Photooxidative degradation of polymers by HO• and HO_2• radicals generated during the photolysis of H_2O_2, $FeCl_3$, and Fenton reagents

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Dedicated to ***Professor Vittorio Carassiti***

This paper summarizes data available so far on the progress made in the study of photooxidative degradation of polymers by HO•, HO_2• radicals generated during the photolysis of H_2O_2, $FeCl_3$, and Fenton ($FeCl_3$-H_2O_2 and $FeCl_3$-H_2O_2) reagents. Experimental results obtained in our laboratories with two polymers, poly(ethylene dioxide) and poly(acrylic acid) are discussed.

The paper presents results, so far, of an extensive, long-term (1991-1995) project, involving international cooperation between:

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1. Introduction

In the project definition stage, the three institutes established five key areas of research:

1. Study of the mechanisms and kinetics of Fe(II) and Fe(III) photoinitiated degradation of water-soluble polymers.
2. Development of photodegradable polymers (for packaging industry) and agriculture (mulch films).

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3. Utilization of controlled and accelerated photodegradation of polymeric waste materials.
4. Application of inorganic salt-polymer complexes in dentistry (Swedish project only).
5. Application of inorganic salt-polymer complexes for the synthesis of semi-conducting polypyrroles.

2. The role of HO•, HO_2•, and POO• radicals in the photooxidative degradation of polymers

When investigating the primary reactions involved in the photooxidative degradation of almost all polymers, the following scheme has been generally accepted:

Initiation step:	Formation of polymer radicals
Propagation step:	Reaction of free polymer radicals with oxygen, and the production of polymer oxy and peroxy radicals, resulting in chain scission.
Termination step:	Reaction of free polymer radicals, resulting in cross-linking.

2.1 Initiation step

Polymers (PH) containing intra-molecular chromophoric groups and light absorbing impurities (RH) (inter-molecular impurities) can produce free radicals [1] in the presence of air (oxygen) under UV/VIS (visible) irradiation:

$$\mathrm{PH} \xrightarrow{+h\nu(O_2)} \mathrm{P\bullet} + \mathrm{HO_2\bullet} \qquad (1)$$

$$\mathrm{RH} \xrightarrow{+h\nu(O_2)} \mathrm{R\bullet} + \mathrm{HO_2\bullet} \qquad (2)$$

$$\mathrm{PH} + \mathrm{R\bullet} \longrightarrow \mathrm{P\bullet} + \mathrm{RH} \qquad (3)$$

If hydroperoxy (HO_2•) radicals are formed, they can react with each other to produce hydrogen peroxide (H_2O_2), which can be further photolyzed into hydroxy (HO •) radicals, which, in turn, can react with polymer (PH) to produce polymer alkyl (P•) radicals:

$$\mathrm{HO_2\bullet} + \mathrm{HO_2\bullet} \longrightarrow \mathrm{H_2O_2} + \mathrm{O_2} \qquad (4)$$

$$\mathrm{H_2O_2} \xrightarrow{+h\nu} \mathrm{HO\bullet} + \mathrm{\bullet OH} \qquad (5)$$

$$\mathrm{PH} + \mathrm{HO\bullet} \longrightarrow \mathrm{P\bullet} + \mathrm{H_2O} \qquad (6)$$

So far, however, there is no direct proof for the participation of HO• and HO_2• radicals in the initiation step.

2.2 Propagation step

Polymer alkyl (P•) radicals react immediately with oxygen (very fast reaction) to produce polymer peroxy (POO•) radicals, which can further abstract hydrogen from the same or neighboring macromolecules to produce polymer hydroperoxide (POOH):

$$P\bullet + O_2 \longrightarrow PO_2\bullet \tag{7}$$

$$PO_2\bullet + PH \longrightarrow POOH + P\bullet \tag{8}$$

It is likely that hydroxy (HO•) radicals and/or hydroperoxy (HO$_2$•) radicals (if they are produced in the initiation step) can also abstract hydrogen from polymer (PH) molecules, reaction (6), and reaction (9) respectively:

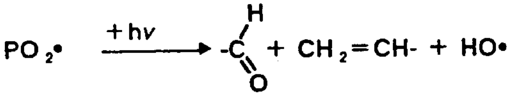
$$PH + HO_2\bullet \longrightarrow P\bullet + H_2O_2 \tag{9}$$

Many other (secondary) reactions of HO• and HO$_2$• radicals in the propagation step have been proposed [1]:

$$PO_2\bullet + PH \xrightarrow{+h\nu} P\bullet + HO_2\bullet + P\bullet \tag{10}$$

$$HO_2\bullet + PH \longrightarrow H\bullet + HO_2\bullet + P\bullet \tag{11}$$

$$PO_2\bullet \xrightarrow{+h\nu} \bullet P\bullet \text{ (biradical)} + HO_2\bullet \tag{12}$$



$$PO_2\bullet \xrightarrow{+h\nu} -\overset{H}{\underset{O}{C}} + CH_2{=}CH- + HO\bullet \tag{13}$$

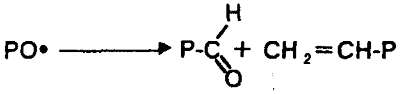
Polymer hydroperoxide (POOH) is further photolyzed by UV radiation into polymer oxy (PO•) radicals and hydroxy (HO•) radicals, with a quantum yield close to unity [2]:

$$POOH \xrightarrow{+h\nu} PO\bullet + \bullet OH \tag{14}$$

Polymer alkyloxy (PO•) radicals are capable of abstracting hydrogen from the same and neighboring macromolecules to produce polymer with hydroxy group (POH). In these reactions water can also be produced, reaction (6):

$$PO\bullet + PH \longrightarrow POH + P\bullet \tag{15}$$

The β-scission process of polymer alkyloxy (PO•) radicals causes degradation of polymer macromolecules:



$$PO\bullet \longrightarrow P\text{-}C(H){=}O + CH_2{=}CH\text{-}P \qquad (16)$$

$$PO\bullet \longrightarrow P\text{-}C({=}O)\text{-}P + CH_2{=}CH\text{-}P \qquad (17)$$

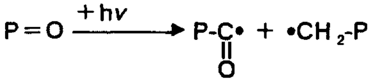
The secondary polymer hydroperoxide (POOH$_s$ and tertiary polymer hydroperoxide (POOH)$_t$ can be photolyzed by the following reactions:

$$(POOH)_s + PH \xrightarrow{+h\nu} P{=}O + H_2O + PH \qquad (18)$$

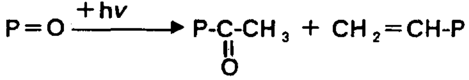
$$(POOH)_t \xrightarrow{+h\nu} P\text{-}C({=}O)\text{-}P + CH_2{=}CH\text{-}P + H_2O \qquad (19)$$

$$(POOH)_t + P_1\text{-}CH_2CH_2\text{-}P_2 \xrightarrow{+h\nu} POH + P_1\text{-}CH{=}CH\text{-}P_2 + H_2O \qquad (20)$$

