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Photo-Fenton Degradation of Poly(ethyleneglycol)

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Polietilenoglicol (PEG) foi fotooxidado usando o sistema foto-Fenton e comparando com a reação no escuro. Os produtos foram analisados por GPC e HPLC. As amostras tratadas na ausência de luz necessitaram 490 min para que a $\overline{M}_w$ decrescesse em 50%, enquanto que sob irradiação UV essa mesma proporção foi obtida em 10 min. O decaimento exponencial de $\overline{M}_w$ com um concomitante aumento na polidispersividade e o número de quebras de cadeia caracteriza um mecanismo de quebra de cadeia aleatório. Os produtos da degradação de PEG em ambos os casos mostram a presença de produtos de massa molecular menor, incluindo etilenoglicóis menores e o ácido fórmico. O mecanismo da fotodegradação corresponde a processos consecutivos, onde etilenoglicóis de maior massa molar geram outros de menor massa, envolvendo quebras sucessivas das cadeias do polímero. O estudo demonstra que o processo de foto-Fenton com irradiação UV é um bom método para a decomposição de PEG.

Polyethyleneglycol (PEG) was photooxidized in a photo-Fenton system and results compared with the dark reaction. The products were analysed using GPC and HPLC. In the absence of light, PEG samples needed 490 min to reduce their $\overline{M}_w$ by 50%, whereas under UV irradiation, only 10 min were necessary. The exponential decay of $\overline{M}_w$ with a concomitant increase in polydispersity and number of average chain scission, characterized a random chain scission mechanism. The degradation products of PEG in both systems showed the presence of lower molecular weight products, including smaller ethyleneglycols and formic acid. The mechanism involves consecutive processes, were the larger ethyleneglycols give rise, successively, to smaller ones. This suggests that the mechanism involves successive scissions of the polymer chain. Irradiated samples decomposed faster than those kept in the dark This study proves that the foto-Fenton method associated with UV-light is a good reactant for PEG photodegradation.

Keywords: polyethyleneglycol, Fenton, photo-Fenton

Introduction

Polyethylene glycol (PEG) is a polymer largely used in several applications. It is soluble in water and in many polar organic solvents, and shows hydrophilicity and biocompatibility.[1] After use, it is generally discarded into the aqueous environment. This is due to the difficulty in recovering or recycling the polymer. Its fate in the environment is not well known, as it is not biodegradable, neither are known its toxicity and that of possible degradation products. Moreover, as it is not used generally in packaging industry, it has received less attention than other high-polluting packaging plastics like polyethylene, polystyrene and others. The thermo-oxidative degradation of PEG has been extensively reported.[1-3] However, there are very few reports about the oxidative photodegradation of PEG[4-6] and PEO (poly(ethylene oxide).[7,8]

Studies of polymer degradation have shown that practically all polymers and polymer-based materials are oxidized by atmospheric oxygen. It is known that the reactions induced in polymers by UV irradiation depend on different factors such as chain structure, internal and external impurities, physical state of the sample, characteristics of the radiation source, etc. On the other hand, as polymer degradation leads to chemically irreversible reactions or physical changes, the knowledge of the involved processes is important to prevent the premature failure of these materials.[9]

It has been found that the initiation of the degradation of poly(ethylene oxide) is not due only to internal structural defects, such as carbonyls and tail-to-tail structures, but might also be induced by UV irradiation with sufficient energy to cause chain scission. These studies also showed

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that macro-radicals formed in the primary degradation of poly(ethylene oxide) react readily with atmospheric oxygen to form oxidation products (hydroperoxides and peroxides), which undergo further fast photolysis.[10] Kasczmarek *et al.*[11] studied the UV degradation of pure poly(ethylene oxide) and its complexes with inorganic salts, such as poly(ethylene oxide)-$CuCl_2$ and observed that the polymer-inorganic complex shows a higher rate of photodegradation than the pure polymer.

