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# The Photodegradation of a Polyamidehydroxyurethane Type Polymer in Aqueous Solution. The Influence of Metal Ions on the Process of Degradation

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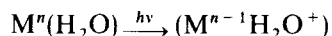
The photodegradation of a polyamidehydroxyurethane type polymer in aqueous solution in the presence of various metal ions has been studied. It has been ascertained, that  $\text{Fe}^{3+}$  ions accelerate the process of photodegradation;  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$  ions retard the process of degradation of the polymer. With increasing  $\text{Fe}^{3+}$  concentration, there increase the rate of the degradation and the values of the quantum yield of chain scission,  $\Phi_{cs}$ . At greater  $\text{Fe}^{3+}$  concentrations, there is observed a stabilization of the degradation by the end of the process, that fact means that in this case the number of macroradicals recombinations is greater than that, at less  $\text{Fe}^{3+}$  concentrations. The photocatalytic role of  $\text{Fe}^{3+}$  ions has been related to the formaion of the  $\cdot\text{OH}$  radicals.

**Keywords:** Photodegradation; polyamidehydroxyurethane; aqueous solution; metal ions

## INTRODUCTION

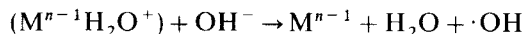
It is known that among the compounds, which are capable of sensitizing (initiating) and accelerating the reactions of photodegradation of polymers, there are also metal oxides and metal salts [1–5]. In literature there exists information concerning the production of polymeric materials containing as additives, this type of compounds [6, 7]. It has

been shown, that under ultraviolet irradiation some of metal ions ( $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ce}^{4+}$ ) can undergo the process of photoreduction, which proceeds through electron transfer [8]. Aqueous solutions of these ions demonstrate a strong absorption. It has been assumed that the electron, necessary for the photoreduction, comes, probably, from the hydrated metal ions [8]:



where  $\text{M}^n$  and  $\text{M}^{n-1}$  are metal ions in oxidized and reduced states, respectively.

Also, the following transformations are possible:

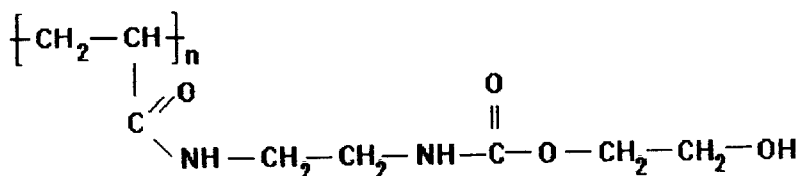


The formed  $\cdot\text{OH}$  radicals can initiate a great number of radical reactions in polymer macromolecules, and they can contribute the formation and decomposition of hydroperoxides in the case of ultraviolet irradiation in the presence of oxygen [9].

This paper presents some aspects of the photodegradation of a polyamidehydroxyurethane (PAHU) in aqueous solution in the presence of various metal ions. Previous studies of the authors concern the photodegradation of PAHU in aqueous solutions in isothermic conditions [10], under temperature influence [11], and in the presence of some dyes [12].

## EXPERIMENTAL

For the study we used a sample of polyamidehydroxyurethane with the structure:



The method of its obtaining was described before [13].

The molecular weight of PAHU was determined by osmometry, and appeared to be  $\bar{M}_n = 18700$  g/mol [10]. The following salts were used:  $\text{MnCl}_2$ , (Merck);  $\text{CoCl}_2$  (Merck);  $\text{CrCl}_3$  (Merck);  $\text{Cu}(\text{NO}_3)_2$  (Merck);  $\text{Fe}(\text{NO}_3)_3$  (Merck).