Polymers formed with carbonyl groups (P=O), absorb intensively UV irradiation and are photolyzed by the Norrish type I (reaction (21)), and the Norrish type II (reaction (22)) mechanisms, resulting in chain scission (degradation):



$$P{=}O \xrightarrow{+h\nu} P\text{-}\underset{\underset{O}{\|}}{C}\bullet + \bullet CH_2\text{-}P \qquad (21)$$



$$P{=}O \xrightarrow{+h\nu} P\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_3 + CH_2{=}CH\text{-}P \qquad (22)$$

2.3 Termination step

In air, only polymer alkylperoxy ($PO_2\bullet$) radicals exist, because of the very high reactivity of oxygen with polymer alkyl (P•) radicals, reaction (7). It can be expected that the main termination reaction occurs between two polymer alkylperoxy ($PO_2\bullet$) radicals, reaction (23):

$$PO_2\bullet + PO_2\bullet \longrightarrow POOP + O \qquad (23)$$

$$PO_2\bullet + PO_2\bullet \longrightarrow P{=}O + P\text{-}OH + O_2 \qquad (24)$$

If the hydroxy (HO•) and hydroperoxy ($HO_2\bullet$) radicals exist in the neighborhood of $PO_2\bullet$ radicals, the following termination reactions may occur:

$$PO_2\bullet + HO\bullet \longrightarrow POH + O_2 \qquad (25)$$

$$PO_2\bullet + HO_2\bullet \longrightarrow POOH + O_2 \qquad (26)$$

$$PO_2\bullet + HO_2\bullet \longrightarrow P{=}O + H_2O + O_2 \qquad (27)$$

The termination step can also include the reaction of polymer alkylperoxy ($PO_2\bullet$) radicals with polymer alkyloxy (PO•) radicals:

$$PO_2\bullet + PO\bullet \longrightarrow POP + O_2 \qquad (28)$$

Finally, both PO• and PO_2• radicals can be terminated by low molecular (R•) radicals formed e.g. from photolysis of impurities or photoinitiators (RR), reactions (29) or (3):

$$R_1R_2 \xrightarrow{+h\nu} R_1\bullet + R_2\bullet \qquad (29)$$

$$PO\bullet + R\bullet \longrightarrow POR \qquad (30)$$

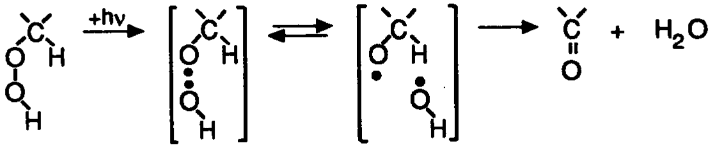
$$PO_2\bullet + R\bullet \longrightarrow POOR \qquad (31)$$

The termination step is responsible for the crosslinking reactions. Hydroxy (HO•) and hydroperoxy (HO_2•) radicals are very small in comparison with the polymeric macroradicals (P•, PO•, or PO_2•).

Because of their mobility, they readily recombine (terminate) by two mechanisms:

1. Primary recombination, which occurs in a period of the order of a vibration, i.e. 10^{-13} seconds This recombination is so rapid that free radicals can not escape from the cage or diffuse into bulk.
2. Secondary recombination, which occurs within about 10^{-9} seconds. Diffusion from cage into bulk, however, can compete with the secondary recombination.

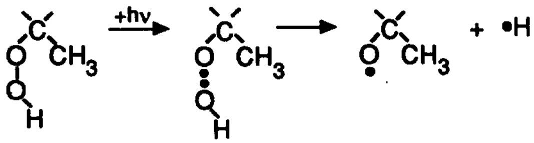
Polyethylene segments can form a cage, which allows fast reactions between polymer alkyloxy (PO•) radicals and hydroxy (HO•) radicals, formed in reaction (14), resulting in the formation of carbonyl groups and water:



(32)

cage reaction

The cage reaction explains the absence of the photoinduction period during the decomposition of secondary hydroperoxides in polyethylene [3,4]. The inductive role of polypropylene hydroperoxides is attributed to the fact that the cage reaction does not occur, and that hydroxy (HO•) radicals diffuse rapidly from the place where they were formed:



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It has also been proposed [5], that charge-transfer (CT) complexes, which can be formed between polymer alkylperoxy ($PO_2\bullet$) radicals and other polymer molecules (PH), result in the formation of hydroperoxy ($HO_2\bullet$) radicals and two polymer alkyl (P•) radicals:

$$POO\bullet + PH \longrightarrow [POO^{-}\bullet \cdots {}^{+}HP] \longrightarrow P\bullet + HO_2\bullet + P\bullet \tag{34}$$

In such a reaction, two polymer alkyl (P•) radicals are left in proximity of each other and they can immediately terminate, giving a crosslinked structure:

$$P\bullet + P\bullet \longrightarrow P\text{-}P \tag{35}$$

All of these reactions (1) — (35) well describe the mechanism of the photooxidative degradation of common polymers. However, many of them are only theoretical speculations, without experimental proof.

3. Photolysis of hydrogen peroxide (H_2O_2) in the presence of polymers

Hydrogen peroxide (H_2O_2) is easily photolyzed in the region 200-300 nm [6-10]:

$$H_2O_2 \xrightarrow{+h\nu} 2\,HO\bullet \tag{36}$$

The quantum yield of the disappearance of H_2O_2 is 1.7 ± 0.4. In the secondary reaction (37), hydroperoxy ($HO_2\bullet$) radicals are formed:

$$H_2O_2 + HO\bullet \longrightarrow HO_2\bullet + H_2O \tag{37}$$

The main products of H_2O_2 photolysis are water and oxygen, which are formed in the termination reactions:

$$2\,HO\bullet \longrightarrow H_2O + \tfrac{1}{2}O_2 \tag{38}$$

$$HO\bullet + HO_2\bullet \longrightarrow H_2O + O_2 \tag{39}$$

However, the termination of HO• and $HO_2\bullet$ radicals can produce hydrogen peroxide:

$$2\,HO\bullet \longrightarrow H_2O_2 \tag{40}$$

$$2\,HO_2\bullet \longrightarrow H_2O_2 + O_2 \tag{41}$$

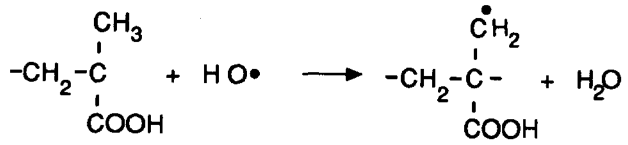
Oxygen does not react with hydroxy (HO•) and hydroperoxy ($HO_2\bullet$) radicals. Hydroxy (HO•) and hydroperoxy ($HO_2\bullet$) radicals may also participate in the following chain reaction:

$$HO\bullet + H_2O_2 \longrightarrow HO_2^{-} + H_2O \tag{42}$$

$$HO_2\bullet \rightleftarrows H^{+} + O_2^{-} \tag{43}$$

$$\begin{aligned} H_2O_2 + O_2^- &\longrightarrow HO\bullet + HO^- + O_2 \\ H^+ + OH^- &\longrightarrow H_2O \\ H^+ + HO_2^- &\longrightarrow H_2O_2 \end{aligned} \qquad (44)$$

