

## The UV/H<sub>2</sub>O<sub>2</sub> - Photodegradation of Poly(ethyleneglycol) and Model Compounds

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O mecanismo geral para a fotodegradação do polietilenoglicol (PEG) usando o sistema H<sub>2</sub>O<sub>2</sub>/UV foi determinado por GPC e HPLC, analisando o comportamento de moléculas modelo, como por exemplo os etilenoglicóis de baixa massa molar (tetra-, tri-, di-, e etilenoglicol). Após 30 min de irradiação, a massa molar ponderal média ( $M_w$ ) do PEG degradado, analisada por GPC, cai para metade do seu valor inicial com um aumento concomitante na polidispersidade e número médio de quebra de cadeia (S). Essa queda acentuada caracteriza uma quebra de cadeia aleatória, formando oligômeros e etilenoglicóis de menor massa molar. A análise da fotodegradação de etilenoglicóis modelo por HPLC permitiu sugerir um mecanismo que envolve processos consecutivos, em que etilenoglicóis maiores originam menores, sucessivamente. A fotodegradação do etilenoglicol formou ácidos carboxílicos de baixa massa molar, como por exemplo os ácidos glicólico, oxálico e fórmico.

The general mechanism for the photodegradation of polyethyleneglycol (PEG) by H<sub>2</sub>O<sub>2</sub>/UV was determined studying the photooxidation of small model molecules, like low molecular weight ethyleneglycols (tetra-, tri-, di-, and ethyleneglycol). After 30 min of irradiation the average molar mass ( $M_w$ ) of the degraded PEG, analysed by GPC, fall to half of its initial value, with a concomitant increase in polydispersity and number of average chain scission (S), characterizing a random chain scission process yielding oligomers and smaller size ethyleneglycols. HPLC analysis of the photodegradation of the model ethyleneglycols proved that the oxidation mechanism involved consecutive reactions, where the larger ethyleneglycols gave rise, successively, to smaller ones. The photodegradation of ethyleneglycol lead to the formation of low molecular weight carboxylic acids, like glycolic, oxalic and formic acids.

**Keywords:** photooxidative degradation, H<sub>2</sub>O<sub>2</sub>/UV system, poly(ethyleneglycol), ethyleneglycols

### Introduction

Studies of polymer degradation are performed with two main objectives: on one side, envisaging the improvement of the photostability and prolongation of the lifetime of polymers, and on the other side, finding methods to improve the polymer degradation, aiming to reduce pollution originated from discarded materials. Many of the synthetic polymers are not very sensitive to biodegradation and, sometimes, also very resistant to photodegradation, so that frequently additives have to be added to increase their degradability.<sup>1</sup>

Polymer oxidation is improved by various factors, such as sunlight, ozone, heat, radiation, mechanical stress, traces of transition metal ions, water, pollutants and microorganisms. Lately, great attention has been given

to advanced oxidation processes (AOPs),<sup>2</sup> which involve oxidation mechanisms that are initiated by active free radicals that play the role of oxidative agents. AOPs, which may also involve photochemically initiated degradation processes, have been proposed for the treatment of ground, surface and wastewaters containing biocidal or non-biodegradable organic compounds. These processes are generally based on oxidative degradation reactions, often initiated by hydroxyl radicals generated by several methods (UV photolysis of hydrogen peroxide, TiO<sub>2</sub> photocatalysis, vacuum ultraviolet (VUV) photolysis of water, Fenton and photo-Fenton reactions).<sup>3</sup> Due to its high oxidation potential ( $E^0 = +2.80$  V), hydroxyl radicals oxidize almost all organic substances and mineralize them to carbon dioxide and water.

In the presence of UV radiation (*ca.* 250 nm) hydrogen peroxide decomposes efficiently forming short-lived oxidizing hydroxyl radicals. These radicals react with

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organic compounds abstracting hydrogen and generating organic radicals that by addition of molecular oxygen yield peroxy radicals. These intermediates initiate thermal chain reaction that leads to the oxidative degradation of the polymers, yielding eventually carbon dioxide, water and inorganic salts. Oxidative degradation can also be initiated by electron transfer to the hydroxyl radicals.

