Accelerating effects of ferrocene in polymerization reactions

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In the present paper there are described the kinetic measurements of the polymerization velocity in styrene on the initiation with dibenzoyl peroxide, the decomposition of which to the reactive radicals is accelerated by ferrocene. The measurements gave a ferrocene-concentration dependence of styrene polymerization velocity at 30—60 °C. At the same time the optimum values of temperature and, ferrocene-accelerator concentration were obtained for the polymerization of styrene as running in the reaction system styrene—dibenzoyl peroxide—ferrocene.

The chemistry of organometallic compounds has found broad application possibilities in various industrial branches in recent years. A representative of these compounds is ferrocene. In this compound an iron atom is closed between two cyclopentadiene rings. Such an arrangement is described as a sandwich structure [1, 2]. The bonds in a ferrocene molecule between the cyclopentadiene residues and the iron atom are due to the π-electrons of cyclopentadiene rings [3].

The studies of oxidation-reduction effects of ferrocene are of great value for practice as the accelerating reactions in the polymerization and copolymerizations under normal and mean temperatures find ever increasing applications and are of great value from the viewpoints of achievable economy and potential improvements of the working and living environment.

The present paper has aimed at examining the oxidation-reduction effects of ferrocene in the polymerizations of styrene and proposing a mechanism of interactions between the accelerator (ferrocene) and the initiator (dibenzoyl peroxide) in the polymerization. The studies of kinetics and mechanism of these reactions are of great importance for the use of ferrocene as an accelerator in the hardening reactions of unsaturated polyester resins with styrene.

In a series of papers published earlier [4—11] the present authors report on the effects of ferrocene in the hardening reactions in polyester resins. This paper aims at supplementing the results reported with the data on the kinetics of homopolymerizations which run besides the copolymerization reactions, to a lesser extent, also in the hardening of unsaturated polyester resins.

Experimental

In this work we performed the kinetic measurements of polymerization of styrene using a reversible single-electron transition of ferrocene to its cation. The polymerization velocity was followed working with a styrene—dibenzoyl peroxide—ferrocene polymerization system. The polymerization of styrene was performed in a temperature range of 30—60 °C, the polymerization velocity being followed by a dilatometric method based on evaluating the volume contraction of polymerization mixture in course of time. The styrene and dibenzoyl peroxide concentrations were constant, the ferrocene concentration and the polymerization temperature being variables. For each temperature experiment there were prepared nine polymerization mixtures differing in ferrocene concentration.

In the measuring operations there was followed the volume contraction of polymerization mixture as depending on time which is directly proportional to the degree of conversion. The conversion dependences in initial polymerization stages are of straight-line nature, the slope giving the polymerization velocity at low conversion degrees. The regression analysis performed gave the polymerization velocities for all the systems examined, the correlation coefficient being in no case below 0.98. This high value of correlation coefficient documents the accuracy of dilatometric measurements and the straight-line character of conversion dependences in the initial stages of styrene polymerization run in the presence of ferrocene as an accelerator.

For the ferrocene—dibenzoyl peroxide interaction studies there were used spectral measurements in the visible region. These measurements based on a colour change in the polymerization mixture allow to make conclusions regarding the reaction mechanism of the dibenzoyl peroxide decomposition due to ferrocene.

Results and discussion

Using the results of spectral measurements as a basis a mechanism of ferrocene effects on dibenzoyl peroxide was proposed. In the first stage an intensely green ferricinium complex and an active radical are formed. In the second stage the green colour turns to yellow-orange colour, the colour change being connected with the decomposition of ferricinium to ferrocene and a second radical. The ferrocene thus recovered is able to start another reaction with dibenzoyl peroxide.

It was also found that an equivalent amount of dibenzoyl peroxide and ferrocene, in an amount in which ferrocene was fed, is not able to start either polymerization or copolymerization reaction of styrene. This shows also that ferrocene is recovered *via* the reaction with dibenzoyl peroxide.

The conclusion regarding the reversible transition of ferrocene to ferricinium is confirmed by the results of copolymerization reactions of styrene with an unsaturated polyester. A rather small amount of ferrocene accelerates the decomposition of up to 100 times higher amount of dibenzoyl peroxide. If ferricinium were a final product in these reactions then only few reactive radicals would be formed, and these could not completely harden the unsaturated polyester. The polymerization and copolymerization velocities would be rather reduced in such a case.

The results indicate that the initiation runs in both polymerization and copolymerization reactions of styrene in accordance with Scheme 1.

The proposed mechanism of ferrocene—dibenzoyl peroxide reaction indicates that it is a mechanism similar to that occurring on treating an organic peroxide with Co(II) salts of organic acids [12].