Hydroxy (HO•) radicals, formed from the photolysis of the hydrogen peroxide in the presence of poly(methacrylic acid), abstract hydrogen mainly from methyl (CH_3) groups rather than from methylene (CH_2) groups, which are sterically hindered [9]:



$$-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{COOH}{|}}{C}} + HO\bullet \longrightarrow -CH_2-\overset{\overset{\dot{C}H_2}{|}}{\underset{\underset{COOH}{|}}{C}}- + H_2O \qquad (45)$$

In experiments carried out with poly (acrylic acid) (PAA) and poly (ethylene oxide) (PEO) dissolved in H_2O_2 (30 wt-%) and UV irradiated (254 nm), we have observed a rapid oxidative degradation of both polymers. The FTIR spectra of the final oxidation products of PAA (Fig. 1C) and PEO (Fig. 2B) show evident differences in comparison to the non-irradiated PAA (Fig. 1A), and PEO (Fig. 2A) samples. Strong absorption bands at 3487 cm^{-1} (Fig. 1C)(PAA) and at 3423 cm^{-1} (Fig. 2B)(PEO) indicates the formation of HO/HOO groups.

In the case of PEO, the formation of two new bands at 1728 cm^{-1} and 1664 cm^{-1} (Fig. 2B) can be attributed to the presence of carbonyl (C=O) and unsaturated end groups (CH_2=CH-), respectively. The UV irradiation of PAA and PEO in water does not significantly change their FTIR spectra, see Fig. 1B and Fig. 2A (broken line) respectively.

Increasing the poly (ethylene oxide) (PEO) concentration in H_2O_2 causes acceleration of the photodecomposition of H_2O_2 (Fig. 3). Similar results have been reported [9] for photolysis of trimethacrylic acid and poly (methacrylic acid) in H_2O_2.

The PAA and PEO samples dissolved in H_2O_2 (30 wt-%) and UV irrradiated (254 nm) are simultaneously exposed to direct photolysis (under UV radiation) and to hydroxyl (HO•) and hydroperoxy (HO_2•) radicals formed from the photolysis of H_2O_2.

Almost all of these reactions (1) - (31) can be responsible for the photooxidative degradation of PAA and PEO. Pure PEO and PAA in the degraded forms are liquids (oligomers with molecular weight not exceeding few thousands). Under UV irradiation, semicrystalline spherulite structures of poly (ethylene oxide)(PEO) (Fig. 4A) are completely destroyed, (Fig. 4B) [11].

In order to separate photooxidative reactions of hydroxy (HO•) and hydroperoxy (HO_2•) radicals that are formed from the photolysis of H_2O_2 from reactions caused by pure UV irradiation, we employed the catalytic decomposition of H_2O_2 by metallic silver (Ag) [12]:

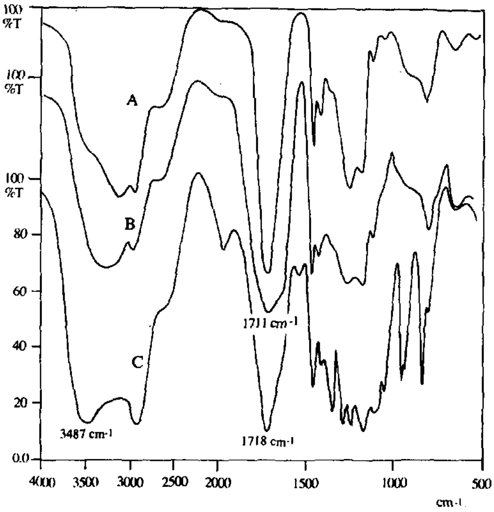


Figure 1. FTIR spectra of poly(acrylic acid)(PAA). (A) sample before irradiation; (B) after UV (254 nm irradiation in water 0 min; (C) after UV (254 nm) irradiation in H_2O_2 30 min

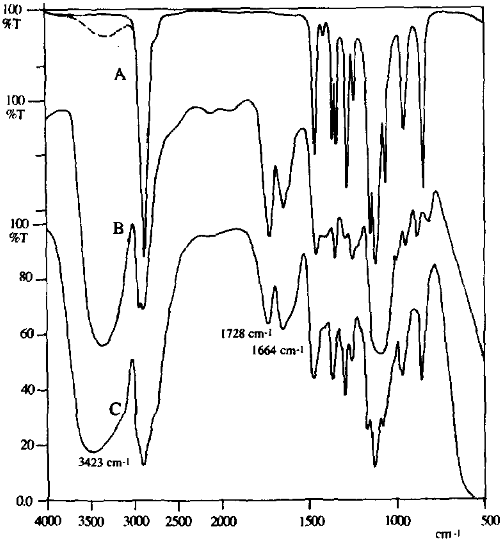


Figure 2. FTIR spectra of poly (ethylene oxide)(PEO). (A) sample before irradiation. The broken line shows change of the spectrum after UV (254 nm) irradiation in water 30 min; (B) after UV (254 nm) irradiation in H_2O_2 30 min; (C) PEO dissolved H_2O_2 after treatment with metallic Ag.

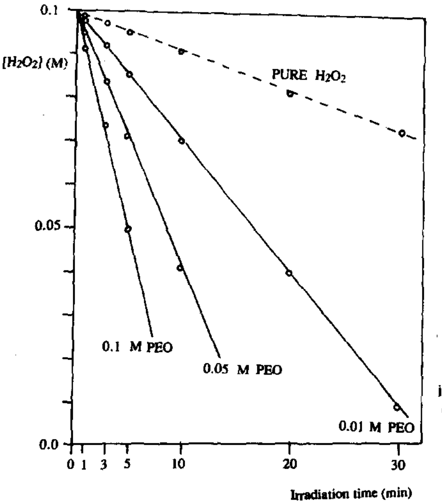


Figure 3. Kinetics of hydrogen peroxide (H_2O_2) photolysis in the presence of various concentrations of poly (ethylene oxide)(PEO)

$$Ag + H_2O_2 \longrightarrow Ag^+ + HO^- + HO\bullet \qquad (46)$$

$$HO\bullet + H_2O_2 \rightleftharpoons HO_2^- + H_2O \qquad (47)$$

$$Ag^+ + HO_2^- \rightleftharpoons (Ag^+\,{}^-OOH) \longrightarrow Ag + HO_2\bullet \qquad (48)$$

