FeSO_4$—ЭДТА с Мерсолом Н повышение концентрации активатора отрицательно влияло на скорость полимеризации стирола, что может быть, кроме прочего, связано с быстрым убытком присутствующей перекиси. Было обнаружено, что

$FeSO_4$—ЭДТА вследствие окисления металлического компонента влияет и на pH среды. Неионный эмульгатор Словасол 2430 может вследствие своего щелочного характера частично ослабить этот эффект активатора, что не было отмечено в случае ионного эмульгатора Мерсола H.

In preceding studies [1, 2], triethylenetetramine was mainly used as activator in the emulsion polymerization of styrene initiated by hydrogen peroxide bonded to isotactic polypropylene (PP). By examining the possibility of using oxidized poly(vinyl chloride) to initiation [3], the effect of other activators of the amine type was investigated. It has been revealed that the $FeSO_4$—disodium salt of ethylenediaminetetraacetic acid complex is more convenient than triethylenetetramine from the viewpoint of the rate of initiator decomposition. Its effect was also examined in modifying isotactic polypropylene with water-soluble vinyl monomers [4] while the formation of homopolymer was simultaneously investigated. However, only minor attention has been hitherto paid to application of a complex type of activator to the emulsion polymerization of styrene initiated by oxidized PP.

In this study we have examined the most convenient conditions for the polymerization of styrene initiated by PP hydrogen peroxide from the viewpoint of the optimum concentration of activator of the type $FeSO_4$—disodium salt of ethylenediaminetetraacetic acid in relation to the type and concentration of emulsifier as well as from the viewpoint of the influence of these two components in the polymerization system.

Experimental

Chemicals

Polypropylene — isotactic, powdered, product of Slovnaft, Bratislava. The remaining atactic portions and stereoblocks were extracted with boiling n-heptane. It was fractionated by fluidization technique and the fraction comprising particle sizes 0.15—0.1 mm was used.

Styrene — purified by shaking with NaOH solution, dried and twice vacuum distilled in nitrogen atmosphere.

EDTA — disodium salt of ethylenediaminetetraacetic acid and $FeSO_4 \cdot 7H_2O$ were anal. grade chemicals. They were used as aqueous solutions of 4.0×10^{-2} mol dm^{-3} concentration and kept in nitrogen atmosphere. $FeSO_4$ was protected against hydrolysis by acidification with HCl solution.

Emulsifiers — ionic type, *i.e.* Mersol H of the composition $CH_3—(CH_2)_{16}SO_3Na$ (Leuna Werke, GDR) and nonionic type, *i.e.* Slovasol 2430 (W. Pieck Chemical Works, Nováky) of the composition $CH_3—(CH_2)_{23}—(CH_2—CH_2—O)_{29}—C_2H_4OH$. They were used as 0.145-M aqueous solutions which had been boiled in inert atmosphere.

All other chemicals were anal. grade.

Nitrogen used as inert atmosphere was deprived of the rest of oxygen by the procedure described in paper [1].

Working procedures

The initiation centres on isotactic PP were obtained by oxidation with oxygen enriched with ozone ($c = 12$ mg dm^{-3}). This oxidation took place in a fluidized bed at laboratory temperature for 60 min. The content of hydrogen peroxides bonded on polypropylene was determined iodometrically ($m(O_2$ in PP$) = 1.83 \times 10^{-2}$ mol kg^{-1}) [5].

The polymerization was performed in glass ampoules by the procedure described in paper [1]. The initiator, *i.e.* oxidized PP, was given into the ampoules in the amount of 0.4 g. It was deprived of oxygen by evacuation. The components of the polymerization system were dosed into the ampoules in nitrogen atmosphere in this order: activator, *i.e.* $FeSO_4$ and EDTA in mole ratio 1 : 1, and emulsifier, *i.e.* anionic Mersol H and/or nonionic Slovasol 2430. The concentrations of individual substances in emulsion (c_{em}) were used according to specification of the planned experiment (Table 1). The monomer was other component ($c_{em} = 1.44$ mol dm^{-3}) and water represented the complement to constant volume (18 cm^3) in each ampoule. The polymerization proceeded at 30 °C. After the completion of polymerization the content of ampoule was quantitatively poured through a fritted glass filter (density S_1) on which the solid initiator was caught. Polystyrene was precipitated from emulsion by methanol. The obtained polymer was purified from the remaining polymerization system by repeated washing with water and methanol. Then it was dried to constant mass. The conversion was expressed in percentage of the initial mass of styrene.

