

Polymerization of styrene in the presence of *N,N*-disubstituted hydroxylamines

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Dedicated to Professor RNDr. J. Gašperík, founder of the Department of Organic Technology and of the Department of Chemical Technology of Plastics and Fibres of the Slovak Technical University on the occasion of the 40th anniversary of their foundation

In this paper the influence of *N,N*-disubstituted hydroxylamines on the radical polymerization of styrene initiated by AIBN or thermally was studied. It has been found that the studied hydroxylamines act mainly as polymerization retarders (their inhibition effect is small). It is possible to evaluate the size of the retardation effect by the transfer constant k_x of the reaction $P^\bullet + HA \xrightarrow{k_x} PH + HA^\bullet$. The study of the styrene oxidation initiated by AIBN in the presence of chosen hydroxylamines has shown, on the other hand, their expressive inhibition effect.

В работе изучали влияние *N,N*-дизамещенных гидроксиламинов на радикальную полимеризацию стирола, инициированную АИБН или термически. Было найдено, что изучаемые гидроксиламины оказывают действие главным образом как замедлители полимеризации (их ингибирующее действие мало). Значение замедляющего действия может быть оценено константой скорости передачи k_x реакции $P^\bullet + HA \xrightarrow{k_x} PH + HA^\bullet$. Изучение инициированного окисления стирола АИБН в присутствии подобранных гидроксиламинов показало наоборот их значительный ингибирующий эффект.

The stabilizing effect of *N,N*-disubstituted hydroxylamines is connected with their ability to decompose peroxides and hydroperoxides giving rise to nitroxyl radicals [1—3]. The decay of nitroxyl radicals can occur by the reaction with free radicals, which are present in the system [4—7], or by their mutual reactions and at the same time forming a nitron [2, 8, 9]. *N,N*-Disubstituted hydroxylamines were also investigated as inhibitors of radical polymerization [10, 11]. The existing

experimental values do not make it possible to evaluate their reactivity with carbon radicals. In this paper are stated the results obtained from the study of chosen *N,N*-disubstituted hydroxylamines with carbon radicals by the polymerization of styrene.

Experimental

Chemicals

N,N-Diethylene hydroxylamine (DEHA) was purified by the procedure described in paper [3]. *N,N*-Dibenzyl hydroxylamine (DBHA) was prepared according to *Schramm* [12] and purified by crystallization from methanol. *N*-Ethyl-*N*-phenyl hydroxylamine (EPHA) was prepared according to *Utzinger* [13] and purified by crystallization from petroleum ether. *N*-Benzyl-*N*-phenyl hydroxylamine (BEPHA) was prepared according to *Bamberger* [14] and purified by crystallization from water. The purity of the prepared hydroxylamines (HA) was evaluated by means of mass spectroscopy.

α,α' -Azobisisobutyronitrile (AIBN) and styrene were purified in the manner commonly used [15]. Nitrogen was purified by leading it through a column packed with a catalyst.

Procedure

The dilatometric method was used to study the influence of *N,N*-disubstituted hydroxylamines on the radical polymerization of styrene. The polymerization was carried out in the presence of AIBN at 60 °C and thermally at 100 °C in glass dilatometers. The dissolved oxygen was removed from styrene by repeated freezing and evacuating in nitrogen atmosphere.

The oxidation of styrene in the presence of AIBN and chosen HA was studied in a 6-channel oxidation device with the recording of oxygen consumption.

Results and discussion

From the characteristic kinetic curves of styrene polymerization initiated by AIBN (Fig. 1) and thermally (Fig. 2) it is evident that all studied hydroxylamines have a retardation and some an inhibition effect. A measurable inhibition period is observed by the styrene polymerization initiated by AIBN, only when DEHA and EPHA were used, while by the thermal polymerization also when DBHA was used.

The change of the polymerization rate, calculated from the linear part of the kinetic curves, with the concentration of HA, is illustrated in Figs. 3 and 4.

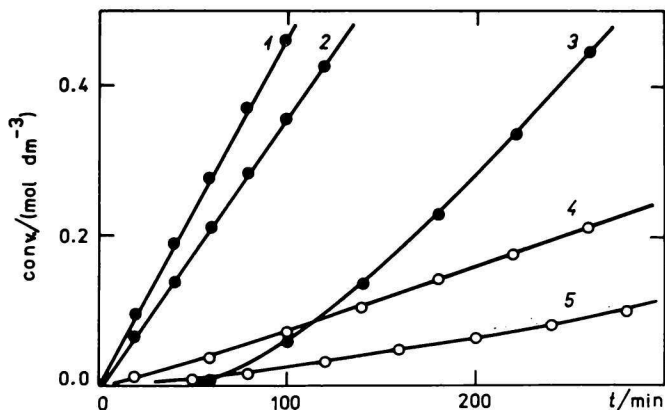


Fig. 1. Polymerization of styrene initiated by AIBN ($c = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$) in the presence of HA at 60°C .