It has been found that the velocity of polymerization of styrene raises with the concentration of ferrocene up to an optimum concentration at which the
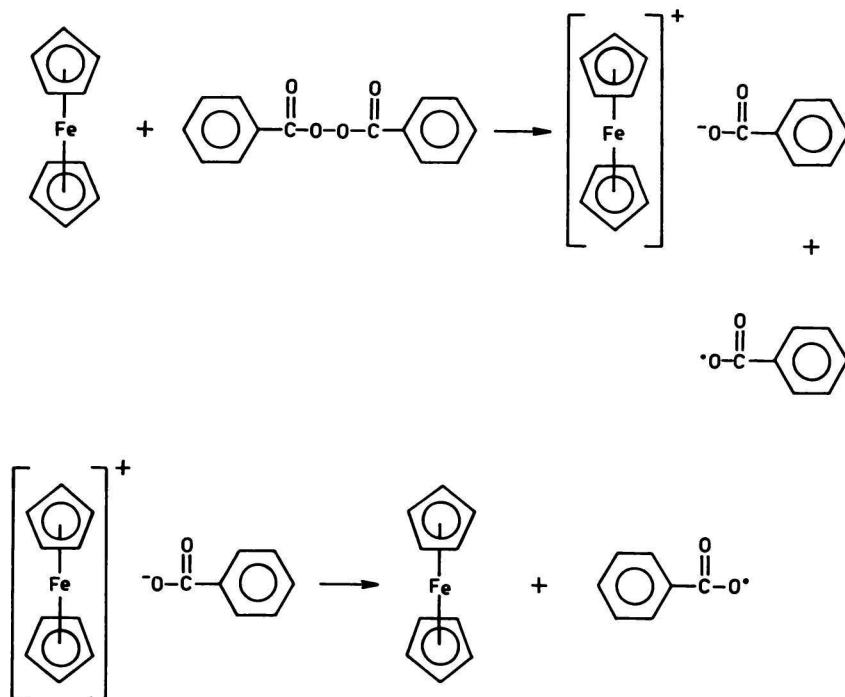
Scheme 1

polymerization velocity reaches its maximum (Fig. 1). The values measured have also revealed that the dependence of the velocity of polymerization on the concentration of accelerator (ferrocene) exhibits a maximum at which the given system reaches its highest polymerization velocity. The dependence shows clearly that the maximum is positioned for various polymerization temperatures in a sharply defined region of ferrocene concentrations. The maximum is sharp especially at high polymerization temperatures and is at about 9×10^{-4} mol dm^{-3} ferrocene concentration, the concentration of peroxide being 0.01 mol dm^{-3}
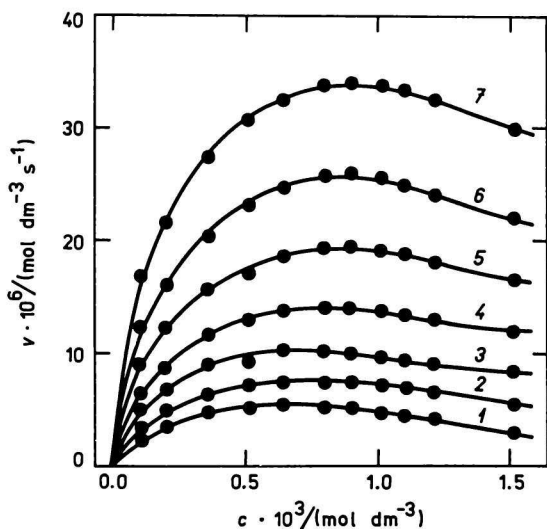

Fig. 1. The ferrocene-concentration dependences of polymerization velocities in the styrene—dibenzoyl peroxide—ferrocene system for various temperatures. 1. 30 °C; 2. 35 °C; 3. 40 °C; 4. 45 °C; 5. 50 °C; 6. 55 °C; 7 60 °C.

The accelerator-concentration dependences of polymerization velocity obtained at all the temperatures in the range used show a sharp growing of the polymerization velocities in the region of low concentrations in a range from a starting point up to a maximum polymerization velocity. Further increases in accelerator concentration lead to a much slower dropping of polymerization velocities.

From the measured results there have been obtained also the polymerization velocities as depending on the styrene-polymerization temperature. In this case each curve represents a single ferrocene concentration used (Figs. 2 and 3).

The results obtained can be expressed as follows. The maximum polymerization velocity gives the optimum ratio of the amount of ferrocene and dibenzoyl peroxide. The initial sharp growth of polymerization velocities is due to the fact

that at a lower ferrocene concentration the competing reactions of the radicals formed are suppressed. In the polymerization mixture the initiation overwhelms the interradical reactions which do not always lead to the regeneration of peroxide but sometimes to the formation of nonreactive compounds. Lower concentrations of the accelerator also start the polymerization of a lower number of styrene molecules, which prefers more the polymerization than the termination reactions, either of disproportionation or recombination nature.

