

Influence of 1,4-dihydropyridine derivatives on the initiated polymerization and oxidation of vinyl monomers

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Dedicated to Professor Ing. J. Beniska, DrSc., in honour of his 60th birthday

In this paper, the influence of 1,4-dihydropyridines on the polymerization of styrene and methyl methacrylate initiated by AIBN and BP was studied. 1,4-Dihydropyridines contained substituents in positions 2,6 and 3,5 and in some cases also in position 4. It was found that during the polymerization of both monomers initiated by AIBN substituted 1,4-dihydropyridines have no influence on the polymerization kinetics and the relative molecular mass of polymers obtained. During the polymerization initiated by BP, 1,4-dihydropyridines influence the polymerization rate of both monomers because a reaction between BP and NH group takes place. The acceleration or retardation of the polymerization is the final effect of this reaction. This effect depends on the reactivity of vinyl monomer. During the oxidation of styrene initiated by AIBN in the presence of 1,4-dihydropyridines retardation was observed.

В работе исследовано влияние 1,4-дигидропиридинов на полимеризацию стирола и метилметакрилата инициированную АИБН и БП. 1,4-Дигидропиридины содержали заместители в положении 2,6; 3,5 или 4. Найдено, что при инициированной полимеризации обоих мономеров с АИБН замещенные 1,4-дигидропиридины не влияют на кинетику полимеризации и изменение молекулярных весов приготовленных полимеров. При инициированной полимеризации с БП влияют исследуемые 1,4-дигидропиридины на скорость полимеризации вследствие реакции между БП и NH группой. В результате этой реакции ускоряется или замедляется полимеризация, которая зависит от реакционной способности и полярности винильного мономера. При инициированном окислении стирола с АИБН мы обнаружили прежде всего их замедляющее влияние.

The chemical properties of dihydropyridines are described in detail in papers [1, 2]. During the last several years, there was drawn attention towards these compounds from the viewpoint of synthesis and application in many fields. In

the polymer chemistry, some of these derivatives have been recommended as light and heat stabilizers for vinyl polymers and copolymers [3—5]. Hitherto, no papers have appeared dealing with the effect of substituted 1,4-dihydropyridines on the initiated polymerization and oxidation of styrene and methyl methacrylate.

Experimental

Chemicals

1,4-Dihydropyridines (DHP): 2,6-dimethyl-3,5-diacetyl-4-(2-furyl)-1,4-dihydropyridine (m.p. = 131 °C; DHP-1); 2,6-dimethyl-3,5-diethoxycarbonyl-4-phenyl-1,4-dihydropyridine (m.p. = 157—159 °C; DHP-2); 2,6-dimethyl-3,5-diethoxycarbonyl-1,4-dihydropyridine (m.p. = 182—183 °C; DHP-3) were prepared according to [6, 7] and they were purified by crystallization from ethanol.

Commercial styrene was washed by aqueous solution of NaOH to remove the stabilizer and then it was dried with anhydride CaCl₂; dry styrene was distilled twice at reduced pressure under nitrogen. Methyl methacrylate was distilled, then prepolymerized and again distilled at reduced pressure under nitrogen before use.

α, α' -Azobisisobutyronitrile (AIBN) was purified by a threefold crystallization from methanol. Benzoyl peroxide (BP) was purified by a threefold precipitation from a chloroform solution by methanol. The initiators were stored in dark at laboratory temperature. Nitrogen was purified by the procedure given elsewhere [8].

Procedures

The polymerization of styrene and methyl methacrylate initiated by AIBN and BP in the presence of substituted DHP was carried out in glass dilatometers 10—12 cm³ in volume, capillary length 60 cm and capillary diameter 0.2 cm. The remaining dissolved oxygen was removed from monomer by repeated freezing, filling with nitrogen, and evacuation of dilatometers.

The oxidation of styrene initiated by AIBN in the presence of DHP was studied in a 6-column oxidation device with automatic record of oxygen consumption at atmospheric pressure and 50 °C [8].

Results and discussion

During the polymerization of styrene and methyl methacrylate initiated by AIBN in the presence of DHP no effects on either the polymerization kinetics or the relative molecular mass of obtained polymers have been observed. This

proves that the radicals formed from the initiator and the growing polymer radicals do not react with the reactive centres, such as N—H groups, C—H groups, and the substituents. It may be concluded that the N—H bond energy in DHP is similar to that in the derivatives of piperidine [9].