The hydrogen peroxide processes have several advantages over other oxidizing sources used for polymer degradation, like commercial availability, minimal capital investment, thermal stability and on-site storage, which renders them very cost-effective systems. Physical properties, like its infinite solubility in water, the lack of mass transfer problems associated with gases, and the readiness of the reactions of the HO• radicals with most organic substrates, also contribute to make these systems very useful.

Poly(ethyleneglycols) (PEGs) are water soluble polymers widely used in industrial and household products, as surfactants, drug release vehicles, colloidal stabilizer. Although these polymers are non toxic and biocompatible, when discarded after use, they will contribute to environmental problems and their disposal is necessary.<sup>4</sup> Low molecular weight ethyleneglycols can be successfully used as model molecules to predict the behaviour of larger molecular mass PEG's. Glastrup<sup>5,6</sup> studied the thermal degradation of tetraethyleneglycol under different conditions and analyzed the degradation products by gas chromatography, proposing a mechanism where formic acid and other oxidation products are formed. McGinnis<sup>7,8</sup> oxidized ethyleneglycol using Fenton's reagent and H<sub>2</sub>O<sub>2</sub>/UV, suggesting a possible pathway for the mineralization of ethyleneglycol, going through glycolic, glyoxylic, oxalic and formic acids. Studies of the rate and extent of the oxidative degradation of diethyleneglycol by both ozone and hydrogen peroxide and a ferric salt allowed the identification of the main reaction products.<sup>9</sup>

In the present work, small molecular weight ethyleneglycols (tetra-, tri-, and diethyleneglycol, as well as ethyleneglycol) were used as models to predict the photo-oxidative degradation mechanism of poly(ethyleneglycol), PEG. The photooxidation reaction was initiated by UV-irradiation of hydrogen peroxide and the degradation products were analysed by high performance liquid chromatography (HPLC).

## Experimental

### Materials

PEG 3350 (Fluka), tetra- and triethyleneglycol (Across Organics), diethyleneglycol (Fenil Química),

and ethyleneglycol (J. T. Baker) were used as supplied. Hydrogen peroxide 30% was purchased from Merck.

### Sample preparation

Hydrogen peroxide was added to solutions containing the ethyleneglycols in Milli-Q water. The solutions were placed in quartz tubes and the photodegradation processes took place in an irradiation chamber using the 254 nm emission of 96-W Ultraviolet Germicidal lamps. For the identification and quantification of the generated products, aliquots were withdrawn at appropriate times from the reaction flasks and analysed.

### Gel permeation chromatography (GPC)

Average molar masses ( $M_w$ ) were determined by GPC on a Shimadzu LC-10 AD chromatographic system with a Shimadzu RID – 6A refractive index detector. 100  $\mu$ L of the solutions were injected in three OHPAK KB-806M columns. Milli-Q water was used as the eluent at a flow rate of 1 mL min<sup>-1</sup>. Narrow-distribution poly(ethyleneglycol) standards (American Polymer Standards Corp.) were used for calibration.

### High performance liquid chromatography (HPLC)

Degradation products were determined using a Shimadzu LC-10 AD chromatographic system with a Rezex 00H-0138-KO Rezex 8 $\mu$  8% 300  $\times$  7.8 mm column using sulphuric acid 0.005 mol L<sup>-1</sup> as mobile phase at a 0.6 mL min<sup>-1</sup> flow rate. A Shimadzu RID – 6A refractive index detector was used and volumes of 100  $\mu$ L of sample were injected.

The reaction products and intermediate species from EG's and PEG photodegradation were identified by comparison with previously injected standard samples. The presence of H<sub>2</sub>O<sub>2</sub> did not affect the retention times of the samples.