The irradiation with ultraviolet light and viscometric measurements were performed on aqueous PAHU solutions with polymer concentration 0,1 g/dl in the absence of salts and aqueous PAHU solutions with the same concentration of polymer in the presence of  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$  ions. The concentration of  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cu}^{2+}$  ions in the irradiated PAHU solutions was  $1 \cdot 10^{-5}$  mol/l. In the case of  $\text{Fe}^{3+}$ , the concentrations were  $1 \cdot 10^{-5}$ ,  $3 \cdot 10^{-5}$ ,  $6 \cdot 10^{-5}$ ,  $1 \cdot 10^{-4}$  mol/l. The volume of solutions was 50 ml. Ultraviolet irradiation and viscometric measurements were carried out at the temperature  $25 \pm 0,25^\circ\text{C}$ .

The apparatus, experimental procedure and method of calculations of the intrinsic viscosity ( $[\eta]$ ), of quantum yield of chain scission ( $\Phi_{cs}$ ) and of number average of chain scissions ( $s$ ) were similar to those used in the study described in the previous paper [11].

## RESULTS AND DISCUSSION

From the obtained data it has been ascertained that among the used ions only  $\text{Fe}^{3+}$  ions accelerate the process of photodegradation of PAHU in aqueous solution. The presence of other ions ( $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cu}^{2+}$ ) retards the proceeding of the process of degradation. Figure 1 shows the changes in the relative viscosity,  $\eta_r$ , with irradiation time,  $\tau$ , for PAHU solutions in the absence and in the presence of some metal ions. It is possible to observe that only in the presence of  $\text{Fe}^{3+}$  the rate of the degradation increases in comparison with that in the absence of metal ions. Also, in the presence of  $\text{Fe}^{3+}$ , there decreases the time, necessary for the termination of the process (when  $\eta_r$  does not decrease with irradiation time). In the presence of  $\text{Fe}^{3+}$  the process of degradation of PAHU ends at approximately 120 minutes irradiation, in the absence of metal ions-at 840 minutes irradiation. In the presence of other ions the rate of PAHU degradation is much less, than in the absence of ions, and the process ends much later (at 1500 minutes irradiation in the presence of  $\text{Cr}^{3+}$  ions).

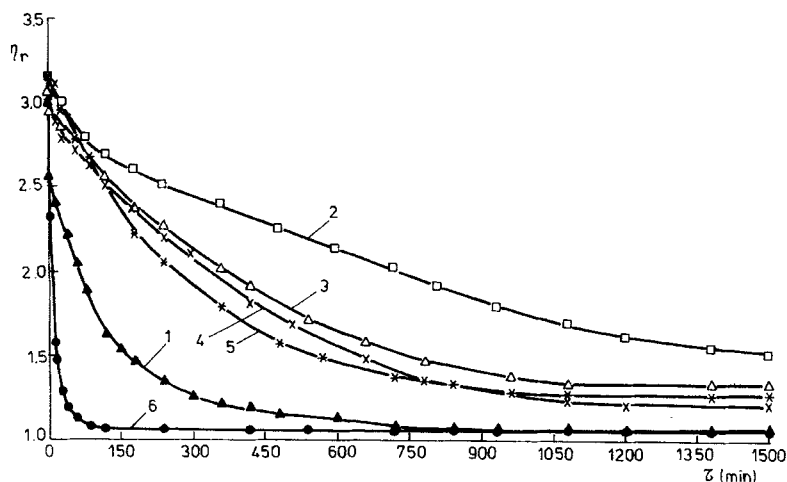


FIGURE 1 Relative viscosity,  $\eta_r$ , of aqueous PAHU solutions (0, 1 g/dl) as a function of irradiation time,  $\tau$ , in the absence (1) and in the presence of metal ions;  $\text{Cr}^{3+}$  (2);  $\text{Mn}^{2+}$  (3);  $\text{Co}^{2+}$  (4);  $\text{Cu}^{2+}$  (5);  $\text{Fe}^{3+}$  (6). Metal ion concentration is  $1 \cdot 10^{-5}$  mol/l.