During the polymerization of both vinyl monomers initiated by BP, the influence of DHP, which differs for the individual monomers (Figs. 1 and 3), has been observed.

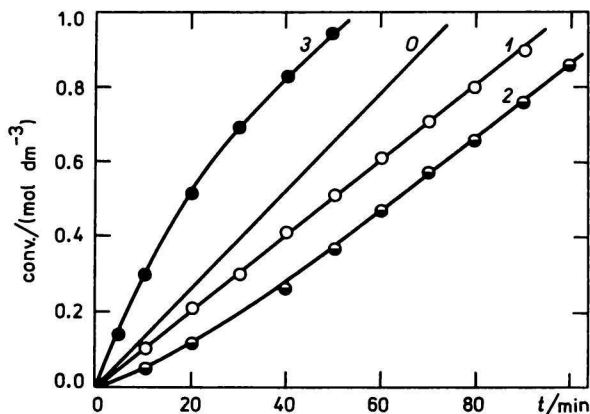


Fig. 1. Polymerization of methyl methacrylate initiated by BP ($c = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$) in the presence of DHP ($c = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$) at 60°C . 0. Without DHP; 1. DHP-1; 2. DHP-2; 3. DHP-3.

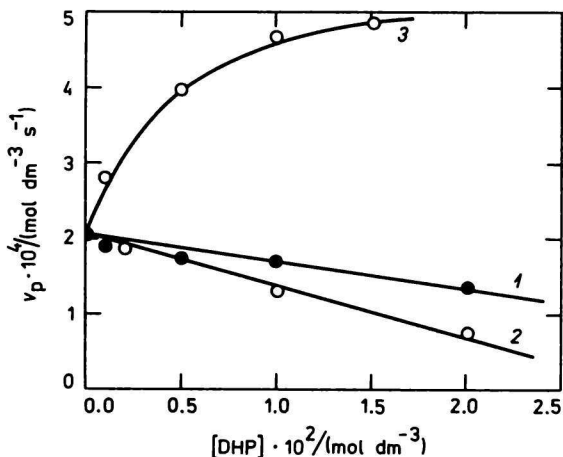


Fig. 2. Dependence of the initial polymerization rate of methyl methacrylate initiated by BP ($c = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$) on the DHP concentration at 60°C . 1. DHP-1; 2. DHP-2; 3. DHP-3.

It is obvious from Fig. 1 that the DHP-1 and DHP-2 derivatives act as retarders during the polymerization of methyl methacrylate, while the DHP-3 derivative, which has no substituents in position 4, accelerates the polymerization in the mentioned conversion range of polymerization. The influence of DHP concentration on the initial polymerization rate v_p of methyl methacrylate is shown in Fig. 2.

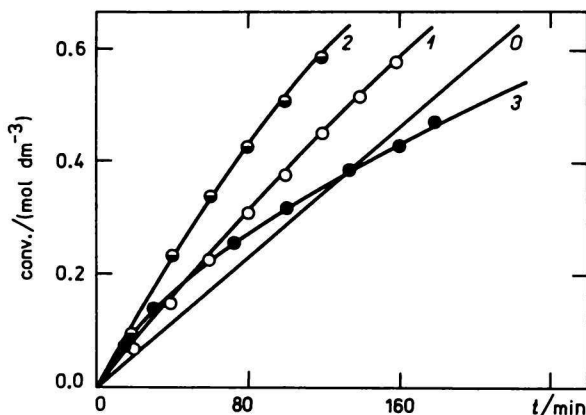


Fig. 3. Polymerization of styrene initiated by BP ($c = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$) in the presence of DHP ($c = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$) at 60°C . 0. Without DHP; 1. DHP-1; 2. DHP-2; 3. DHP-3.