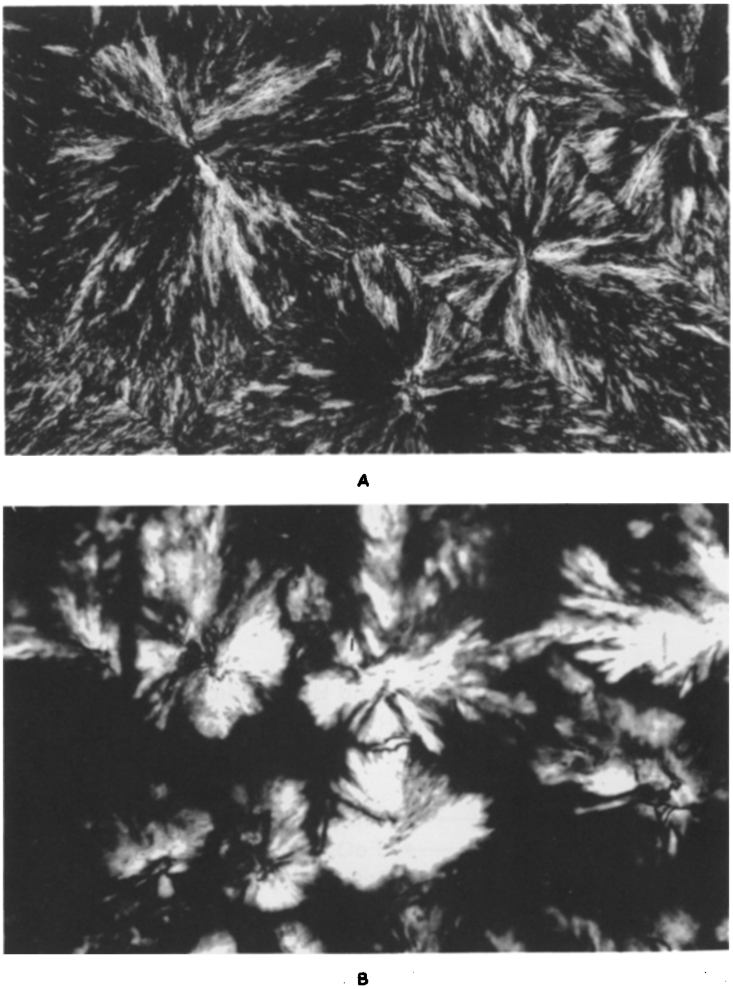
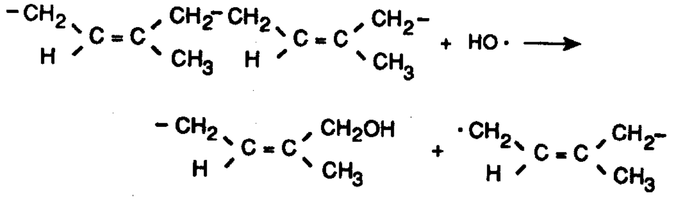


Figure 4. Microphotographs (x300) of: (A) poly(ethylene oxide)(PEO) spherulites and (B) photodegraded PEO spherulites after 60 min UV (254 nm) irradiation. Reproduced from [11].

In this chain reaction, the decomposition of H_2O_2 occurs at the surface of metallic silver. This is the "cleanest" method for the generation of HO• and HO_2• radicals. The FTIR spectrum of poly(ethylene oxide)(PEO) after treatment in H_2O_2 (30 wt-%) with metallic silver powder (Fig. 2C) is almost the same as the FTIR spectrum of PEO obtained after UV photolysis in H_2O_2, Fig.2 (B).

This is direct proof that hydroxy (HO•) and hydroperoxy (HO_2•) radicals react with PEO and are responsible for their oxidative degradation.

It has also been reported [13] that UV irradiation of natural rubber in the presence of H_2O_2 causes its oxidative degradation with simultaneous hydroxylation, according to the mechanism:



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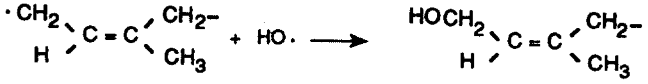

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The results presented above show that polymers in solutions are very susceptible to reactions with HO• and HO_2• radicals. However, we did not observe any reaction between HO• and HO_2• radicals and solid polyethylene film immersed in H_2O_2 (30-wt %) and UV irradiated (254 nm) during 3 hours, or treated in H_2O_2 with metallic silver. It is, therefore, doubtful that HO• and HO_2• radicals play an important role in the oxidative degradation of the solid polymers.

4. Reactions of iron chlorides (Fe^{3+}) and (Fe_2^{2+}) with H_2O_2 (Fenton reagents)

These reactions form the source of HO• and HO_2• radicals. A rapid and exothermic reaction of ferric chloride ($FeCl_3$) with H_2O_2 occurs by the following mechanism [14-16]:

$$Fe^{3+}\ H_2O_2 \longrightarrow FeO_2H^{2+} + H^+ \tag{51}$$
$$FeO_2H^{2+} + H_2O \longrightarrow FeO_2H + HO\bullet + H^+ \tag{52}$$
$$Fe^{3+} + H_2O + HO\bullet \longrightarrow FeO_2H^+ + 2H^+ \tag{53}$$
$$FeO_2H^+ + H_2O_2 \longrightarrow Fe^{2+} + HO\bullet + HO^- + H_2O + O_2 \tag{54}$$

Another mechanism postulates the following reactions:

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + H^+ + HO_2\bullet$$
$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO^- + HO\bullet$$
$$HO^- + H_2O_2 \longrightarrow H_2O + HO_2\bullet$$
$$HO_2\bullet + Fe^{3+} \longrightarrow Fe^{2+} + H^+ + O_2$$
$$HO_2\bullet + Fe^{2+} \longrightarrow Fe^{3+} + HO_2^-$$

The above mechanism is dependent on pH, presumably because of prior equilibria:

$$Fe^{3+} + H_2O_2 \rightleftharpoons [FeOOH^{2+} + H^+] \longrightarrow Fe^{2+} + HO_2\bullet \tag{60}$$

$$HO_2\bullet \longrightarrow H^+ + O_2^{-}\bullet \xrightarrow{Fe^{3+}} Fe^{2+} + O_2 \tag{61}$$

The above mechanisms predict a rate of H_2O_2 decomposition proportional to $[H_2O_2[Fe^{3+}] / [H^+]$ at high $[H_2O_2] / [Fe^{3+}]$ ratios. Ferrous ions (Fe^{2+}) formed in the reactions (55) and (58) are immediately oxidized to ferric ions (Fe^{3+}) by the Haber-Weiss rapid and exothermic reactions [14,17]:

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + HO\bullet \tag{62}$$
$$HO\bullet + H_2O_2 \longrightarrow HO_2\bullet + H_2O + O_2 \tag{63}$$

$$HO_2\bullet + H_2O_2 \longrightarrow HO\bullet + H_2O + O_2 \tag{64}$$
$$HO\bullet + Fe^{2+} \longrightarrow Fe^{3+} + OH^- \tag{65}$$
$$HO_2\bullet + Fe^{3+} \longrightarrow Fe^{2+} + H^+ + O_2 \tag{66}$$

Reactions of iron chlorides (Fe^{3+} and Fe^{2+}) with H_2O_2 can be used as sources of $HO\bullet$ and $HO_2\bullet$ for the study of their reactions with polymers.

It has been reported [18] that hydroxy ($HO\bullet$) and hydroperoxy ($HO_2\bullet$) radicals generated by the reaction of ferrous ions (Fe^{2+}) with H_2O_2 attack polyacrylamide molecules in aqueous solution.