Han and co-workers,[2,3] studying the thermal oxidative degradation of PEG, described its susceptibility to free-radical oxidative attack, with reduction of the molecular weight and formation of low molecular weight oxygenated products. PEG degraded more severely in oxygen-rich atmosphere producing low molecular weight oxygenated products by a chain scission process. No degradation was observed for PEG aged in vacuum.[3]

In recent years, several photochemical methods for the disposal of organic pollutants in wastewaters have been developed. Most of them are based on the production of hydroxyl radicals that react readily and decompose most organic species.[12] These processes are generally based on oxidative degradation reactions initiated by hydroxyl radicals generated by several methods, like UV photolysis of hydrogen peroxide, TiO_2 photocatalysis, vacuum ultraviolet (VUV) photolysis of water, Fenton and photo-Fenton reactions.[13]

One way to generate HO$^\bullet$ is by the well known reactions of hydrogen peroxide with Fe^{2+} and Fe^{3+} salts. Mixtures of iron salts with H_2O_2 are known as Fenton process and are potential alternative oxidation methods.[14] It is well-known that the oxidizing processes induced by Fenton type systems can be greatly enhanced by irradiation with UV light.[15]

In the present work the oxidative degradation of PEG started by Fenton and photo-Fenton systems is studied. Degradation products were analyzed by high performance liquid chromatography, which allowed to detected the intermediates that confirmed the sequential mechanism.

Experimental

PEG 3350 (Sigma), tetra- and triethyleneglycol (4EG and 3EG) (Across Organics), diethyleneglycol (2EG) (Fenil Química), and ethyleneglycol (EG) (J. T. Baker) were used as supplied. Hydrogen peroxide 30% was from Merck.

Sample preparation

The samples were prepared using PEG solutions (5 g L^{-1}), iron (III) chloride hexahydrate (2% m/m) in Milli Q water. The concentration of H_2O_2 was 0.19 mol L^{-1} and it was added at once at the beginning of the reaction. The experimental set-up is similar to conditions described by Bossmann *et al.*[16] The solutions (initial pH 4.5) were placed in quartz tubes and the photodegradation processes took place in an irradiation chamber.

The chamber is equipped with 16 ultraviolet germicidal lamps (total power of 96 W) and the temperature was kept at 25 °C. The lamps emitted predominantly 254-nm radiation and the photon flux was 1.78×10^{21} photons *per* m^2 s. The photon flux was determined using the equation described for Neumann *et al.*[17] The emission spectrum shown in Figure 1, together with the absorption spectra on the sample, was determined using SPR-01 spectroradiometer (Luzchem).
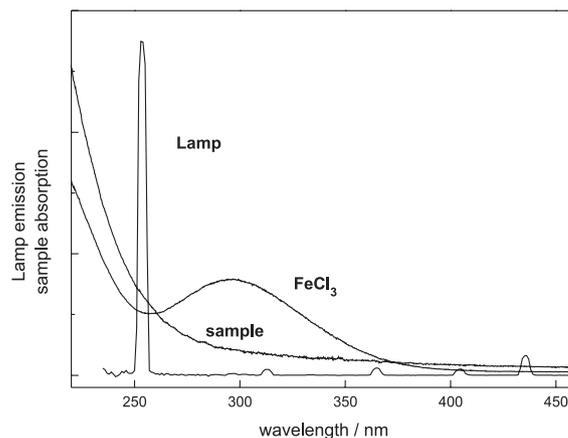

Figure 1. Emission spectrum of the irradiating lamp, and absorption spectra of the reaction mixture and $FeCl_3$ ($\times 200$).

For the identification and quantification of the generated products, aliquots were withdrawn from the reaction flasks at different times and analysed. The aliquots were analyzed immediately after withdrawing from the reaction vessel and filter. The dark reaction was sufficiently slow not to affect significantly the decomposition during this interval.

Gel permeation chromatography (GPC)

Average molar masses were determined by GPC on a Shimadzu LC-10 AD chromatographic system with a Shimadzu RID-6A refractive index detector. 20 µL of the sample solutions were injected in three OHPAK KB-806M columns. Millipore (Milli Q) water was used as the eluent at a flow rate of 1 mL min^{-1}. 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 8μ 8% 300×7.8 mm column using sulfuric acid 0.0025 mol L^{-1} as mobile phase at a 0.6 mL min^{-1} flow rate. A Shimadzu RID-6A refractive index detector was used and sample of 20 μL were injected. The reaction products and intermediate species from EG's and PEG photodegradation were identified by comparison with previously injected standard samples. All samples were injected under the same conditions, in the presence and absence of H$_2$O$_2$ and their retention time remained the same.