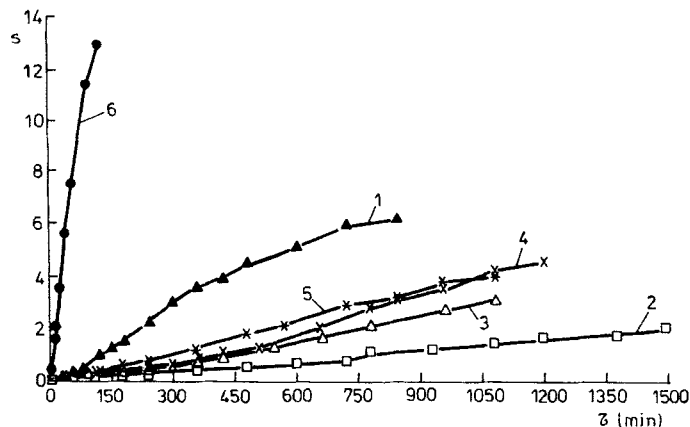


FIGURE 2 Number average of chain scissions,  $s$ , as a function of irradiation time,  $\tau$ , for the photodegradation of PAHU in aqueous solutions (0, 1 g/dl) in the absence (1) and in the presence of metal ions;  $\text{Cr}^{3+}$  (2);  $\text{Mn}^{2+}$  (3);  $\text{Co}^{2+}$  (4);  $\text{Cu}^{2+}$  (5);  $\text{Fe}^{3+}$  (6). Metal ion concentration is  $1 \cdot 10^{-5}$  mol/l.

Figure 2 illustrates the dependences of the values of the number average of chain scissions,  $s$ , as a function of irradiation time,  $\tau$ , for the process of degradation of PAHU in the absence and in the presence of metal ions. It can be observed that in the presence of  $\text{Fe}^{3+}$  the process

of polymer degradation proceeds without induction period, in this case the values of  $s$  increase abruptly from the very initial moments of the process, and in the absence of the metal ions there exists an induction period (the values of  $s$  increase very slightly), of approximately 20 minutes. In the presence of  $\text{Fe}^{3+}$  the maximum values of  $s$  become greater ( $s = 13,5$ ) in comparison with the other cases. It should be noticed that in the presence of  $\text{Fe}^{3+}$  ions, the dependence  $s = f(\tau)$  is fairly linear, this means that in the system the processes of chain scissions predominate. This is reflected in Figure 3, showing the dependences of the values of the quantum yield of chain scission,  $\Phi_{cs}$ , as a function of irradiation time,  $\tau$ , in the absence of metal ions as well as, in the presence of  $\text{Fe}^{3+}$  ion at the concentration  $1 \cdot 10^{-5}$  mol/l. The values of  $\Phi_{cs}$  in the presence of  $\text{Fe}^{3+}$  increase abruptly, from the initial moments of the process of degradation, but after reaching a certain maximum,  $\Phi_{cs}$  values decrease slightly.

Figure 4 illustrates changes in the values of the relative viscosity,  $\eta_r$ , with irradiation time,  $\tau$ , both in the absence of metal ions and in the