In the presence of dissolved oxygen a chain scission reaction occurs with a consequent decrease in solution viscosity, whereas in the absence of oxygen, chain scission does not occur. The oxidative degradation of polyacrylamide is initiated by the reactions (6) and (9). However, it has been suggested that polymer alkyl radicals ($P\bullet$) can also participate in the reduction of Fe^{3+} ions (reaction (67) and the oxidation of Fe^{2+} ions, reaction (68):

$$P\bullet + Fe^{3+} \longrightarrow P^+ + Fe^{2+} \tag{67}$$
$$P\bullet + Fe^{2+} \longrightarrow P^- + Fe^{3+} \tag{68}$$
$$P^+ + OH^- \longrightarrow POH \tag{69}$$
$$P^- + H^+ \longrightarrow PH \tag{70}$$
$$H^+ + OH^- \longrightarrow H_2O \tag{71}$$

In experiments carried out with poly(ethylene oxide)(PEO) and Fenton reagents (Fe^{3+} and H_2O_2 (30 wt-%)), we have observed rapid oxidative degradation of polymers. The diffusion scattering FTIR spectra of PEO before treatment (Fig. 5A) and after reaction of PEO with $HO\bullet$ and $HO_2\bullet$ radicals (Fig. 5B), show the formation of two new bands at 3396 cm:$^{-1}$ and 1664 cm^{-}, attributed to the formation of HO/HOO and unsaturated end groups ($CH_2{=}CH{-}$, respectively.

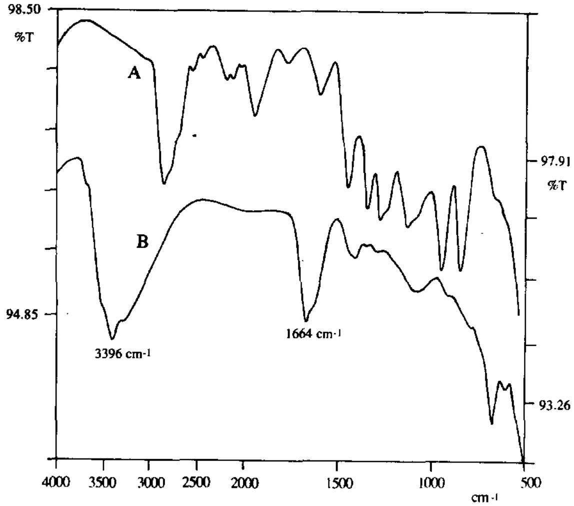


Figure 5. Diffusion reflectance FTIR spectra of poly(ethylene oxide) (PEO):. (A) sample before treatment and (B) after reaction with HO• and HO_2• radicals produced in Fenton reactions ($FeCl_3$ and H_2O_2).

5. Photochemical reactions of iron chlorides

Inorganic salts participate in a number of photochemical reactions [19]. The transfer of electrons from one ion to another ion, or to solvent molecules, plays an important role in the majority of inorganic photoreactions. A number of observations suggest that water of hydration participates in the electron transitions, e.g.:

$$X^{n}H_2O \xrightarrow{+h\nu} (X^{n+1}H_2O^-) \tag{72}$$

It is assumed that the latter species dissociates or reacts in various ways, for example:

$$(X^{n+1}H_2O^-) + H^+ \longrightarrow X^{n+1} + H_2O + H\bullet \tag{73}$$

$$(X^{n+1}H_2O^-) \longrightarrow X^{n+1} + HO^- + H\bullet \tag{74}$$

Cations which are photoreduced through an electron transfer process include: Hg^{2+} (180 nm), Cu^{2+}: (200 nm), Pb^{2+} (308 nm), Fe^{3+} (230 nm) and Ce^{4+} (320 nm). Aqueous solutions of these cations show a strong absorption; the electrons apparently originate from the water of hydration:

$$X^{n}H_2O \xrightarrow{+h\nu} (X^{n-1}H_2O^+) \tag{75}$$

$$(X^{n-1}H_2O^+) + OH^- \longrightarrow X^{n-1} + H_2O + HO\bullet \tag{76}$$

$$(X^{n-1}H_2O^+) \longrightarrow X^{n-1} + H^+ + HO\bullet \tag{77}$$

The absorption spectra of ion pairs of these cations with various anions are shifted towards the visible region and the magnitude of that shift is almost directly proportional to the decrease in the electron affinity of the anion. Thus for:

$Fe^{3+}Cl^-$, $\lambda_{max} = 320$ nm
$Fe^{3+} + Br^-$, $\lambda_{max} = 380$ nm
$FeSCN^-$, $\lambda_{max} = 460$ nm.

It may be concluded that in such ion pairs the anion carries the electron and the primary result of absorption is for example:

$$Fe^{3+}X^- \longrightarrow Fe^{2+}X \tag{78}$$

This is followed by various reactions of the intermediate compound, including its dissociation:

$$Fe^{2+}X \longrightarrow Fe^{2+} + X \tag{79}$$

The association of the Fe^{3+} (ferric) ion with chloride ions in water solution at pH1, excluding the hydration of the metal and complex ions, is as follow [20]:

$$Fe^{3+} + Cl^- \rightleftharpoons FeCl_{2+} \tag{80}$$
$$FeCl_{2+} + Cl^- \rightleftharpoons FeCl_2^+ \tag{81}$$
$$FeCl_{2+} + Cl^- \rightleftharpoons FeCl_3 \tag{82}$$
$$FeCl_3 + Cl^- \rightleftharpoons FeCl_4^- \tag{83}$$

Absorption spectra of $FeCl_3$ and these complex ions are shown in Fig.6. Solutions of ferric chloride ($FeCl_3$) in water contain, in addition to the chloro-complexes, the hydroxy-complexes $Fe(OH)^{2+}$,$Fe(OH)_2^+$ and $Fe(OH)_3$, which have been extensively investigated [21,22]. The absorption by the hydroxy-complexes is sufficiently large to interfere with the spectra of the chloro-complexes, even when the former are present in very small quantities [21].

Increase of pH causes formation of different iron hydroxy-complexes such as $FeOH^{2+}$, $Fe(OH)_2^+$, $Fe_2(OH)_4^+$, and $Fe(OH)_3$ [23-25], which causes additional complications of the investigated system. It is well known that $FeCl_4^-$ is formed in several solvent (S) systems, according to the reaction:

$$nS + 2Fe^{3+}(Cl_3^-)_3 \longrightarrow S_n(Fe^{3+}(Cl^-)_2)^+(Fe^{3+}(Cl^-)_4^- \tag{84}$$

The $FeCl_2^-$ is easily photolyzed with formation of reactive chlorine radicals:

$$FeCl_4^- \longrightarrow FeCl_2 + Cl^- + Cl\bullet \tag{85}$$

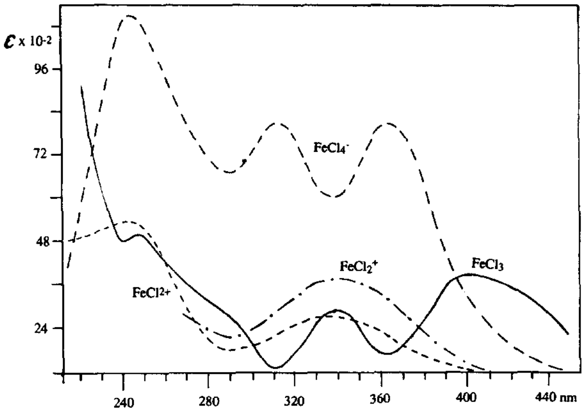


Figure 6. Absorption spectra of $FeCl_3$ and complex ions in water. Reproduced from [20].