The pH measurements were carried out with a pH-meter, type OP 205 (Radelkis). A combined glass electrode (type OP 807, Radelkis) consisting of a thick-walled glass indication electrode and a saturated silver/silver chloride reference electrode was used.

Table 1

Basic data of the planned experiment for the heterogeneously initiated polymerization of styrene*

x_i	Factor	Level of factor			I_i
		−1	0	1	
x_1	Activator				
	c_{em}(FeSO$_4$—EDTA)·10^3/(mol dm^{-3})	0.22	0.89	1.56	0.67
x_2	Emulsifier				
	c_{em}(Slovasol 2430)·10^2/(mol dm^{-3})	2.4	4.8	7.2	2.4

* The polymerization system contained 0.4 g of oxidized PP. The contents of hydrogen peroxides and styrene were $m(O_2$ in PP$) = 1.83 \times 10^{-2}$ mol/kg and $c_{em} = 1.44$ mol dm^{-3}, respectively; $t_{pol} = 1$ h, $\theta = 30$ °C.

Results and discussion

It has been found by investigating the effect of triethylenetetramine in the heterogeneously initiated polymerization of styrene that this substance has several

functions. In the region of low concentrations, it accelerates the decomposition of polypropylene hydrogen peroxide [6], polarizes the double bond of styrene and thus facilitates its bonding to the growing radical, and positively influences the polymerization system by its basic character [1]. On the basis of this knowledge, we determined the optimum concentration of the activator of the type $FeSO_4$—EDTA and we also investigated its further effects in the polymerization system. For this purpose, we used the two-factor planned experiment of the orthogonal type in which the second parameter was emulsifier concentration, which also significantly influenced the result of polymerization.

The experimental results obtained are given in Table 1 where the concentration change of activator is coded in the coordinate (x_1) and concentration of emulsifier Slovasol 2430 in the coordinate (x_2). The experimental results of nine experiments were processed by regression analysis and are presented in Table 2. The regression expression for Y_{theor} is

$$Y_{theor} = 79.58 - 0.03x_1 + 19.87x_2 - 5.15x_1x_2 - 10.84x_1^2 - 9.98x_2^2 \qquad (1)$$

The standard deviation is ± 1.6 %.

Table 2

Description of the planned experiment and the degrees of styrene conversion (Y/%) for 1 h reaction time obtained experimentally (Y_{exp}) and calculated according to regression eqn (*1*) (Y_{theor})

i	1	2	3	4	5	6	7	8	9
x_1	−1	−1	−1	0	0	0	1	1	1
x_2	−1	0	1	−1	0	1	−1	0	1
Y_{exp}	31.0	73.5	81.8	52.4	75.7	90.7	44.0	67.8	74.2
Y_{theor}	33.7	68.8	83.8	49.7	79.6	89.5	44.0	68.7	73.4

On the basis of the obtained relations, we constructed a contour diagram with a result area expressing the yield of polystyrene as a function of the concentration of activator and emulsifier (Fig. 1). The numerical values of each isoline represent the theoretically expected degree of styrene conversion (Y_{theor}).

As follows from the results of the planned experiment the maximum yield of polystyrene is 90.7 % after 1 h polymerization under given conditions. This maximum yield may be obtained in the concentration region of the $FeSO_4$—EDTA activator $c_{em} = 0.89 \times 10^{-3}$ mol dm^{-3} and emulsifier Slovasol 2430 $c_{em} = 7.4 \times 10^{-2}$ mol dm^{-3}. While the concentration of activator passes through a maximum, the optimum concentration of emulsifier is on the border of experimental space.