Results and Discussion

Average molar mass ($\overline{M}_w$) of PEG in the photo-Fenton system and in the dark was determined by GPC. Figure 2A shows the results for degradation of PEG ($\overline{M}_w$ 3330 Da) kept in the dark and Figure 2B shows the degradation of PEG in the photo-Fenton system. The reaction causes chain scission and a progressive decrease of the average molar mass in both cases. No degradation occurred when PEG was submitted to photolyzed without iron or hydrogen peroxide.
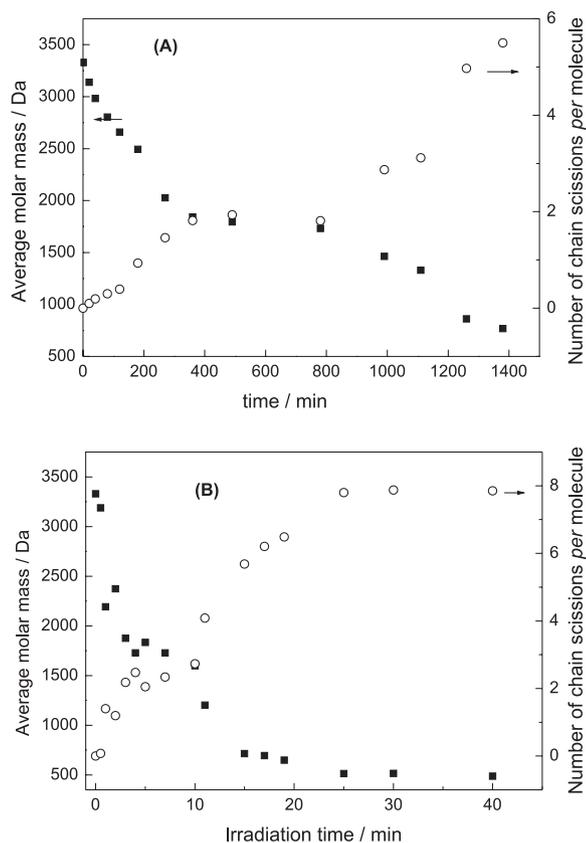

Figure 2. Time course of the alteration of the average molar mass, $\overline{M}_w$, of PEG and the number of chain scissions, S, for the dark (A) and photo-Fenton (B) systems. Points shown correspond to two independent runs for each system.

When kept in the dark, PEG samples in the presence of H$_2$O$_2$ and Fe^{3+} needed 490 min to reduce their $\overline{M}_w$ by 50% of the initial value. In contrast, the same reduction in $\overline{M}_w$ could be obtained in 10 min under UV irradiation. For the samples kept in the dark there is a steady drop of the molar mass during the first 360 min of the reaction, whereas for the irradiated samples, the $\overline{M}_w$ shows an abrupt reduction during the first 15 min, after which the $\overline{M}_w$ remains practically constant.

The progress of the PEG degradation processes could also be assessed by the number of average chain scissions (S) *per* molecule.[9,18,19] This parameter can be calculated according to the model developed by Madras and McCoy, using[20,21]

$$S = \frac{\overline{M}_n(0)}{\overline{M}_n(t)} - 1 \qquad (1)$$

It can be seen in Figure 2 that *S* increases with irradiation time, matching the exponential decay of the molecular weight, confirming a random chain scission mechanism.

The chain scission reactions can also be expressed in terms of the number of scission events *per* gram of the material N(t), it can be calculated using[22]

$$N(t) = \frac{1}{\overline{M}_n(t)} - \frac{1}{\overline{M}_n(0)} \qquad (2)$$

The change of N(t) at different reaction times is shown in Table 1 for the photo-Fenton system and the solutions kept in the dark. As expected, there is an increase with time, which is more pronounced for the irradiated system than for the system in the dark.

The mechanism for oxidative photodegradation of PEG by H$_2$O$_2$/UV systems was proposed in a previous work.[4] For the photodegradation of PEG in the H$_2$O$_2$/UV system a fast drop of the molar mass was observed during the first 70 min of irradiation. A strong similarity can be noticed in the behaviour of the $\overline{M}_w$ decay comparing the use of photo-Fenton and H$_2$O$_2$/UV systems.[4] On the other hand, irradiated samples using Fenton's reagent presented a faster degradation process than samples irradiated in the presence of H$_2$O$_2$ alone. The degradation of PEG with the same reagents kept in the dark proceeded with a clearly lower rate than the irradiated samples.