$[\text{HA}] \cdot 10^2 / (\text{mol dm}^{-3})$: 1. without HA; 2. [DBHA] = 1.0; 3. [DEHA] = 0.5; 4. [BEPHA] = 2.0; 5. [EPA] = 0.5.

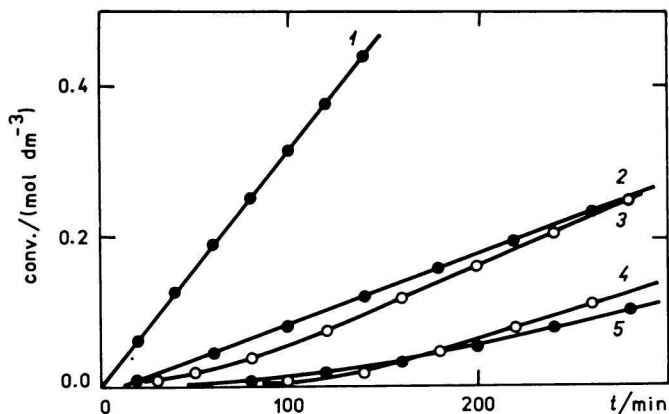


Fig. 2. Thermal polymerization of styrene in the presence of HA at 100°C .

$[\text{HA}] \cdot 10^2 / (\text{mol dm}^{-3})$: 1. without HA; 2. [DBHA] = 1.0; 3. [DEHA] = 0.5; 4. [BEPHA] = 2.0; 5. [EPA] = 0.5.

These dependences enable to evaluate the size of the secondary inhibition (retardation), whereby it seems that EPA is the most effective retarder. It is possible to propose the following reaction scheme for the studied *N,N*-disubstituted hydroxylamines in the polymerization system initiated by AIBN

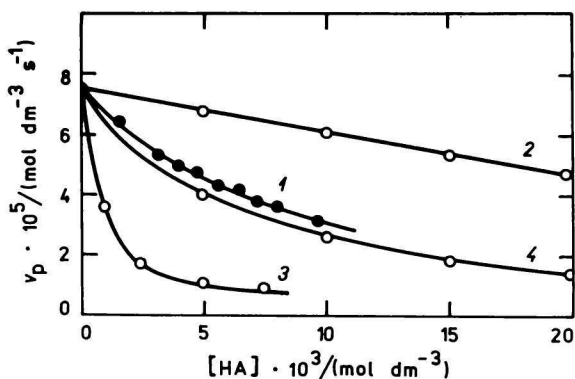


Fig. 3. Dependence of the rate of polymerization of styrene initiated by AIBN ($c = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$) on the concentration of HA at 60 °C.
1. DEHA; 2. DBHA; 3. EPHA; 4. BEPHA.

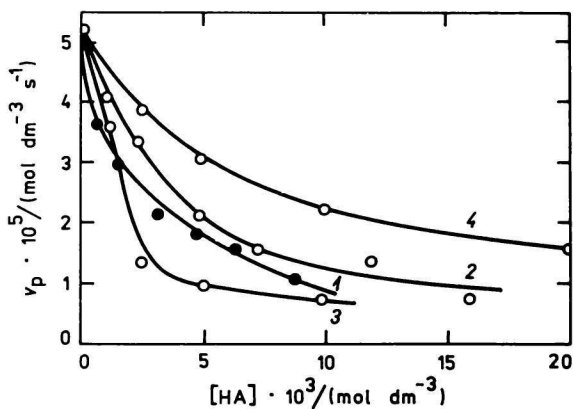
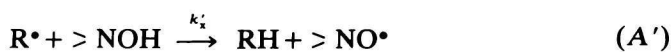


Fig. 4. Rate dependence of thermal polymerization of styrene on HA concentration at 100 °C.
1. DEHA; 2. DBHA; 3. EPHA; 4. BEPHA.





HA[•] can be > NO[•] radicals but also $\begin{array}{c} \cdot \\ | \\ \text{---C---N---OH} \\ | \quad | \\ \text{H} \end{array}$ radicals.

Since the primary inhibition in the studied hydroxylamines is manifest to a smaller extent (it is possible to neglect the reactions A'—A'', in comparison with the reaction B) and it shows more the retardation, then, considering a stationary state it is possible to derive the equation

$$\frac{1}{v_p} = \frac{1}{v_{p0}} + \frac{k_x [HA]}{k_p [M] v_{\text{init}}} \quad (1)$$

where v_p and v_{p0} are rates of the retarded and nonretarded polymerization, k_x and k_p are rate constants of transfer and propagation, v_{init} is the initiation rate, [HA] and [M] — molar concentration of hydroxylamine and monomer.