Like for the couple $FeSO_4$—EDTA and Slovasol, we tried to find the optimum concentration for the case in which the activator was again $FeSO_4$—EDTA but as an ionic emulsifier was used earlier described Mersol H [6]. The planned experiment for this pair of parameters was performed at equal basic data as stated in Table 1. The obtained relations were used for constructing the diagram with result area expressing the yield of polystyrene as a function of concentration of activator and Mersol H (Fig. 2). The regression equation for calculation of the theoretical degree of conversion is under Fig. 2.

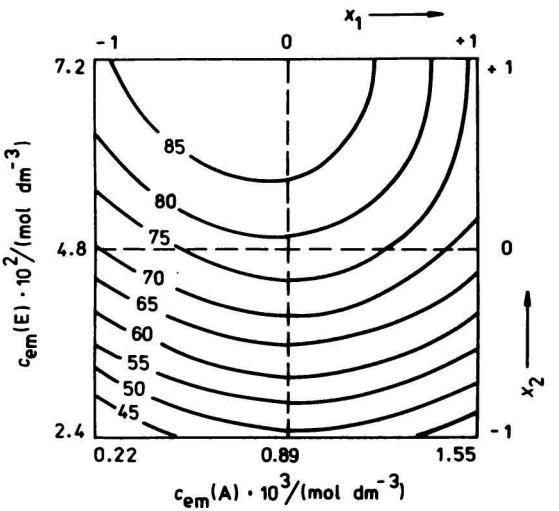
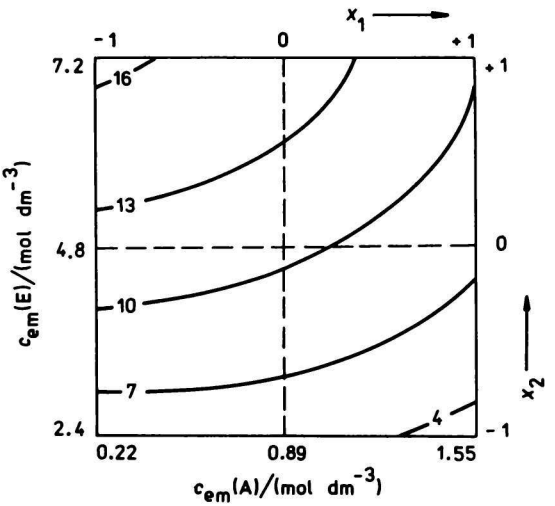


Fig. 1. Contour diagram expressing the influence of $FeSO_4$—EDTA concentration (x_1) and Slovasol 2430 concentration (x_2) on the degree of conversion of styrene (Y_{theor}) in the polymerization system initiated by oxidized PP, $m(O_2 \text{ in PP}) = 1.83 \times 10^{-2}$ mol/kg, for 1 h polymerization at 30 °C.

It has been found that the degree of conversion increases with an emulsifier concentration in the investigated region, but an increase in activator content over the lowest chosen limited value (Table 1) has a negative influence on the formation of polystyrene. Therefore we investigated for a wider concentration range how a change in content of activator and emulsifier affects the yield of polystyrene. It follows from the results presented in Fig. 3 that the $FeSO_4$—EDTA activator has a positive effect on styrene conversion only in a certain and very narrow concentration range ($c_{em} < 0.22 \times 10^{-2}$ mol dm^{-3}). If the content of activator is higher, the percentage of styrene conversion is not growing even if Mersol H concentration is increased. The most convenient concentration of emulsifier is in the range $c_{em} = 7.4 \times 10^{-2}$ mol dm^{-3} for all investigated amounts of activator.