## Results and Discussion

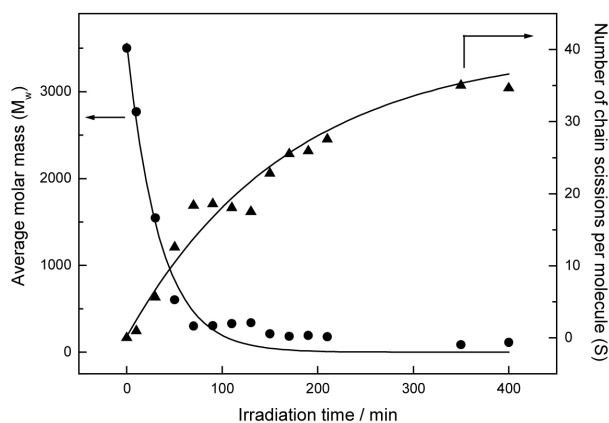
### PEG photodegradation

#### GPC analysis

The average molar mass of the polymers were determined by GPC, before and during UV irradiation. A calibration curve was obtained previously using known molecular weight PEG samples. The results for the oxidative photodegradation of PEG are shown in Table 1, and prove that irradiation causes chain scissions

**Table 1.** Average molar mass ( $M_w$ ), polydispersity ( $M_w/M_n$ ), average chain scissions per molecule ( $S$ ) and number of scission events ( $N_t$ ) per gram of PEG

Irradiation time (min)	$M_w$ (mol g <sup>-1</sup> )	$M_w/M_n$	$S$	$N_t$
0	3500	1.0	0	0
10	2770	1.7	1	$3 \times 10^{-4}$
30	1550	3.0	6	$2 \times 10^{-3}$
50	600	2.5	13	$4 \times 10^{-3}$
70	300	-	18	$6 \times 10^{-3}$
90	300	-	19	$6 \times 10^{-3}$
110	330	-	18	$6 \times 10^{-3}$
130	340	-	18	$5 \times 10^{-3}$
150	210	-	23	$7 \times 10^{-3}$
170	180	-	26	$8 \times 10^{-3}$
190	190	-	26	$8 \times 10^{-3}$
210	180	-	28	$8 \times 10^{-3}$
320	85	-	35	$1 \times 10^{-2}$
350	110	-	40	$1 \times 10^{-2}$
400	120	-	35	$1 \times 10^{-2}$



**Figure 1.** Evolution of the molar mass and the number of chain scissions during photodegradation of PEG.

and the decrease of the  $M_w$ . Undegraded samples are characterized by average molar masses in the range of 3500 D. A fast drop of the molar mass can be observed during the first 70 min of irradiation, after which the  $M_w$  remains practically constant (Figure 1).

The exponential decay indicates a random chain scission process rather than a depolymerization process, which would lead to a slower decrease of the  $M_w$ .<sup>10</sup>

The number of average chain scission ( $S$ ) per molecule can be calculated from:<sup>11</sup>

$$S = [M_n(0)/M_n(t)] - 1 \quad (1)$$

where  $M_n(0)$  and  $M_n(t)$  are the number average molar mass of the polymer before and after  $t$  min of UV irradiation, respectively.

The number of scission events per gram of PEG,  $N_t$ , is calculated using<sup>10,11</sup>

$$N_t = [1/M_n(t)] - [1/M_n(0)] \quad (2)$$

The change of  $N_t$  for different times irradiations is shown in Table 1 and shows an increase during the first 70 min of irradiation. The progress of the PEG's photodegradation processes could also be assessed by the number of average chain scissions ( $S$ ) per molecule. It can be seen in Figure 1 that  $S$  increases with irradiation time, matching the exponential decay of the  $M_w$ , confirming a random chain scission mechanism.