The $FeCl_2$ in the presence of oxygen and HCl is oxidized to $FeCl_3$:

$$FeCl_2 + O_2 \longrightarrow Fe^{3+}(Cl^-)_2 + O_2^- \qquad (86)$$

$$O_2^- + HCl \longrightarrow HO_2\bullet + Cl^- \qquad (87)$$

$$Fe^{3+}(Cl^-)_2 + Cl^- \longrightarrow FeCl_3 \qquad (88)$$

In solvents (S), $HFeCl_4$ can be formed according to the reaction:

$$S_n(Fe^{3+}(Cl^-)_2)^+(Fe^{3+}(Cl^-)_4)^- + 2HCl \longrightarrow nS + 2HFeCl_4 \qquad (89)$$

The Fe_2^+ (ferrous) ions can also directly absorb UV radiation and produce free electrons according to the reactions:

$$Fe^{2+} \longrightarrow (Fe^{2+})^* \text{ (excited state)} \qquad (90)$$

$$(Fe^{2+})^* \text{ (in solid)} \xrightarrow{+h\nu} Fe^{3++} + e \qquad (91)$$

$$(Fe^{2+})^* \text{ (in liquid)} \xrightarrow{+h\nu} Fe^{3+} + e_{(solvated)} \qquad (92)$$

Electrons can freely move through a polymer matrix, until they are trapped [26]. In the presence of water the following reaction may occur:

$$(Fe^{2+})^* + H_3O^+ \longrightarrow Fe^{3+} + H_2O + H\bullet \qquad (93)$$

Photochemical reactions of polymers with $FeCl_3$ are discussed in section 7.

6. Complexes between polymers and ferric chloride ($FeCl_3$)

A number of polymers such as poly(ethylene oxide)(PEO) [27], poly(methyl methacrylate) [28], and poly(vinyl chloride)(PVC) [29] form complexes with $FeCl_3$. Absorption spectra of PEO-$FeCl_3$ (Fig. 7), and PVC-$FeCl_3$ (Fig. 8.) complexes show three peaks at 240, 312, and 364 nm (Fig. 8) that belongs to the $FeCl_4^-$ ion.

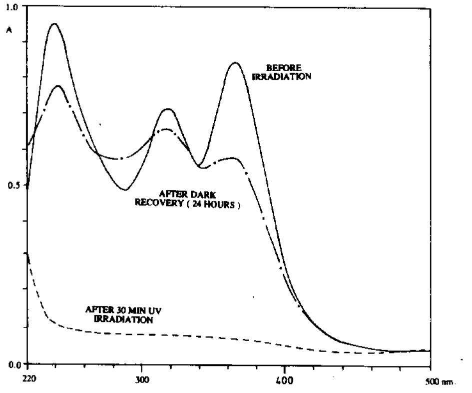


Figure 7. Change of UV/VIS absorption spectra of poly(ethylene oxide). (PEO)-$FeCl_3$ complex under UV irradiation. Reproduced from [27].

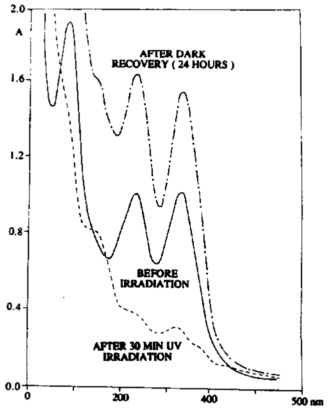
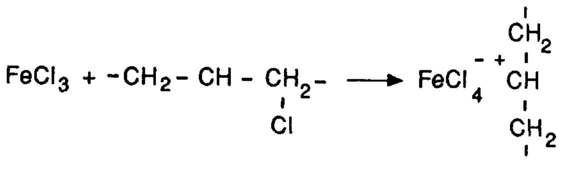


Figure 8. Change of UV/VIS absorption spectra of poly(vinyl chloride). (PVC)-$FeCl_3$ complex under UV irradiation. Reproduced from [29].

Under UV irradiation, all of these strongly colored complexes which contain $FeCl_4^-$ ions are bleached and their UV/VIS absorption decreases (Fig. 7 and Fig. 8). However, the yellow color and absorption spectra are reverted in the dark after 25 hours (Fig. 7 and Fig. 8). This photochromic effect is a result of the photo- reduction process due to a rapid electron exchange between ions $Fe^{2+} \cdots FeCl_4^-$ in the ion pair $FeCl_2^+ \cdots FeCl_4^-$ generated in the photoreduction of $FeCl_4^-$:

$$FeCl_2^+ \ldots FeCl_4^- \xrightarrow{+h\nu} \left[FeCl_2^+ \overset{+e}{\cdots\cdots} FeCl_3^-\right] + Cl\bullet \longrightarrow FeCl^+ \ldots FeCl_4^- \quad (94)$$

The polymer complex matrix plays an important role in $FeCl_3$ photoreduction kinetics. In poly(vinyl chloride)-$FeCl_3$ complexes, the $FeCl_4^-$ ions are formed by the direct reaction of $FeCl_3$ with polymer molecules[29]:



$$FeCl_3 + -CH_2-CH-\underset{\underset{Cl}{|}}{CH_2}- \longrightarrow \overset{-}{FeCl_4}\ \begin{array}{c} | \\ CH_2 \\ | \\ \overset{+}{C}H \\ | \\ CH_2 \\ | \end{array} \qquad (95)$$

The photochromic effect in the PVC-$FeCl_3$ complex has only been observed in the presence of oxygen.

In poly(ethylene oxide)(PEO)-$FeCl_3$ complexes, different crystalline structures are formed at different weight ratios of PEO:$FeCl_3$. For example, dendritic crystals are formed at a weight ratio of PEO:$FeCl_3$=7:3. (Fig. 9).

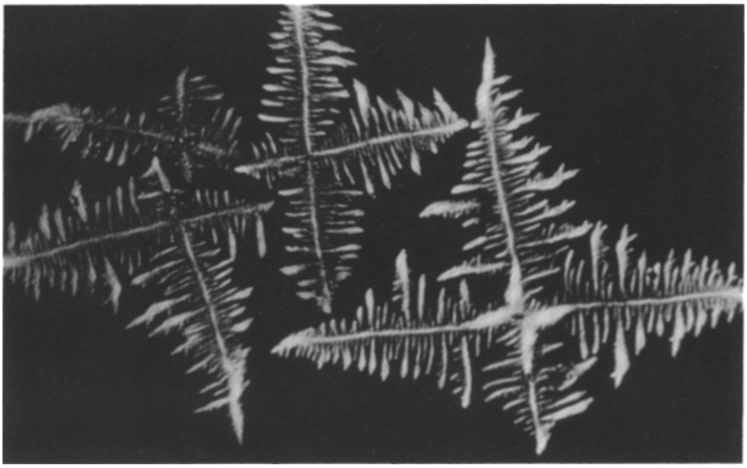
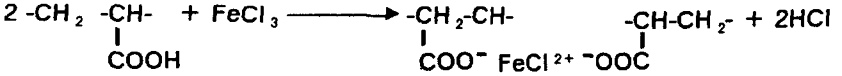


Figure 9. Microphotograph of dendritic crystals formed in poly(ethylene oxide). (PEO)-$FeCl_3$ (7:3) complex (scale bar, 100μm).