Eqn (1) enables to determine graphically the ratio of the rate constants k_x/k_p and to calculate according to Tüdös [16] also the stoichiometrical inhibition coefficient. The constants quoted by Matheson [17] for the temperature of 60 °C (Table 1) were used for the calculation of v_{init} and the stoichiometrical coefficient (μ).

From the study of the styrene oxidation in the presence of DEHA and DBHA at 50 °C (Figs. 5 and 6) it was found that the investigated hydroxylamines behave, before all, as inhibitors, whereby their secondary retardation influence is small. It is

Table 1

Values of the ratio of constants k_x/k_p and μ for the polymerization of styrene initiated by AIBN ($c = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$) in the presence of *N,N*-disubstituted hydroxylamines at 60 °C

| HA | k_x/k_p | μ |
|-------|-----------|-------|
| DEHA | 2.5 | 1.7 |
| DBHA | 0.5 | 1.8 |
| EPHA | 20.5 | 1.6 |
| BEPHA | 3.8 | 1.3 |

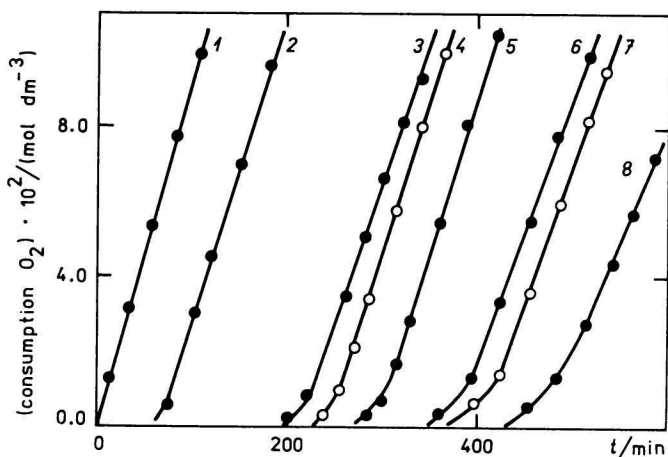


Fig. 5. Styrene oxidation initiated by AIBN ($c = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$) at 50°C in the presence of DEHA.
 $[\text{DEHA}] \cdot 10^4 / (\text{mol dm}^{-3})$: 1. without HA; 2. 2.5; 3. 4.0; 4. 5.4; 5. 7.5; 6. 9.8; 7. 12.8; 8. 19.0.

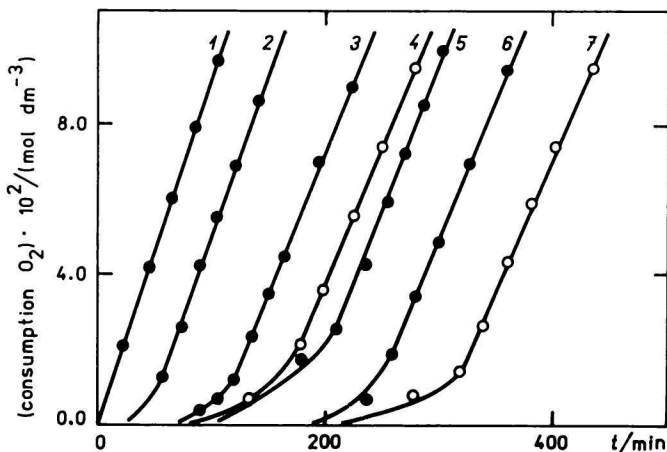


Fig. 6. Styrene oxidation initiated by AIBN ($c = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$) at 50°C in the presence of DBHA.
 $[\text{DBHA}] \cdot 10^4 / (\text{mol dm}^{-3})$: 1. without HA; 2. 1.0; 3. 1.5; 4. 1.9; 5. 2.3; 6. 2.7; 7. 3.1.

evident from the figures that DBHA is, in the oxidation system, more effective than DEHA, unlike their influence by polymerization.

The experimental results obtained enabled to evaluate the reactivity of the studied *N,N*-disubstituted hydroxylamines as inhibitors or retarders of styrene

polymerization. On the basis of the transfer constants it is possible to classify the efficiency of the hydroxylamines by the following sequence: DBHA, DEHA, BEPHA, EPHA. Hitherto the results obtained by the initiated styrene oxidation indicate that hydroxylamines in this case manifest themselves as effective antioxidants.

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