The polydispersity ( $M_w/M_n$ ) of the UV-irradiated samples is also shown in Table 1. It can be seen that the system starts off from a solution where all the chains have almost the same length, and under irradiation changes to a wider distribution of  $M_w$ , indicating that the system becomes less uniform. This behaviour is expected for degraded polymers, as irradiation will promote an increase in the number of polymer chains, lowering the  $M_n$ , and consequently increasing the polydispersity. These results are similar to those obtained by Hoekstra *et al.*<sup>11</sup> for the oxidation of high density polyethylene (HDPE), where the oxidized polymers presented higher polydispersity than the original samples.

#### HPLC analysis

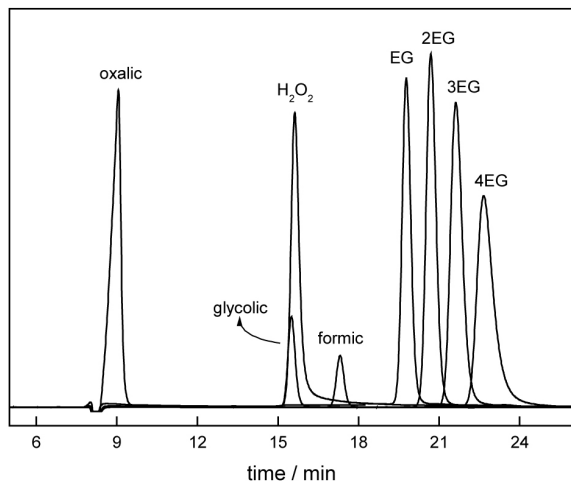
After 10 min of irradiation of the PEG samples, practically all the lower molecular weight products shown in Table 2 were detected, *i.e.*, 4EG, 3EG, 2EG, EG, glycolic, oxalic and formic acids. All of them were identified using the retention times of standard samples, as shown Figure 2.

A chromatographic peak at larger retention time (25.8 min) was also observed, suggesting the formation of

**Table 2.** Retention times for ethyleneglycols and some oxidation products

Compound	Retention time (min)
Oxalic acid	8.7
Glycolic acid	15.5
H <sub>2</sub> O <sub>2</sub>	15.6
Formic acid	17.3
EG	19.8
2EG	20.7
3EG	21.6
4EG	22.7

a species with molecular weight higher than 4EG, probably an oligomer arising from a PEG scission. All the degradation products remain in solution even after 120 h of irradiation, indicating that practically all the initially present H<sub>2</sub>O<sub>2</sub> is consumed during the initial 60 min of irradiation.



**Figure 2.** Chromatographic analysis of ethyleneglycols and photodegradation products.

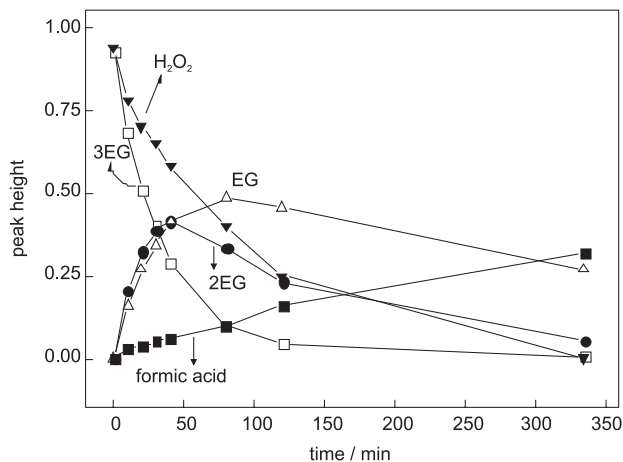
#### Photodegradation of model compounds

4EG, 3EG, 2EG and EG were used as model molecules to ascertain the degradation mechanism of the photooxidation of PEG polymers. The lower molar weight ethyleneglycols always appear as primary decomposition products in the photodegradation of PEG, so that the degradation mechanism of these smaller molecules can reasonably be extended to the photodegradation of the higher molecular weight polymers.