Fig. 2. The temperature dependences of polymerization velocities for various ferrocene concentrations $c\,/\,(\mathrm{mol\,dm^{-3}})$: *0.* 0.0000; *1.* 1.0207×10^{-4}; *2.* $2.0414 \times 10^{-}$; *3.* $5.1036 \times 10^{-}$; *4.* 8.1658×10^{-4}
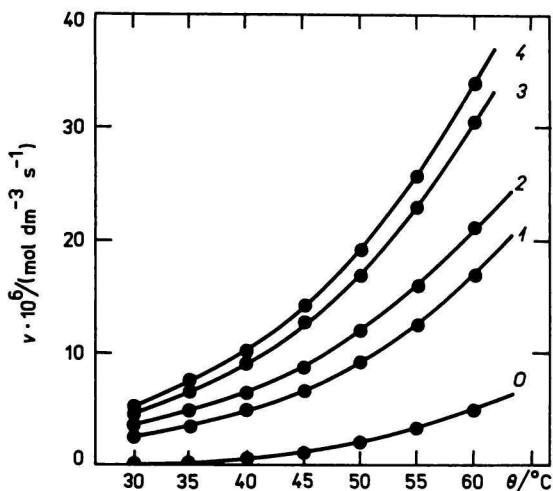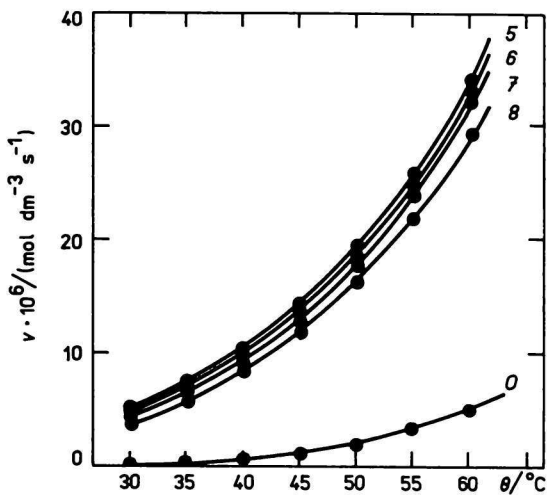

Fig. 3. The temperature dependences of polymerization velocities for various ferrocene concentrations $c/(\mathrm{mol\,dm^{-3}})$: *0.* 0.0000; *5.* 9.1864×10^{-4}; *6.* 1.1228×10^{-3}; *7.* $1.2249 \times 10^{-}$; *8.* 1.5311×10^{-3}

For practice these results mean that the polymerization and copolymerization reactions require the precise dosing of individual components of the initiation system; keeping this requirement results in well running oxidation-reduction initiation reactions.

From the obtained values of polymerization velocities of styrene the comparative accelerations for all the ferrocene concentrations used were calculated, considering as a base the velocity of styrene polymerization reduced to the zero ferrocene concentration. The comparative acceleration values as depending on the accelerator concentration are given in Table 1. It is evident that the highest acceleration is reached at a ferrocene concentration of $9.186 \times 10^{-4} \, mol \, dm^{-3}$ and at a dibenzoyl peroxide concentration of $0.01 \, mol \, dm^{-3}$ at a polymerization temperature of $35 \, °C$.

Table 1

Comparative acceleration of the polymerization of styrene

c (ferrocene)	$\theta/°C$						
$mol \, dm^{-3}$	30	35	40	45	50	55	60
0.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
1.021×10^{-4}	7.336	9.400	9.894	5.894	4.370	3.902	3.483
2.041×10^{-4}	10.488	12.884	12.603	7.848	5.859	4.998	4.351
5.104×10^{-4}	13.591	17.341	17.657	11.469	8.002	7.073	6.190
8.166×10^{-4}	14.872	19.718	19.469	12.657	9.260	7.986	6.898
9.186×10^{-4}	14.899	19.797	19.525	12.660	9.391	8.069	6.996
1.123×10^{-3}	14.612	18.913	19.242	12.376	9.201	7.937	6.973
1.225×10^{-3}	13.862	18.443	18.298	11.904	8.978	7.697	6.820
1.531×10^{-3}	13.318	17.572	17.792	11.569	8.673	7.502	6.621

From the viewpoint of applicability to practice the results described in this paper are usable for the homopolymerizations of styrene and for the copolymerizations of styrene with an unsaturated polyester. On the basis of the optimum concentrations new initiation systems, nontoxic in contradiction to hitherto used cobalt salts and N,N-dimethylaniline, can be formulated, which leads to improvements in the working and living environment. Replacing cobalt with the organoiron compound leads also to substantial economies of cobalt which is considered nowadays a strategically important material.

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