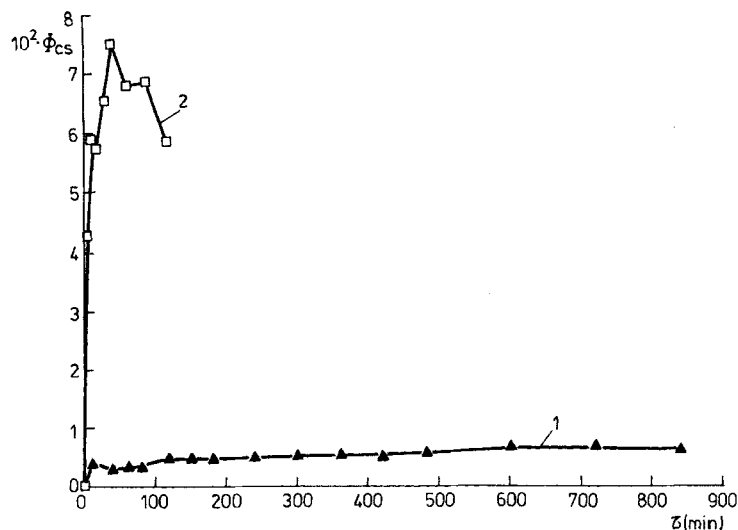


FIGURE 3 Quantum yield of chain scission,  $\Phi_{cs}$ , as a function of irradiation time,  $\tau$ , for the photodegradation of PAHU in aqueous solutions (0, 1 g/dl) in the absence of metal ions (1) and in the presence of  $\text{Fe}^{3+}$  (2)  $\text{Fe}^{3+}$  ion concentration is  $1 \cdot 10^{-5}$  mol/l.

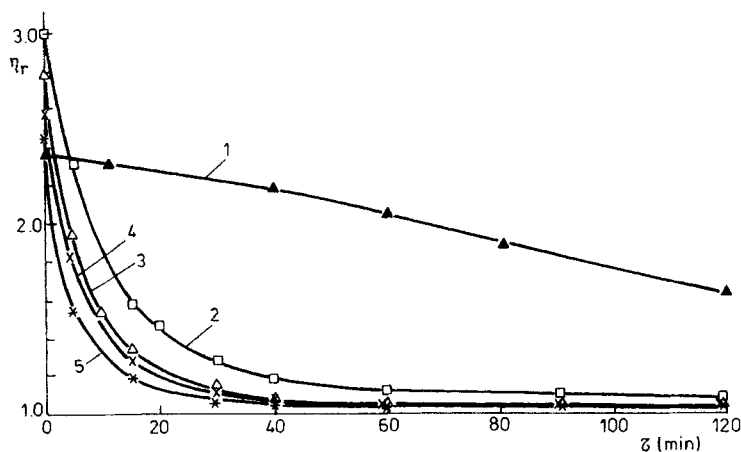


FIGURE 4 Relative viscosity,  $\eta_r$ , as a function of irradiation time,  $\tau$ , for aqueous PAHU solutions (0.1 g/dl) in the absence of metal ions (1) and in the presence of  $\text{Fe}^{3+}$ , at various concentrations:  $1 \cdot 10^{-5}$  mol/l (2);  $3 \cdot 10^{-5}$  mol/l (3);  $6 \cdot 10^{-5}$  mol/l (4);  $1 \cdot 10^{-4}$  mol/l (5). The values of  $\eta_r$  in the case of the degradation in the absence of metal ions are shown till 120 minutes.

presence of  $\text{Fe}^{3+}$  ions at various concentrations. Note an increase in the rate of the degradation of PAHU with increasing  $\text{Fe}^{3+}$  concentration in solution, with exception of  $\text{Fe}^{3+}$  concentration of  $6 \cdot 10^{-5}$  mol/l. From Figure 4 it can be noted that at  $\text{Fe}^{3+}$  concentrations  $3 \cdot 10^{-5}$  mol/l,  $6 \cdot 10^{-5}$  mol/l and  $1 \cdot 10^{-4}$  mol/l, the process of degradation ends at 90 minutes irradiation.

Figure 5 presents the number average of chain scissions,  $s$ , plotted as a function of irradiation time,  $\tau$ , in the absence of metal ions and in the presence of  $\text{Fe}^{3+}$  ions at various concentrations. In general, the values of  $s$  increase with increasing  $\text{Fe}^{3+}$  ion concentration, but not at the end of the process. By the end of the process a clear dependence of the values of  $s$  on  $\text{Fe}^{3+}$  ion concentration is not observed: at  $\text{Fe}^{3+}$  concentration  $6 \cdot 10^{-5}$  mol/l by the end of the process the values of  $s$  become smallest, and at  $\text{Fe}^{3+}$  concentration of  $1 \cdot 10^{-4}$  mol/l the values of  $s$  by the end of the process increase. They are, however, smaller than those, at  $\text{Fe}^{3+}$  concentration  $3 \cdot 10^{-5}$  mol/l but higher than those at  $1 \cdot 10^{-5}$  mol/l. The Figure 5 also shows that at larger  $\text{Fe}^{3+}$  concentrations ( $6 \cdot 10^{-5}$  mol/l and  $1 \cdot 10^{-4}$  mol/l) the values of  $s$  by the end of the process of degradation approach a certain limit, which means that the process of degradation stabilizes. This stabiliza-