Triethyleneglycol and tetraethyleneglycol, as well as their degradation products, are small enough to be analysed directly by HPLC. It is expected that these molecules will undergo the same type of reactions found on larger molecular weight PEG. Besides the two end hydroxyl groups they bear two vicinal ether groups which might be under the influence of the hydroxyl groups. There is also a central ether group that should be under the only influence of other ether groups.<sup>6</sup>

**Triethyleneglycol.** The peak attributed to 3EG with retention time of 21.6 min decreases continuously during UV-irradiation, and new peaks with retention times around 20.7 and 19.8 min develop simultaneously, characterizing the formation of 2EG and EG (Figure 3).

The consumption of hydrogen peroxide is slightly faster than the simultaneous disappearance of the 3EG peak. It can be noticed that after the initial growth, the 2EG and the EG peaks start to fall off, due to their degradation process. It can also be noticed that the maximum reached by the diethyleneglycol occurs at shorter times than that



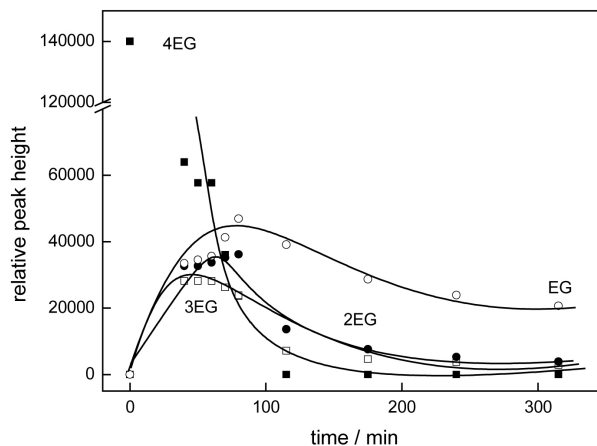
**Figure 3.** Time evolution of the concentration of the reaction products during the photodegradation of triethyleneglycol.

of ethyleneglycol, confirming a sequential degradation process. Formic acid, which is one of the final products, grows steadily during all the photodegradation process. The global degradation process for triethyleneglycol can be characterized by the sequence:

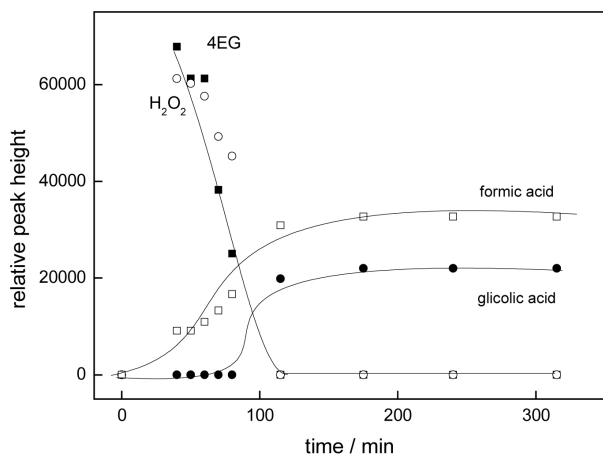


**Tetraethyleneglycol.** After 10 min of irradiation of 4EG, the chromatograms showed the formation of 3EG, 2EG, EG, and oxalic and formic acid, simultaneous to the 4EG consumption, as shown in Figure 4. The degradation pattern is similar to that obtained for the photo-oxidation of 3EG, as well as for the other EG's, that is, the presence of smaller EG's and carboxylic acids simultaneous to the disappearance of the original EG.

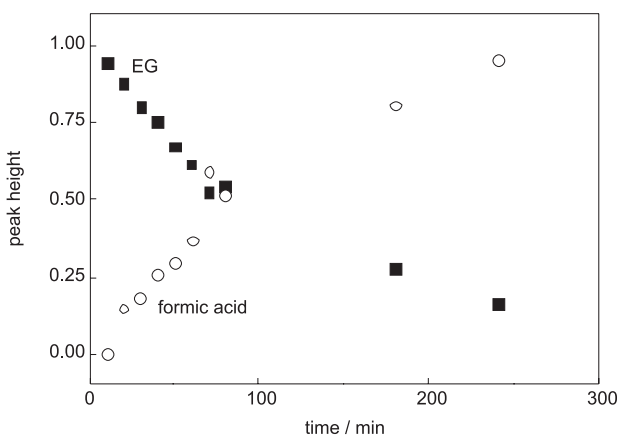
**Ethyleneglycol.** The photodegradation of EG was monitored by the behaviour of the 19.8 min retention time peak (Figure 5).