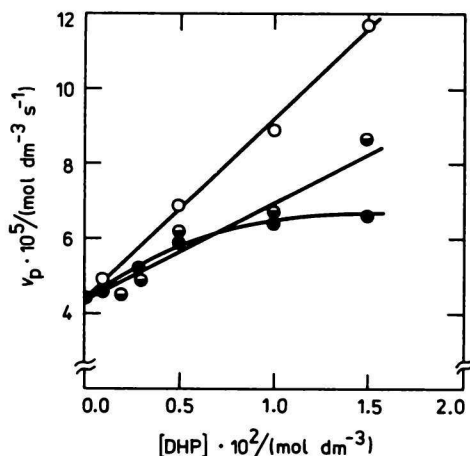
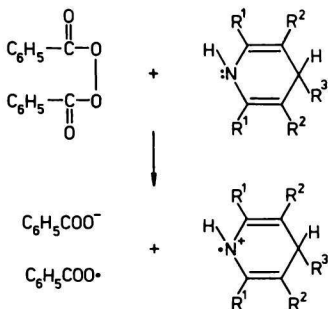


Fig. 4. Dependence of the initial polymerization rate of styrene initiated by BP ($c = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$) on the DHP concentration at 60°C . 1. DHP-1; 2. DHP-2; 3. DHP-3.

In contrast to methyl methacrylate, DHP derivatives accelerate the polymerization of styrene (Fig. 3). With increasing concentration of DHP, their influence on the polymerization rate is increasing (Fig. 4). DHP-3 derivative behaves anomalously, decreasing the polymerization rate v_p at higher conversions (Fig. 3, curve 3).

On the basis of the results obtained it is possible to conclude that DHP accelerate the decomposition of BP due to the presence of N—H group. Decomposition of BP in the presence of DHP-3 in acetonitrile at 30 °C was studied [10]. It was proved that the main reaction products are corresponding pyridine and benzoic acid. As the confirmation of BP decomposition in the presence of DHP serves the fact that polymer formation was observed in methyl methacrylate polymerization initiated by BP in the presence of DHP-2 at 25 °C, when no thermal decomposition of BP takes place [11]. The observed BP decomposition in the presence of DHP takes place as a consequence of the complex formation [12, 13] (Scheme 1).



Scheme 1

Further changes of $C_6H_5COO^-$, $C_6H_5CO\dot{O}$, and amine cation radical depend on the monomer reactivity and polarity of the medium. The cation radical, as unstable intermediate product [14], can split off a proton to form a pyridinyl radical, which can decay in the polymerization system by the mutual recombination, in the reaction with the benzoyl radical, but it can be also stabilized by the resonance under the formation of a carbon radical. The reactivity of the pyridinyl radicals is influenced by the type of the substituents in positions 2,6 and 3,5 but also in position 4 [15, 16]. The final products of the chemical changes of the amine cation radical are radicals, which in the presence of reactive monomer participate in the initiation step of polymerization or in the termination of growing radicals. In this way, it is possible to explain either acceleration or retardation effect of DHP in the polymerization of styrene or methyl methacrylate initiated by BP.

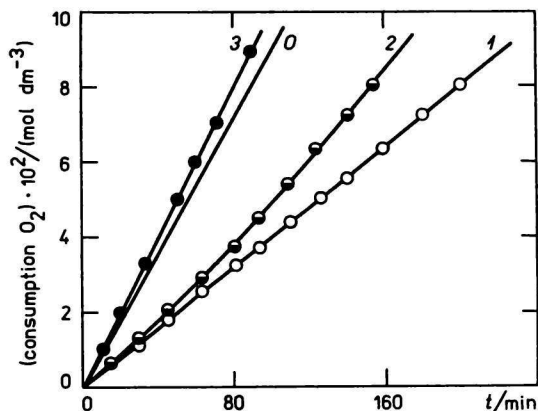


Fig. 5. Oxidation of styrene initiated by AIBN ($c = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$) in the presence of DHP ($c = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$) at 50°C .
 0. Without DHP; 1. DHP-1; 2. DHP-2; 3. DHP-3.

To gain some additional knowledge about the reactivity of DHP their influence on the oxidation of styrene has been studied (Fig. 5).

It is evident from the course of the kinetic curves of the styrene oxidation initiated by AIBN that DHP-1 and DHP-2 derivatives act as retarders, while DHP-3 derivative has no marked influence on the oxidation. Such a behaviour of DHP in the oxidation system is caused by the preferential reaction of RO_2^\bullet radicals with NH group and C—H bond of DHP.

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