Influence of the composition of the redox initiation system on the kinetics of the solution polymerization of styrene

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

The solution polymerization of styrene initiated by the redox system of cumene hydrogen peroxide, 1-benzoyl-3-n-propylthiourea, or 1-benzoyl--3-isobutylthiourea was studied. On the basis of the study of the influence of the initiation system composition and its total concentration on the polymerization kinetics, a reaction scheme was proposed and a kinetic equation was derived, which describes well the initial polymerization phases. Feeding successively the initiation system, its efficiency is markedly enhanced during polymerization.

Изучена полимеризация стирола в растворе, инициируемая редокс системой, состоящей из гидроперекиси кумола и 1-бензоил-3-н-пропил-тиомочевины или 1-бензоил-3-изобутилтиомочевины. На основании изучения влияния состава инициирующей системы и ее общей концентрации на кинетику полимеризации была предложена реакционная схема и выведено кинетическое уравнение, хорошо описывающее начальные стадии процесса полимеризации. При постоянном пополнении инициирующей системы ее эффективность значительно усиливается в процессе полимеризации.

In the framework of the reactivity study of sulfur and nitrogen compounds the influence of various derivatives of thiourea on the polymerization of vinyl monomers, initiated by organic hydrogen peroxides, was studied as well. The efficiency testing of more than forty various derivatives of thiourea has shown [1, 2] that among the most effective ones are the 1,3-disubstituted thioureas, if one substituent is the benzoyl radical (benzoyl-, methoxybenzoyl-, p-chlorobenzoyl-, etc.). The character of the second substituent influences the efficiency only slightly. Relatively effective has also shown to be the tetramethyl thiourea [3] with tert-butyl hydrogen peroxide. The kinetics of the block polymerization of styrene and methyl methacrylate using the system 1-methoxybenzoyl-3-n-propyl-thiourea—tert-butyl hydrogen peroxide has been widely investigated [1, 2].

In this paper are presented the results of the study of the influence of the redox systems 1-benzoyl-3-n-propylthiourea—cumene hydrogen peroxide and 1-benzoyl-3-isobutylthiourea—cumene hydrogen peroxide on the polymerization of styrene in solution.

Experimental

Styrene — technical grade, stabilized. It was purified by shaking with a 10 % NaOH solution. After washing with distilled water till neutral reaction and drying with $CaCl_2$, it was vacuum-distilled in N_2 atmosphere. It was stored in the dark at $-15\,°C$.

Cumene hydrogen peroxide (CHP) — n.e. Slovnaft. Content of hydrogen peroxide determined iodometrically was 82.7 %. It was stored in the dark at $-15\,°C$.

1-Benzoyl-3-n-propylthiourea (BPTU) was prepared and characterized at the Department of Chemical Technology of Plastics and Fibres [4].

The other chemicals and materials used were of anal. grade.

The dilatometric method was used to study the kinetics of the polymerization in solution.

Results and discussion

The influence of the composition of the initiation system on the kinetics of polymerization was studied at 50 °C, 55 °C, 60 °C, and 65 °C. BPTU was used as the reduction component. The concentration of styrene (the volume fraction of monomer $x_M = 0.4$) and the total concentration of the initial system ($c = 10.59 \times 10^{-2}$ kmol m^{-3}) were during all polymerizations constant. The mole fraction of thiourea in the initiation system was changed in the range of $x_{TU} = 0$—0.8. The conversion was determined dilatometrically. The conversion dependences on time at $x_{TU} = 0$ and at all studied temperatures had a linear course, because the polymerization was initiated only by radicals formed thermally as the consequence of initiator decomposition (CHP), its concentration being very slightly changed. The conversion dependences in the presence of thiourea are bending already at conversions over 2 %. At higher x_{TU} there is a more marked bending, which indicates a faster initiator exhaustion as a consequence of thiourea excess, which acts as an activator for the hydrogen peroxide decomposition. In these cases there were obtained also lower "final" conversions and the polymerization rate was stabilized sooner at a value nearer to the thermal polymerization.

The values of the initial (maximum) rates at the individual temperatures and at x_{TU} of the solution polymerization of styrene are in Table 1. It can be seen from the table that the initial polymerization rates in the presence of thiourea were increased 60 to 90 times compared with rates in the presence of CHP alone at the given concentration.