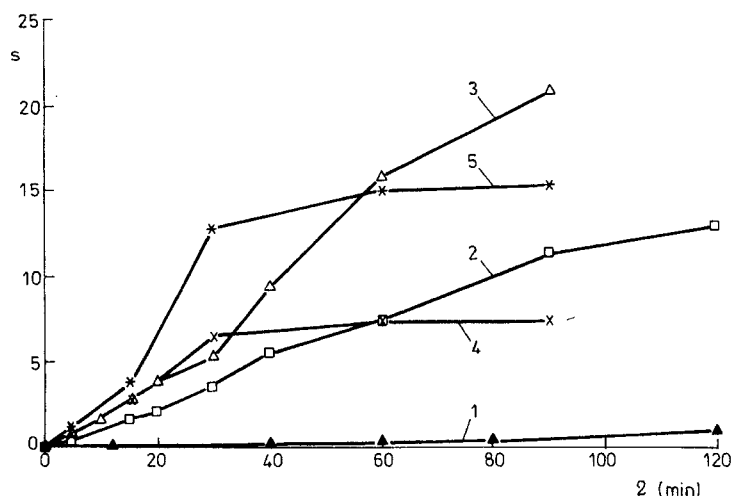


FIGURE 5 Number average of chain scissions,  $s$ , as a function of irradiation time,  $\tau$ , for the photodegradation of PAHU in aqueous solutions (0,1 g/dl) in the absence of metal ions (1) and in the presence of  $\text{Fe}^{3+}$  at various concentrations:  $1 \cdot 10^{-5}$  mol/l (2);  $3 \cdot 10^{-5}$  mol/l (3);  $6 \cdot 10^{-5}$  mol/l (4);  $1 \cdot 10^{-4}$  mol/l (5). The values of  $s$  in the case of the degradation in the absence of metal ions are shown till 120 minutes.

tion could be explained by the fact, that together with primary photochemical reactions—processes of chain scissions there occur also the secondary radical reactions—the recombination of radicals, formed during the scissions. Apparently these processes of recombination proceed more intensely at larger  $\text{Fe}^{3+}$  concentrations ( $6 \cdot 10^{-5}$  mol/l and  $1 \cdot 10^{-4}$  mol/l).

Such a behavior of the system is reflected also, in Figure 6, where is shown the quantum yield of chain scission,  $\Phi_{cs}$ , plotted as a function of irradiation time,  $\tau$ , in the absence of metal ions and in the presence of  $\text{Fe}^{3+}$  ions at various concentrations. It can be observed, that at  $\text{Fe}^{3+}$  concentrations of  $1 \cdot 10^{-5}$  mol/l and  $3 \cdot 10^{-5}$  mol/l, the values of  $\Phi_{cs}$  increase continuously, practically, during the entire process, with only a slight decrease in  $\Phi_{cs}$  at the process end. With  $\text{Fe}^{3+}$  concentrations of  $6 \cdot 10^{-5}$  mol/l and  $1 \cdot 10^{-4}$  mol/l, the values of  $\Phi_{cs}$ , reach, however a maximum and then begin to decrease till the end of the process. Figure 5 also shows that the values of  $\Phi_{cs}$  increase with increasing  $\text{Fe}^{3+}$  concentration, except the case at  $\text{Fe}^{3+}$  concentration  $6 \cdot 10^{-5}$  mol/l. It should be noted that in the presence of  $\text{Fe}^{3+}$  ions with the concentration of  $1 \cdot 10^{-4}$  mol/l,  $\Phi_{cs}$  reaches its maximum