The exponential decay of $\overline{M}_w$ indicates a random chain scission process rather than a depolymerization process, which would lead to a slow decrease of $\overline{M}_w$.[23] This behaviour is similar to that observed by Han and co-workers[2,3] and Lai and Liau[1] for the thermal degradation of PEG. They found that the thermal degradation of PEG in air at 80 °C followed a random chain scission oxidation mechanism.

Table 1. Average molar mass ($\overline{M}_w$), polydispersivity ($\overline{M}_w / \overline{M}_n$), and number of scission events (N(t)) *per gram of PEG*

	Fenton				Photo-Fenton		
Reaction time / min	$\overline{M}_w$ / Da	$\overline{M}_w / \overline{M}_n$	N(t)	Irradiation time / min	$\overline{M}_w$ / Da	$\overline{M}_w / \overline{M}_n$	N(t)
0	3300	1.09	0	0	3300	1.09	0
20	3100	1.13	3.2×10^{-5}	0.5	3200	1.12	2.6×10^{-5}
40	3000	1.16	6.3×10^{-5}	1	2200	1.72	4.6×10^{-4}
80	2800	1.19	9.8×10^{-5}	2	2400	1.70	3.9×10^{-4}
120	2700	1.21	1.3×10^{-4}	3	1900	1.95	7.1×10^{-4}
180	2500	1.58	3.1×10^{-4}	4	1700	1.96	8.1×10^{-4}
270	2000	1.63	4.8×10^{-4}	5	1800	1.82	6.7×10^{-4}
360	1800	1.69	5.9×10^{-4}	7	1700	1.89	7.6×10^{-4}
490	1800	1.72	6.3×10^{-4}	10	1600	1.95	8.9×10^{-4}
780	1700	1.59	5.9×10^{-4}	11	1200	1.99	1.3×10^{-3}
990	1500	1.85	9.4×10^{-4}	15	710		1.9×10^{-3}
1110	1300	1.79	1.0×10^{-3}	17	700		2.0×10^{-3}
1260	900		1.6×10^{-3}	19	600		2.1×10^{-3}
1380	800		1.8×10^{-3}	25	500		2.6×10^{-3}
				30	500		2.6×10^{-3}
				40	500		2.6×10^{-3}

The model for polymer degradation described by Marimuthu and Madras[21] leads to a correlation between the change number-average molecular weight M_n with time and the degradation rate constant k_d

$$\frac{\overline{M}_n(0)}{\overline{M}_n(t)} - 1 = \overline{M}_n(0)k_d t \qquad (3)$$

This relationship is plotted in Figure 3. The degradation reaction in photo-Fenton, in the dark and H_2O_2/UV systems were followed up to 25, 1400 and 400 min, respectively. The degradation rate coefficients, k_d, for the degradation of PEG, which are independent of the initial molecular weight, in photo-Fenton, H_2O_2/UV and in the dark were 1.0×10^{-4}, 3.6×10^{-5} and 1.1×10^{-6} Da^{-1} min^{-1} respectively. Under the conditions used, the degradation rate coefficient for the photo-Fenton system is 100 times larger than in the dark.

GPC analysis also showed that the rate of degradation is much higher for the photo-Fenton system, followed by UV/H_2O_2 system. The dark reaction has the lowest degradation rate.

The polydispersity ($\overline{M}_w / \overline{M}_n$) *of* the samples is also shown in Table 1. The polydispersity increases from 1.09 to 1.99 for photo-Fenton system, and in the dark the variation of $\overline{M}_w / \overline{M}_n$ goes from 1.09 to 1.79. This increase of the polydispersity also indicates random scission.