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Table 1

Values of maximum (initial) rates of styrene polymerization in benzene
dependent on x_{TU} and temperature

x_{TU}	$R_{p,max} \cdot 10^4/(kmol\ m^{-3}\ s^{-1})$			
	50 °C	55 °C	60 °C	65 °C
0.0	0.13	0.19	0.31	0.41
0.2	6.43	7.04	9.47	10.89
0.3	6.47	9.00	10.85	12.13
0.4	7.26	9.15	11.14	13.00
0.6	6.43	8.50	10.75	11.62
0.8	5.23	5.80	8.28	7.62

The apparent total activation energies of polymerization at the individual x_{TU} values were estimated from the slope of the dependence $\ln(R_{p,max}/(kmol\ m^{-3}\ s^{-1})) = f(T^{-1})$ and they are in Table 2.
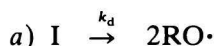
Table 2

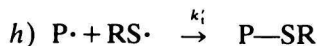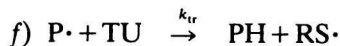Values of the effective activation energies of styrene polymerization at various x_{TU}

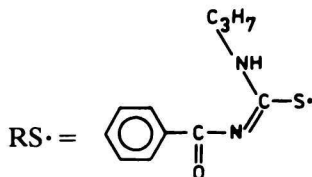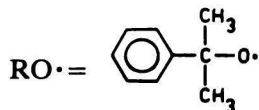| x_{TU}	0.0	0.2	0.3	0.4	0.6	0.8
$\dfrac{E_a}{kJ\ mol^{-1}}$	80.0	36.1	38.3	38.9	36.7	37.5
r_{xy}	0.986	0.876	0.984	0.999	0.980	0.862

The effective activation energy of the initiated polymerization (80 ± 4) kJ mol^{-1} corresponds to the values from the literature [5, 6]. The effective activation energy in the presence of thiourea (BPTU) is not dependent on its mole fraction x_{TU} and its mean value is $E_{ap} = (37.5 \pm 4)$ kJ mol^{-1}, which indicates that in this studied system a redox initiation takes place.

On the basis of the estimated dependences of the initial (maximum) polymerization rates on x_{TU} at various temperatures, for the initial stages of the styrene polymerization the following simplified reaction scheme was proposed

$$a)\ I\ \overset{k_d}{\rightarrow}\ 2RO\cdot$$

$$b)\ I + TU\ \overset{k_a}{\rightarrow}\ RO\cdot + RS\cdot + H_2O$$

c) $RO \cdot + M \overset{k_i}{\rightarrow} P \cdot$

d) $RS \cdot + M \overset{k'_i}{\rightarrow} P \cdot$

e) $P \cdot + M \overset{k_p}{\rightarrow} P \cdot$

f) $P \cdot + TU \overset{k_{tr}}{\rightarrow} PH + RS \cdot$

g) $P \cdot + P \cdot \overset{k_t}{\rightarrow} P\!-\!P$

h) $P \cdot + RS \cdot \overset{k'_t}{\rightarrow} P\!-\!SR$

i) $RS \cdot + RS \cdot \overset{k''_t}{\rightarrow} RSSR$

where

$$RO \cdot = \text{benzene ring} - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - O \cdot \qquad\qquad RS \cdot = \text{benzene ring} - \underset{\|}{\overset{}{C}} - N \overset{\overset{C_3H_7}{|}}{\underset{}{\overset{NH}{|}}}\!\!\diagup\!\! \overset{}{C} - S \cdot$$

In the initial, stationary polymerization phase the set of the differential equations for the concentration of the individual types of radicals is changed to a set of linear and quadratic equations, the sum of which gives the relation

$$v_{ii} + v_{ia} = k_t [P\cdot]^2 + 2k'_t [P\cdot]\cdot[RS\cdot] + k''_t [RS\cdot]^2 \qquad (1)$$

where v_{ii} is the initiation rate at spontaneous initiator decomposition and v_{ia} is the rate of activated initiation.

After accepting the simplified assumptions that $k'_t = \sigma\, k_t$, $k''_t = \sigma^2\, k_t$ and under the assumption that the rate of transformation of $P\cdot$ radicals to $RS\cdot$ ones is equal to the rate of transformation of $RS\cdot$ radicals to $P\cdot$ ones, i.e.

$$k_{tr} [P\cdot]\cdot[TU] = k'_i [RS\cdot]\cdot[M] \qquad (2)$$

it is possible to express from eqn (1) the concentration of $P\cdot$ radicals and we obtain for the initial polymerization rate the following equation

$$R_{p,max} = \frac{(R^2_{p,io} + R^2_{p,ao})^{1/2}}{1 + \dfrac{k'_t \cdot k_{tr} [TU]}{k_t \cdot k'_i [M]}}$$

where

$$R_{p,io} = \left(\frac{2fk_d}{k_t}\right)^{1/2} \cdot k_p \, [M] \cdot [I]^{1/2}$$

$$R_{p,ao} = \left(\frac{2uk_a}{k_t}\right)^{1/2} \cdot k_p \, [M] \cdot [I]^{1/2} \cdot [TU]^{1/2}$$

f is the efficiency of initiation by $RO\cdot$ radicals and u is the efficiency of initiation by $RS\cdot$ radicals.