We may expect with respect to previous knowledge [1, 7] that like triethylenetet-


x_1
-1
0
+1
7.2
4.8
2.4
16
13
10
7
4
+1
0
-1
x_2
0.22
0.89
1.55
$c_{em}(E)/(mol\ dm^{-3})$
$c_{em}(A)/(mol\ dm^{-3})$

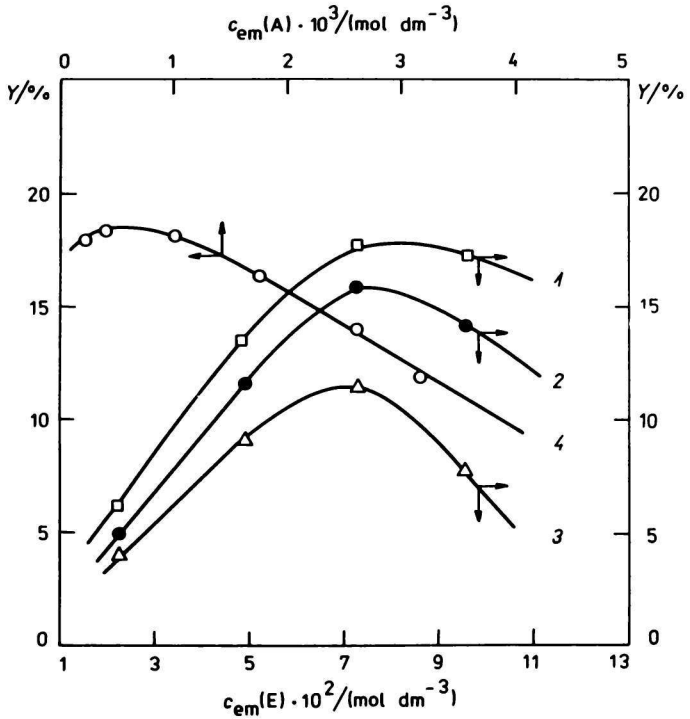

$c_{em}(A) \cdot 10^3/(mol\ dm^{-3})$
0
1
2
3
4
5
Y/%
20
15
10
5
0
1
3
5
7
9
11
13
$c_{em}(E) \cdot 10^2/(mol\ dm^{-3})$
1
2
4
3

Fig. 2. Contour diagram expressing the influence of $FeSO_4$—EDTA concentration (x_1) and Mersol H concentration (x_2) on the degree of conversion of styrene in the polymerization system initiated by oxidized PP, $m(O_2 \text{ in PP}) = 1.83 \times 10^{-2}$ mol/kg, for 20 min polymerization at 30 °C.

$$Y_{theor} = 12.31 - 1.81x_1 + 4.50x_2 - 1.07x_1x_2 - 0.86x_1^2 - 1.05x_2^2 \quad (2)$$

ramine the complex type of activator used in this case must have several functions in the polymerization system. In order to examine its action in a deeper manner, we investigated the kinetics of styrene polymerization and studied the content of residual hydrogen peroxide for both types of the used emulsifiers (Fig. 4). It has been shown that hydrogen peroxide bonded on PP decomposed more rapidly in the presence of the $FeSO_4$—EDTA activator (approximately after 15 min polymerization) than in the presence of triethylenetetramine (after 30 min polymerization) [2]. If the content of the $FeSO_4$—EDTA activator increases, the peroxides are decomposed more deeply. An increase of the primary radicals formed from the initiator decomposition in the presence of Mersol H does not cause an increase in polymerization rate but a decrease in polymerization rate. It may be connected with the observation [8] that an increase in concentration of very active amines results in a more rapid consumption of the peroxides available for the reaction, which manifests itself by a decrease in polymerization rate. In our case, besides activator we must take into account the simultaneous influence of emulsifier on the overall polymerization rate. It follows from previous results [9] that the nonionic Slovasol 2430 is more convenient for the heterogeneously initiated emulsion polymerization of styrene than the ionic emulsifier Mersol H. It is due to the character of emulsifier, different structure and length of its chain as well as to the fact that the emulsifier together with the activator can, to a certain extent, influence further important factor of emulsion polymerization, *i.e.* the pH value of medium. From Table 3 it is evident that the $FeSO_4$—EDTA activator with a monomer produces an acid medium in contrast to triethylenetetramine which was used earlier as activator [1]. The nonionic emulsifier Slovasol 2430 with its basic character, in a certain degree, compensates the influence of activator on the pH value of the emulsion, which is not, however, valid for the ionic emulsifier Mersol H. If Slovasol 2430 is present in the polymerization system, pH is approximately corresponding to neutral point and that medium is convenient for the emulsion polymerization of styrene [3, 10].