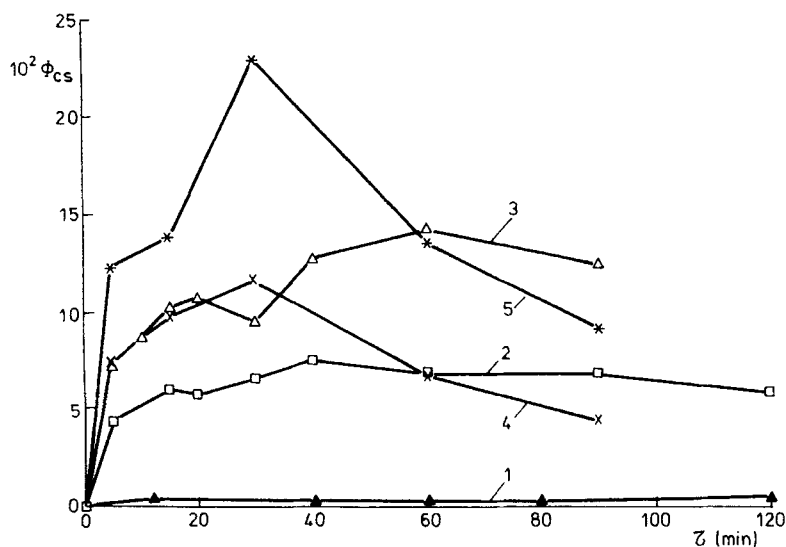


FIGURE 6 Quantum yield of chain scission,  $\Phi_{cs}$ , as a function of irradiation time,  $\tau$ , for the photodegradation of PAHU in aqueous solutions (0,1 g/dl) in the absence of metal ions (1) and in the presence of  $\text{Fe}^{3+}$  at various concentrations:  $1 \cdot 10^{-5}$  mol/l (2);  $3 \cdot 10^{-5}$  mol/l (3);  $6 \cdot 10^{-5}$  mol/l (4);  $1 \cdot 10^{-4}$  mol/l (5). The values of  $\Phi_{cs}$  in the case of the degradation in the absence of metal ions are shown till 120 minutes.

value ( $\Phi_{cs} \approx 0,23$ ), which is much larger, than that in the absence of  $\text{Fe}^{3+}$  ions ( $\Phi_{cs} \approx 0,69 \cdot 10^{-2}$ ).

Since the irradiation of PAHU solutions in the absence and in the presence of  $\text{Fe}^{3+}$  ions was carried out in the presence of oxygen, it could be expected that together with polymer photodegradation via chain scissions, there can proceed also the photo-oxidation with hydroperoxides formation and decomposition.

Previously it has been ascertained [10] that during the processes of PAHU photodegradation in aqueous solution under ultraviolet irradiation changes in conformation of PAHU molecules can take place, caused by the break of hydrogen bonds. It is not excluded, that in the presence of  $\text{Fe}^{3+}$  ions together with the processes of chain scissions and macro-radicals recombination changes in conformation are also possible.

It has been reported that the presence of  $\text{Fe}^{3+}$  ions accelerates the photodegradation in aqueous solutions of hydroxyethyl cellulose, carboxymethyl cellulose, poly(oxyethylene) and poly(methacrylic acid) [14, 15]

Rabek and co. [1] have demonstrated that in the presence of iron trichloride ( $\text{FeCl}_3$ ) the photodegradation of poly(oxyethylene) is greatly accelerated. It has been assumed, that the formation of a complex between the polymer and  $\text{FeCl}_3$  occurs, and that  $\cdot\text{Cl}$  radicals, obtained from  $\text{FeCl}_4^-$  ions, present in the complex polymer- $\text{FeCl}_3$  are responsible for the acceleration of the degradation.