The original PEG has a narrow distribution of molecular weights, with $\overline{M}_w / \overline{M}_n = 1.09$. On the other hand, degraded PEG has a broader polydispersity range reaching values of $\overline{M}_w / \overline{M}_n$ near 2. This broad distribution can be attributed to the low molecular weight species produced by the oxidative degradation.[3] Bond scissions in the backbone of the polymer result in the reduction of the molecular weight and the decrease of the chain length.[1] The results show that the system starts as a solution where all the chains have almost the same length, and under irradiation changes to a wider distribution of $\overline{M}_w$, 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 $\overline{M}_w$, and consequently, increasing the polydispersity. These results are similar to those obtained by Hoekstra *et al.*[22] and David *et al.*[24] for the oxidation and photo oxidation of polyethylene, where the oxidized polymers presented higher polydispersity than the original samples.

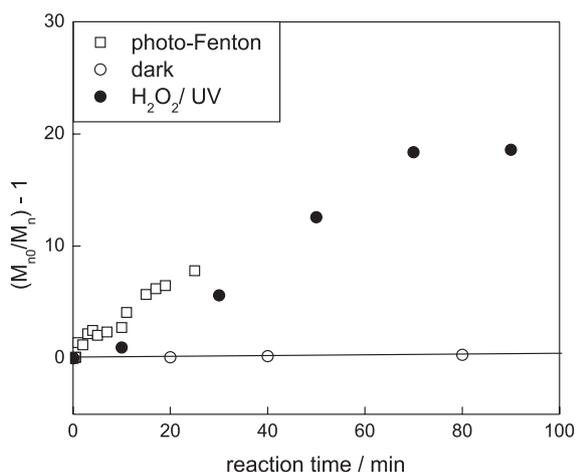The degradation products of PEG by the photo-Fenton method and in the dark were analysed by HPLC. The

Figure 3. Variation of $[\overline{M}_n(0)/\overline{M}_n(t)] - 1$ *vs.* reaction time for the degradation of PEG in photo-Fenton (□), Fenton (○), and UV/H_2O_2 (●) systems.

photo-oxidation of polymers produces a complex mixture of products and their precise identification is the key for the proposal of an overall degradation mechanism. During the degradation of PEG, several changes were observed, like the consumption of reagents, the formation of oxidation products, as well as the formation and disappearance of intermediates, as can be seen in Figure 4. The peak at 15.7 min, attributed to hydrogen peroxide, decreases continuously during the reaction, but new peaks with retention times around 21.7, 20.8, 19.8, 19.2, and 17.4 min develop simultaneously, characterizing the formation of 4EG, 3EG, 2EG, EG, and formic acid respectively. The peaks due to 4EG, 3EG, 2EG, and EG and the low molecular weight acids were identified by comparison with chromatograms of the pure samples.
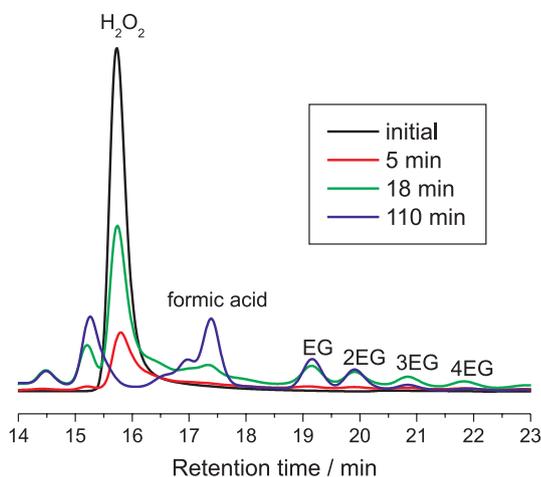

Figure 4. Chromatogram of PEG submitted to degradation in a photo-Fenton system.

All the degradation products remain in solution even after 100 min of reaction, whereas all the initially present H_2O_2 is consumed in this period. The same products found when the PEG samples were kept in the dark in the presence of the Fenton reagent, but its detection was only possible after longer reaction times (*ca.* 3500 min).

The time evolution of the lower molecular weight ethyleneglycols is shown in Figure 5A. It can be seen that all of them show the same behaviour, that is, an initial increase followed by a decrease. The concentration maxima of these species are observed at times inversely to their molecular masses (*i.e.*, 4EG at approximately 10 min, 3EG at 20 min, 2EG at 30 min, and EG at 60 min). This indicates that the smaller species arise from the larger ones, as would be expected in a successive scission mechanism.