Fig. 3. Degree of conversion of styrene after 20 min polymerization initiated by oxidized PP, $m(O_2 \text{ in PP}) = 1.83 \times 10^{-2}$ mol/kg, at 30 °C as a function of $FeSO_4$—EDTA concentration (*4*) at constant Mersol H concentration, $c_{em} = 7.4 \times 10^{-2}$ mol dm^{-3} or as a function of emulsifier concentration at the content of activator c_{em}/(mol dm^{-3}): *1.* 0.22×10^{-3}; *2.* 0.89×10^{-3}; *3.* 1.56×10^{-3}.

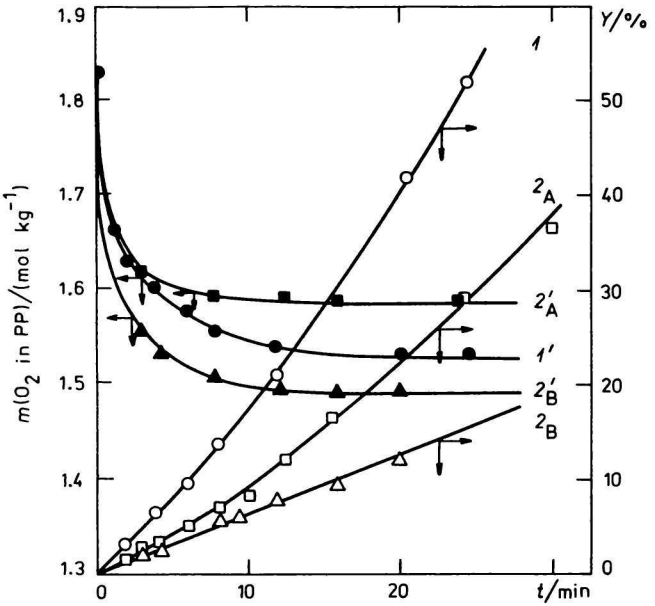


Fig. 4. Content of residual hydrogen peroxide in PP (*1'*; $2'_A$; $2'_B$) and degree of conversion (*1*, 2_A, 2_B) as a function of time for emulsion polymerization of styrene at 30 °C; c_{em}/(mol dm^{-3}): *1*, *1'*. $FeSO_4$—EDTA (Slovasol 2430) 0.89×10^{-3} (7.4×10^{-2}); 2_A, $2'_A$. $FeSO_4$—EDTA (Mersol H) 0.22×10^{-3} (7.4×10^{-2}); 2_B, $2'_B$. $FeSO_4$—EDTA (Mersol H) 1.56×10^{-3} (7.4×10^{-2}).

Table 3

Determinations of pH of the medium used for polymerizations and particular components of the polymerization systems

No.	c_{em}(styrene) / mol dm^{-3}	c_{em}(FeSO$_4$—EDTA) $\cdot 10^3$ / mol dm^{-3}	c_{em}(Slovasol 2430) $\cdot 10^2$ / mol dm^{-3}	c_{em}(Mersol H) $\cdot 10^2$ / mol dm^{-3}	pH
1	1.44	—	7.4	—	8.18
2	↓	0.89	7.4	—	7.27
3	↓	0.89	—	—	4.02
4	↓	—	—	7.4	6.90
5	↓	0.22	—	↓	5.15
6	↓	1.56	—	↓	3.55
7	↓	1.56	—	—	3.06

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