In the case of the polymer poly(acrylic acid), completely different complexes are formed, in which two carboxylic groups are involved in the reaction with $FeCl_3$[30]



$$2\ \text{-}CH_2\ \text{-}\underset{\substack{|\\ COOH}}{CH}\text{-}\ +\ FeCl_3 \longrightarrow \text{-}CH_2\text{-}\underset{\substack{|\\ COO^-}}{CH}\text{-}\ \ FeCl^{2+}\ \ \text{-}\underset{\substack{|\\ {}^-OOC}}{CH}\text{-}CH_2\text{-}\ +\ 2HCl \qquad (96)$$

Theoretically, $FeCl^{2+}$ ions can form intramolecular or inter molecular complexes with two carboxyl groups attached to one or two polymer molecules (Fig. 10).

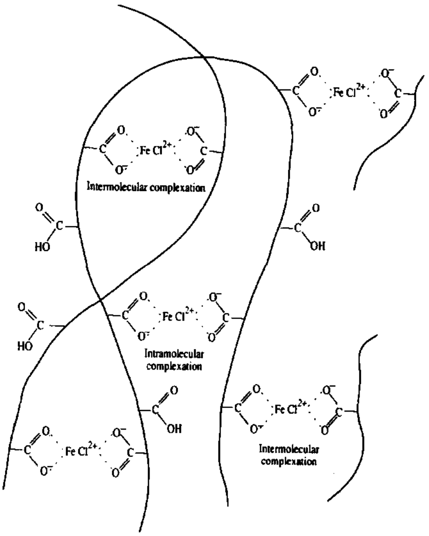


Figure 10. Probable structure of poly(acrylic acid). (PAA)-$FeCl_3$ complexes.

The FTIR spectra of poly(acrylic acid)-$FeCl_3$ complex (Fig. 11) show disappearing of the band at 1711 cm^{-1} (attributed to the carboxyl groups COOH) and formation of a new band at 1592 cm^{-1}. This is characteristic of the formation of ionized corboxyl groups (complexed with Fe^{2+}). The poly(acrylic-$FeCl_3$) complexes are strongly ionically crosslinked structures, which form a hydrogel that is completely nonsoluble in water. It is, however, hydrolysed by concentrated HCl. These gels have the ability to tighten channels in the dentin of human teeth and thereby decreases fluid transportation through the channels [30].

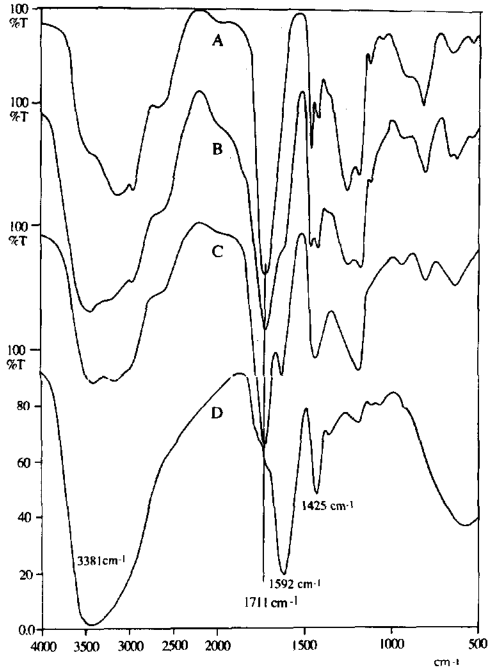


Figure 11. FTIR spectra of poly(acrylic acid). (PAA)-FeCl $_3$ complexes; (A) pure PAA; (B) PAC-FeCl $_3$ (100:1); (C) PAA-FeCl $_3$ (10:1) and (D) PAA-FeCl $_3$ (2:1).

7. Degradation of polymers photoinitiated by ferric chloride (FeCl$_3$)

Iron(III)chloride (ferric chloride, FeCl$_3$) markedly accelerate photodegradation of: polyethylene [31], polypropylene [32,33] poly(methyl methacrylate) [28,34-40], poly(vinyl alcohol) [41,42], poly(vinyl chloride) [29,43], poly(ethylene oxide) [11,27], poly(ethylene glycols) [44], polycaproamide [45], and cellulose [46-50].

The introduction of FeCl$_3$ into non-soluble polymers in water is a serious practical problem. Polymer samples (films or powders) can be immersed in acetone or nitromethane solutions of FeCl$_3$ of known concentration and then dried under vacuum. The amount of FeCl$_3$ adsorbed in the polymer samples, (pale yellow in color) can be determined by iodometric titration. However, the adsorbed FeCl$_3$ is observed to be limited mainly to the surface of the polymer samples.

On the other hand, there is no problem with the preparation of water soluble polymer samples with FeCl$_3$ at any given concentration directly from the water solution. Introduction of FeCl$_3$ to melted polymers is almost impossible, because ferric chloride accelerates thermal degradation. Chlorine radicals (Cl•) formed during photolysis of $FeCl_3$ are very reactive species and can abstract hydrogen at any carbon group in a polymer, causing a rapid degradation. Fig. 12 shows the kinetic curves of poly(ethylene oxide)(PEO) degradation in the presence of different concentrations of $FeCl_3$ [11].

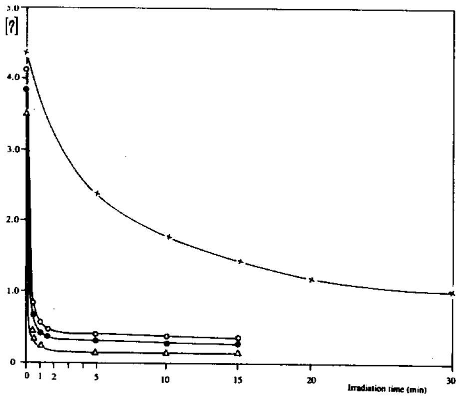


Figure 12. Changes of intrinsic viscosities for. (x) pure poly(ethylene oxide)(PEO); (o) PEO-$FeCl_3$ (9:1), (o) PEO-$FeCl_3$ (7:3); and (Δ) PEO-$FeCl_3$ (5:5) in nitromethane solutions (1 wt-%) during UV irradiation (254 nm). Reproduced from [11].