Linden and co. [2] have reported that the presence of  $\text{FeCl}_3$  and Fenton reagent promotes greatly the process of photodegradation of poly(oxyethylene). It has been supposed that in the process of degradation hydroxyl and hydroperoxyl radicals play an important role.

Gafurov and co. [3] have shown that the mixture of anthracene and Mohr's salt ( $\text{Fe}^{2+}$ ) has a photosensitizing effect on the process of photodegradation of polyethylene.

Besides, there exists information concerning the fact, that the process of photodegradation of some polymers can be accelerated in the presence of various metal-organic compounds of iron [16, 17].

In the case of the studied system it could be assumed, that under ultraviolet irradiation there takes place the photoreduction of  $\text{Fe}^{3+}$  ions to  $\text{Fe}^{2+}$  ions. This process can be followed by the formation of hydroxyl  $\cdot\text{OH}$  radicals. The  $\cdot\text{OH}$  radicals can abstract hydrogen atoms from the groups  $-\text{CH}_2-$  and  $-\text{CH}-$  along the polymer chain of PAHU with macroradicals formation. These macroradicals, under ultraviolet irradiation, can disproportionate, causing the main chain scission. On the other hand, since the irradiation of solutions has been carried out in the presence of oxygen, from the formed macroradicals, through a series of transformations, hydroperoxides, can be formed which subsequently decompose during ultraviolet irradiation.

The stabilization of the process of PAHU photodegradation at greater  $\text{Fe}^{3+}$  concentrations ( $6 \cdot 10^{-5}$  mol/l and  $1 \cdot 10^{-4}$  mol/l), that is reflected by: (i) smaller values of  $s$  by the end of the process in comparison with those at smaller  $\text{Fe}^{3+}$  concentrations, and (ii) the decrease in the values of  $\Phi_{cs}$ , at greater  $\text{Fe}^{3+}$  concentrations, after a maximum in  $\Phi_{cs}$  is reached, could be explained by the increase in the number of  $\cdot\text{OH}$  radicals and therefore of macroradicals which recombine.

The behaviour of the studied system in the presence of other ions ( $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cr}^{3+}$ ) is difficult to explain only on the basis of this study. It is possible, that the retardant effect of these ions on the photodegradation of PAHU could be caused by the changes in

conformation of PAHU polymer chains in the presence of the used electrolytes. This effect has been used to explain the decrease in the degree of photodegradation of polyvinylpyrrolidone in aqueous solution in the presence of  $\text{Cu}^{2+}$  ions [18].

## CONCLUSIONS

The photodegradation of PAHU in aqueous solution is accelerated in the presence of  $\text{Fe}^{3+}$  ions. The presence of  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$  ions retard the process.

With increasing  $\text{Fe}^{3+}$  concentration, there is an increase in the rate of degradation of PAHU and the values of  $\Phi_{cs}$ . The values of  $s$  by the end of the process, at greater  $\text{Fe}^{3+}$  concentrations, are less than those, at lower  $\text{Fe}^{3+}$  concentrations; a stabilization of the process at greater  $\text{Fe}^{3+}$  concentrations was observed.

The photodegradation of PAHU in aqueous solution in the presence of  $\text{Fe}^{3+}$  ions proceeds through chain scissions. Parallel to chain scissions the reactions of macroradicals recombination also take place.

The photocatalytic effect of  $\text{Fe}^{3+}$  ions on the photodegradation of PAHU in aqueous solution can be explained by  $\cdot\text{OH}$  radicals formation. Through the abstraction of hydrogen atoms from PAHU polymer chain, these radicals cause the formation of macroradicals, which through their disproportionation, lead to main chain scissions.

The stabilization of the process of degradation at greater  $\text{Fe}^{3+}$  ion concentrations can be explained in the following way: with increasing  $\text{Fe}^{3+}$  concentration, the number of  $\cdot\text{OH}$  radicals increases, and this leads to increases of the number of the macroradicals, which recombine.

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