Because $v_{ii} \ll v_{ia}$, or $R_{p,io} \ll R_{p,ao}$, it is possible to neglect the first term in the nominator of eqn (3) and after rearrangement we obtain for the polymerization rate the following equation in the form

$$R_{p,max} = \frac{\left(\frac{2uk_a}{k_t}\right)^{1/2} \cdot k_p \, [M] \cdot [I]^{1/2} \cdot [TU]^{1/2}}{1 + \dfrac{k_t' \cdot k_{tr}}{k_t \cdot k_i'} \cdot \dfrac{[TU]}{[M]}} \qquad (4)$$

Introducing into eqn (4) the mole fraction of thiourea x_{TU}, whereby the total concentration of the initiation system $c = [I] + [TU]$ was constant, we obtain for the polymerization rate eqn (5), where

$$x_{TU} = \frac{[TU]}{[I] + [TU]} = \frac{[TU]}{c}$$

and for the mole fraction of the initiator mixture it is valid

$$x_I = 1 - x_{TU}$$

$$R_{p,max} = \frac{\left(\frac{2uk_a}{k_t}\right)^{1/2} \cdot k_p \, [M] \cdot c \cdot ((1 - x_{TU}) \cdot x_{TU})^{1/2}}{1 + \dfrac{k_t' \cdot k_{tr}}{k_t \cdot k_i'} \dfrac{c}{[M]} \cdot x_{TU}} \qquad (5)$$

Since the experiments were made at constant monomer concentration and at steady total concentration of the initiator mixture, it is possible to introduce into eqn (5) the complex constants A and B, whereby

$$A = \left(\frac{2uk_a}{k_t}\right)^{1/2} \cdot k_p \, [M] \cdot c$$

$$B = \frac{k_t' \cdot k_{tr}}{k_t \cdot k_i'} \cdot \frac{c}{[M]}$$

The rate equation (5) is then transformed into the form

$$R_{p,max} = \frac{A \cdot ((1 - x_{TU}) \cdot x_{TU})^{1/2}}{1 + B \cdot x_{TU}} \qquad (6)$$

From the linear form of eqn (6)

$$\frac{1}{x_{TU}} = -B + A \frac{((1 - x_{TU}) \cdot x_{TU})^{1/2}}{x_{TU} \cdot R_{p,max}} \qquad (7)$$

it is possible graphically to estimate the complex constants A and B on the basis of experimental values.

The estimated values of the complex constants A and k_a for the individual polymerization temperatures are in Table 3.

Table 3

Values of complex constants A and rate constants of the activated CHP decomposition
(under the assumption that $u = 1$)

$\theta/°C$	50	55	60	65
$\dfrac{A \cdot 10^3}{\text{kmol m}^{-3}\,\text{s}^{-1}}$	1.74	2.18	2.48	2.85
$\dfrac{k_a}{\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}}$	0.057	0.059	0.061	0.063

The complex constants B have a considerable experimental error, because they are estimated from the linear section on the y axis. Their mean value for the studied temperature is $B = 0.35 \pm 0.09$.

In Fig. 1 are illustrated the dependences $R_{p,max} = f(x_{TU})$ for the individual temperatures. The mentioned polymerization rates were calculated from eqn (6) by means of the estimated values of the complex constants A and B. The points are experimental values and the curves represent calculated values $R_{p, max}$. This proves the validity of the reaction scheme in spite of the introduced simplified assumptions.

From the dependence $\ln (k_a/(\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1})) = f(T^{-1})$ the activation energy of the activated decomposition of the initiator $E_a = (5.7 \pm 2)$ kJ mol^{-1} was determined. This value is rather low, but it correlates with the estimated effective activation energy of the polymerization $E_{ap} = (37.5 \pm 4)$ kJ mol^{-1}.

The reaction scheme is valid only for the initial stages of the polymerization; it does not describe the fast consumption of the initiation system, which is shown by the fast decrease of the polymerization rate.

The study of the influence of the composition of the redox initiation system on the course of the solution polymerization of styrene in benzene has shown that the dominant reaction during the initiation is the activated decomposition of CHP. This reaction is characterized by a very low activation energy of termination. The values of the rate constants of the activated CHP decomposition at the individual temperatures are by three to four orders higher in comparison with the rate

Fig. 1. Dependence $R_{p.max} = f(x_{TU})$ at various temperatures.
1. 50 °C; *2.* 55 °C; *3.* 60 °C; *4.* 65 °C.
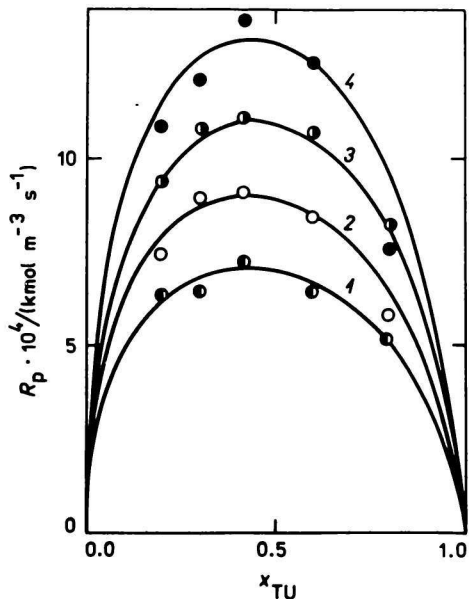
constants of the spontaneous CHP decomposition. On the consumption of components of the initiation system the (nonradical) side reactions participate in a great measure.

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