The evolution of the hydrogen peroxide and formic acid concentrations are shown in Figure 5B. As expected,
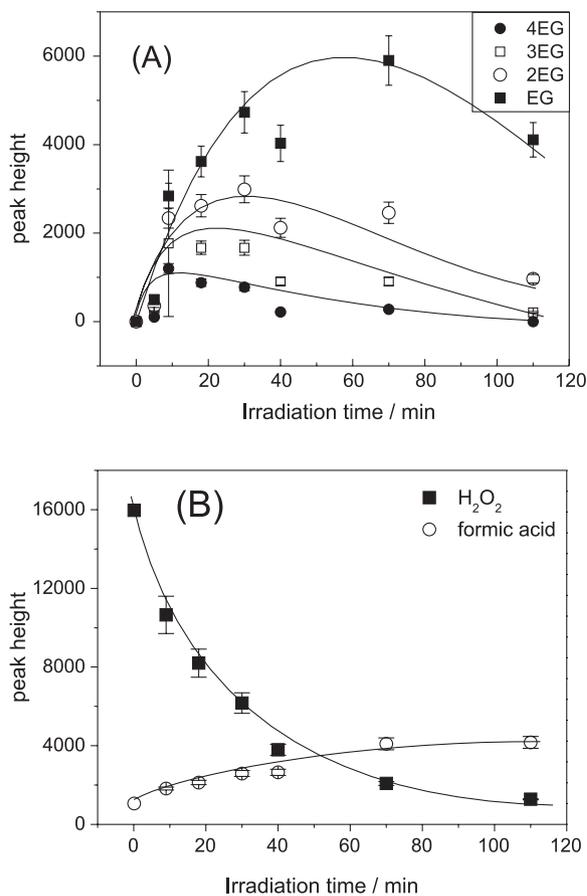

Figure 5. Time evolution of the concentration of (A) reaction products during the photodegradation of PEG and (B) consumption of H_2O_2 and formation of formic acid.

the peak due to H_2O_2 decreases steadily and that of formic acid increases. In the system studied it was difficult to identify the presence of glycolic acid because its retention time (15.6 min) is very similar to that of hydrogen peroxide.

Photodegradation of PEG in the UV/H_2O_2 system was studied previously.[4] In that work, the small molecular weight ethyleneglycols (4EG, 3EG, and 2EG) were used as models to study the photo-oxidative degradation of poly(ethyleneglycol). The identification of the degradation products lead to the conclusion that the degradation mechanism involved consecutive processes, where the larger ethyleneglycols give rise, successively, to smaller ones, that is, the degradation products of triethyleneglycol included diethyleneglycol, ethyleneglycol and formic acid.

Despite the differences between the UV/H_2O_2 and photo-Fenton systems, it is assumed that the reaction of the hydroxyl radicals produced in both systems would involve production of similar intermediate products. The intermediates detected in both systems were consistent with the pathway previously described for similar compounds.[4,25-27]

Conclusions

Polyethyleneglycol (PEG) was photooxidized using the photo-Fenton method and in the dark. PEG samples treated by the photo-Fenton method irradiating with UV light needed 10 min to reduce their $\overline{M}_w$ by 50%. In contrast, the same reduction was only obtained after 490 min when the system was kept in the dark. Polydispersity increases after photodegradation. The exponential decay of $\overline{M}_w$ with a concomitant increase in polydispersity and number of average chain scission, characterized a random chain scission, yielding low molecular weight species produced by oxidative degradation. The rate degradation coefficient in the photo-Fenton system is 100 times higher than that for the system in the dark (1.0×10^{-4} and 1.1×10^{-6} Da^{-1} min^{-1}, respectively). GPC analysis also showed that the rate of degradation is much higher for the photo-Fenton system, followed by UV/H$_2$O$_2$ system ($k_d = 3.6 \times 10^{-5}$ Da^{-1} min^{-1}). Degradation in the dark showed the slowest degradation rate.

The degradation products of PEG by the photo-Fenton method, EG, 2EG, 3EG, 4EG, glycolic and formic acids where detected by HPLC. The identification of these products confirmed that the photodegradation mechanism involved consecutive processes, were the larger ethyleneglycols give rise, successively, to smaller ones. This suggested that the mechanism involved successive scissions of the polymer chain.

Acknowledgments

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