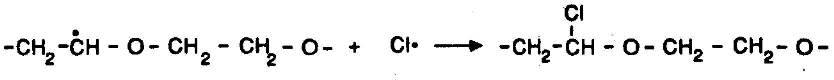
The main reactions responsible for the photodegradation of poly(ethylene oxide)(PEO) in the presence of $FeCl_3$ are as follows:

$$\mathrm{-CH_2-CH_2-O-CH_2-CH_2-O- + Cl\bullet \longrightarrow -CH_2-\dot{C}H-O-CH_2-CH_2-O- + HCl} \quad (97)$$

$$\mathrm{-CH_2-\dot{C}H-O-CH_2-CH_2-O- \longrightarrow -CH_2-\overset{H}{\underset{O}{C}} + \bullet CH_2-CH_2-O-} \quad (98)$$

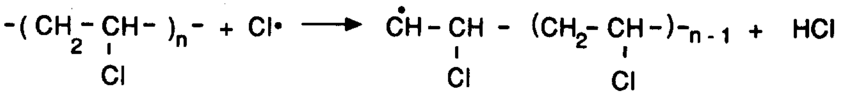
$$\mathrm{-CH_2-CH_2-O-CH_2-CH_2-O- + \bullet CH_2-CH_3-O- \longrightarrow}$$

$$\mathrm{-CH_2-\dot{C}H-O-CH_2-CH-O- + CH_3-CH_2-O-} \quad (99)$$

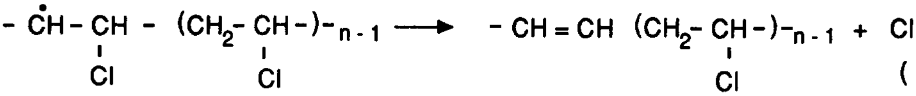


$$\mathrm{-CH_2-\dot{C}H-O-CH_2-CH_2-O- + Cl\bullet \longrightarrow -CH_2-\overset{Cl}{\overset{|}{C}}H-O-CH_2-CH_2-O-} \quad (100)$$

The chlorine radical (Cl) also reacts with poly(vinyl chloride)(PVC) [13,15]. In the absence of oxygen (air) the dehydrochlorination reaction leads to formation of conjugated polyene sequences:



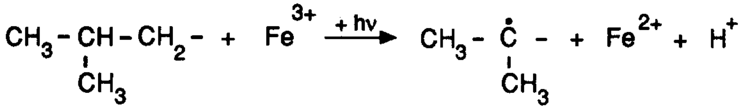
$$-(CH_2-\underset{Cl}{CH}-)_n- + Cl\bullet \longrightarrow \dot{C}H-\underset{Cl}{CH}-(CH_2-\underset{Cl}{CH}-)-_{n-1} + HCl \qquad (101)$$



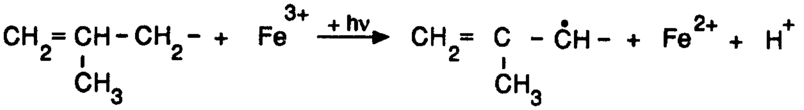
$$-\underset{Cl}{\dot{C}H}-\underset{Cl}{CH}-(CH_2-\underset{Cl}{CH}-)-_{n-1} \longrightarrow -CH=CH\ (CH_2-\underset{Cl}{CH}-)-_{n-1} + Cl\bullet \qquad (102)$$

In the presence of oxygen (air) poly(vinyl chloride)(PVC) alkyl radicals (P•) are oxidized to polymer peroxy (POO•) radicals (reaction (7)), which further participate in chain scission and crosslinking reactions.

It has been reported [31] that $FeCl_3$ suppresses the formation of polymer alkyl (P) radicals in photodegraded polythelene with UV radiation < 300 nm. It does, however, accelerate double bond formation. At radiations > 300 nm, addition of $FeCl_3$ to polyethylene accelerates the formation of polymer alkyl peroxy radicals (POO•). Ferric chloride ($FeCl_3$) accelerates the formation of radicals from hydrocarbons containing a hydrogen atom on a tertiary carbon or an allylic position [32]. These reactions can be explained by the following redox catalytic mechanism:



$$CH_3-\underset{CH_3}{CH}-CH_2- + Fe^{3+} \xrightarrow{+h\nu} CH_3-\underset{CH_3}{\dot{C}}- + Fe^{2+} + H^+ \qquad (103)$$



$$CH_2=\underset{CH_3}{CH}-CH_2- + Fe^{3+} \xrightarrow{+h\nu} CH_2=\underset{CH_3}{C}-\dot{C}H- + Fe^{2+} + H^+ \qquad (104)$$

However, there is no experimental proof for the occurrence of the redox catalytic mechanism.

8. Decomposition of polymeric hydroperoxides by iron salts

Transition metal ions of variable valence readily form complexes with hydroperoxide groups (OOH), which are photodecomposed under UV irradiation with the formation of polymer alkyl peroxy (POO) and polymer alkyl oxy (PO•) radicals [52]:

$$Fe^{3+} + POOH \rightleftarrows (Fe^{3+}\cdots HOOP)\ \text{(complex)} \qquad (105)$$

$$(\mathrm{Fe}^{3+} \cdots \mathrm{HOOP}) \xrightarrow{+h\nu} \mathrm{Fe}^{2+} + \mathrm{POO}\bullet + \mathrm{H}^{+} \quad (106)$$

$$\mathrm{Fe}^{2} + \mathrm{POOH} \rightleftharpoons (\mathrm{Fe}^{2+} \cdots \mathrm{HOOP})\ (\mathrm{complex}) \quad (107)$$

$$(\mathrm{Fe}^{2+} \cdots \mathrm{HOOP}) \xrightarrow{+h\nu} \mathrm{Fe}^{3+} + \mathrm{PO}\bullet + \mathrm{H}^{+} \quad (108)$$

The $FeCl_3$ may also cause decomposition of chain hydroperoxides in polyacrylamide without light [53].

9. Conclusions

The introduction of transition metal ions into polymers reduces the outdoor lifetime of most polymers. The problem is that they cannot be incorporated as salts into polymers because they accelerate thermal degradation of polymers (by catalytic decomposition of polymeric hydroperoxides) during processing. Overcoming this problem is difficult, but not impossible.

On other hand, the recycling of plastic waste into the original application or into the secondary products does not allow the presence of even traces of metal salt contaminants, because they have disastrous effects on outdoor stability.

Application of transition metal ions is very promising for the development of rapid photodegradable polymers, especially for application in agriculture. Large solar photoreactors can be used for photoinitiating (using metal salts) the degradation process of waste polymeric materials.

10. Experimental section

The experiments described in this paper have been carried out with two water soluble polymers: poly(ethylene oxide)(type Polyox WSRN 750,Union Carbide) and poly(acrylic acid)(Aldrich).

Hydrogen peroxide (H_2O_2) solution in water, 30 wt-%)(Aldrich) was used as delivered. Concentrations of H_2O_2 less than 0.001 M, were determined iodometrically. Above 0.001 M, concentrations were determined by titration with potassium permanganate.

Anhydrous iron (III) chloride ($FeCl_3$) (Merck) was used as delivered. UV/VIS and FITR spectra were recorded with Beckman 7500 UV-VIS and FT-IR Perking Elmer 1650 spectrometers, respectively. Some FTIR spectra were made with the diffusion reflectance attachment (Perkin-Elmer). Photomicrographs were made with the Nikon Polarizing Microscope type Optiphot-2 Pol.

Acknowledgements

We would like to thank Alan Bamford who helped with the editing and preparation of this paper.

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