**Figure 4a.** Time evolution of the concentration of the smaller ethyleneglycols during the photodegradation of tetraethyleneglycol.



**Figure 4b.** Time evolution of hydrogen peroxide and formic and glycolic acid during the photodegradation of tetraethyleneglycol.



**Figure 5.** Photodegradation of ethyleneglycol and formation of formic acid.

A continuous decay is observed during the first 60 min of irradiation and the total disappearance occurs between 240 and 570 min. Figure 2 also shows the formation of formic acid resulting from the EG degradation, reaching the highest concentration after 570 min. It was found that even after 24 and 72 h irradiation, the formic acid concentration remained constant. This can be attributed to an extremely slow photodegradation of formic acid in the absence of  $\text{H}_2\text{O}_2$ , as probably all the hydrogen peroxide

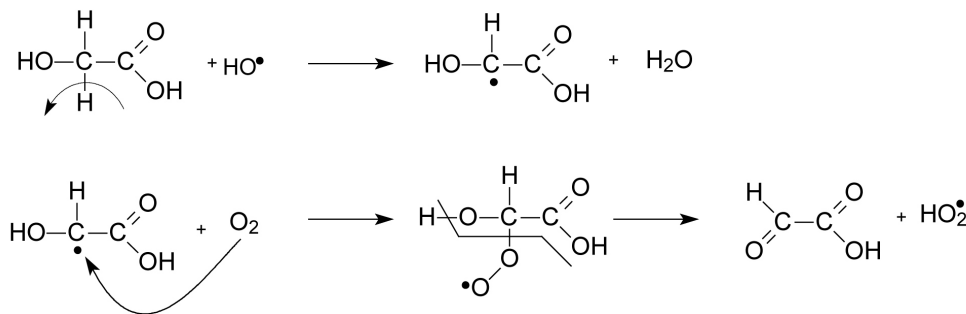
was already consumed after 570 min, proving additionally that all the oxidation processes occurred via the hydrogen peroxide photodecomposition, with no contribution of reactions involving photodecompositions of any of the intermediates or final products. Oxalic acid was found in samples irradiated for at least 570 min.

Although hydrogen peroxide has a similar retention time than glycolic acid (15.6 min), the presence of the latter during the degradation of smaller ethyleneglycols could be confirmed by HPLC. As shown in the Figure 5, the 15.6 min peak increases about 20% after 10 min of UV-irradiation and remains more or less constant up to 72 h thereafter. As hydrogen peroxide will obviously be consumed during the photodegradation process, the increase of the peak should be ascribed to the formation of the glycolic acid.

Thus, under the conditions used in this work, the hydrogen peroxide concentration can be considered to be the limiting factor for the photodegradation during the first 3 h, after which it is totally consumed. The low molecular weight acids formed during the photodegradation (glycolic, oxalic and formic acids), continue to be present as their photodegradation is less efficient than the photodegradation of the smaller ethyleneglycols, which practically consume the whole of the oxidizing agent.

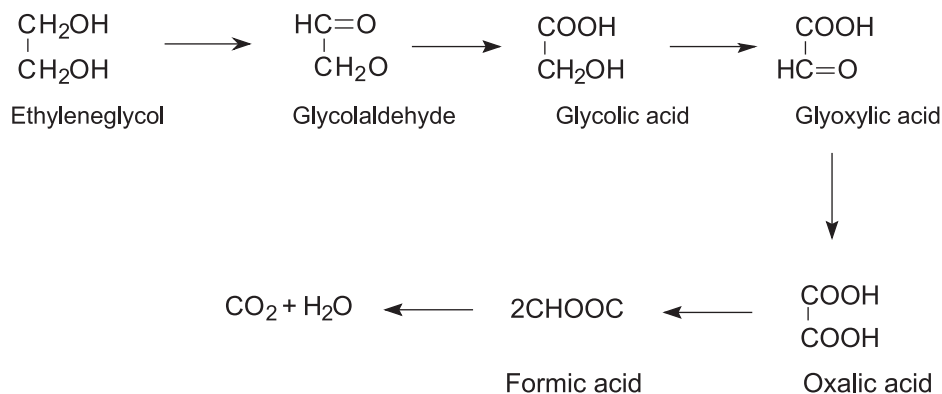
#### *Photodegradation of carboxylic acids*

The irradiation of the carboxylic acids was performed using the same conditions of the previous experiments. Experiments carried out with the  $\text{H}_2\text{O}_2/\text{UV}$  system indicate that the degradation of glycolic acid yields oxalic and formic acids. According to the mechanism proposed by Leitner<sup>12</sup> for the oxidation of glycolic acid, the hydroxyl radicals formed by the UV-irradiation of  $\text{H}_2\text{O}_2$  abstract carbon-bound hydrogen atoms from the substrate. Then, the substrate radicals rapidly add oxygen, forming peroxy radicals that do eliminate  $\text{HO}_2^\bullet$ , which initiates the degradation chain reaction. The glyoxylic acid resulting from the oxidation of glycolic acid is transformed into oxalic acid following the same routes (Scheme 1).



**Scheme 1.** Photooxidation of carboxylic acids.





**Scheme 2.** Mineralization of carboxylic acids.

Although some studies<sup>7,8,12</sup> propose the conversion of oxalic acid into formic acid (Scheme 2), under the conditions used in our experiments, this was not observed.

## Conclusions

The present study proves that the photolysis of hydrogen peroxide is a good source of hydroxyl radicals, which lead to the photodegradation of poly(ethyleneglycol). Chromatographic analysis made it possible to demonstrate that the H<sub>2</sub>O<sub>2</sub>/UV system is efficient in degrading PEG, which undergoes a random chain scission process, yielding oligomers, tetraethyleneglycol, triethyleneglycol, diethyleneglycol, ethyleneglycol and its lower molecular weight decomposition products.

The smaller ethylene glycols were successfully used as model molecules to predict the PEG behaviour. Tetraethyleneglycol, as well as the other ethyleneglycols used, decomposes generating smaller ethyleneglycols. HPLC analysis also proved that the degradation of ethyleneglycol leads to glycolic, oxalic and formic acids

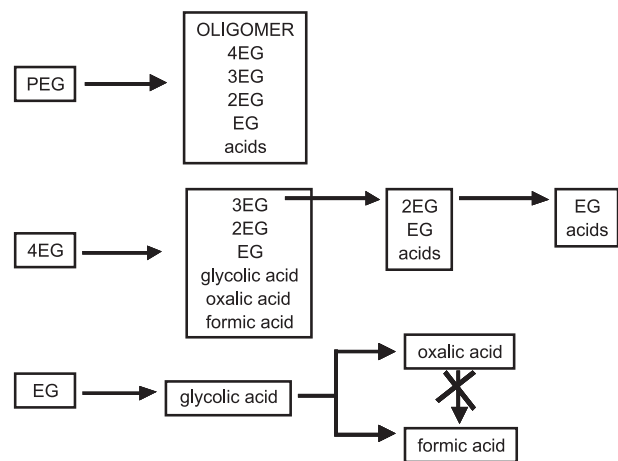
when irradiated in the presence of hydrogen peroxide, as shown in Scheme 3.

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**Scheme 3.** Photodegradation pathways for PEG and small ethyleneglycols.

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