

# Antioxidation activity of several diphosphonates in thermooxidative stability of LDPE

S. JIPA<sup>a,b\*</sup>, L. M. GORGHIU<sup>a</sup>, C. DUMITRESCU<sup>a</sup>, M. BUMBAC<sup>a</sup>, R. L. OLTEANU<sup>a</sup>, T. ZAHARESCU<sup>b</sup>, H. CUTHON- GOURVES<sup>c</sup>

<sup>a</sup>Valahia University Targoviste, Chemistry Department 18-20 Unirii Bd., 130082 Targoviste, Romania

<sup>b</sup>INCIE, ICPE CA, 313 Splaiul Unirii, Bucharest, Romania

<sup>c</sup>Bretagne Occidentale University, 6, av. Victor le Gorgeu – CS 93837, 29238 Brest Cedex 3, France

The thermal degradation of low density polyethylene in the presence of several esters – diphosphonates compounds mostly used in anticancer treatment – was investigated by chemiluminescence at three temperatures: 180 °C, 190 °C and 200 °C. Kinetic parameters that depict the stability of polymer – temporal characteristics (oxidation induction time, half – period of oxidation and maximum oxidation time), oxidation rates and activation energies – were calculated from the dependencies of chemiluminescence intensity on thermal degradation time. The stabilization effectiveness of the tested compounds and other antioxidants, namely SANDOSTAB P-EPQ and TOPANOL OC is presented for comparison. Experimental data have demonstrated that one of the diphosphonates compounds is more efficient than the commercial antioxidants.

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## 1. Introduction

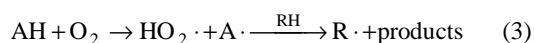
Thermal stability of polymers is of great importance. Due to this reason, stabilization of polymers is an intensively studied subject. Various causes lead to more or less fast oxidation of the polymers. In most of cases, macromolecular materials need protection to improve the oxidation resistance. These practical requirements have stimulated academic research on the stabilization efficiency of various large categories of antioxidants. Starting from the commercial products – like sterically hindered phenols or amines – a large category of compounds has attracted interest. Several new series of antioxidants were prepared and tested [1-10]. The major benefit of this kind of investigation consists of the preparation and the characterization of efficient oxidation protectors under extreme working conditions.

The protection effect of stabilizers is the result of the competitive interaction between peroxy radicals and polymer or antioxidant molecules:



where AH and RH represent antioxidant molecule and polymer macromolecule, respectively.

The ratio of the rates of the two processes characterizes two critical concentrations of antioxidants: the lower value for minimal oxidation prevention and the upper value when oxygen depletes additive according to reaction (3) [11, 12].



The present study reports the main kinetic features of thermal degradation for LDPE stabilized with some diphosphonates compounds, mostly used as active substances in anticancer treatment. The effect of these new synthesized compounds on stabilization efficiency and the values of activation energy is emphasized.

## 2. Experimental

### 2.1. Materials

Low density polyethylene (K322<sup>®</sup>, Brazi Chemical Company, ROMANIA) was the base polymer substrate for all determinations. Some material characteristics are density 0.920, crystallinity 45.5%, number of CH<sub>3</sub>– per 100 carbon atoms 3.1. The purified material was obtained by dissolution of LDPE in hot o-xylene followed by fast precipitation from hot solution by pouring in cool methanol. Supernatant material was removed by filtration. Solids were separated from the suspension by fast filtration and were allowed to dry by gentle heating (30 °C) in air – circulating oven. The resulted powder was rinsed many times with acetone and dried at room temperature.

### 2.2. Additives

The molecular structures of the stabilizing compounds are presented in Table1. These compounds were synthesized in the Organic Chemistry Laboratory of Bretagne Occidentale University of Brest, France.

Table 1. Molecular structures of studied additives.

Molecular structures	Marks
	S1
	S2
	S3
	S4
	S5

For comparison, two kind of commercial antioxidants were selected:

- Antioxidants with phosphor atoms into the molecule as trionil-phenyl-phosphite (RONOX) and Tetra-kis-(2,4-di-t-butyl-phenyl-4,4'-diphenylen-diphosphonite (SANDOSTAB P-EPQ)
- Two hindered phenols as 2-(3',5'-Di-t-butyl-4'-hydroxyphenylpropionil-hydrazino)5-(3'',5''-di-t-butyl-4''hydroxyphenylethyl)-2,3-dihydro-1,2,3,4-oxaphosphatiazol (FAU 13) and 2,6-Di-t-butyl-4-methyl-phenol (TOPANOL OC).

The structures of these antioxidants are presented in Table 2.

Table 2. Molecular structures of commercial antioxidants.

Molecular structures	Commercial denomination
	RONOX
	SANDOSTAB P-EPQ
	FAU 13
	TOPANOL OC

## 2.3. Samples preparation

The addition of each stabilizer to polyethylene powder was carried out by dropwise pouring of a low concentration of additive solution in chloroform under vigorous grinding. Finally, samples contained additive at the concentration of 0.25% w/w. The compounded materials, consisting of polyethylene and stabilizer, were dried in a desiccator at room temperature for 24 hours. Aliquots of 25 mg were placed on an aluminum tray before measurements.

## 2.4. Measurements

Chemiluminescence (CL) investigations were performed on OL-94 unit [13]. Because of high thermal stability of the organic support, isothermal determinations were carried out at various temperatures (180 °C, 190 °C and 200 °C). Oxidation environment for thermal degradation in CL equipment was continuous air stream. A typical chemiluminescence curve and the explanations on the kinetic parameters obtained in this kind of investigation are presented in Fig. 1.

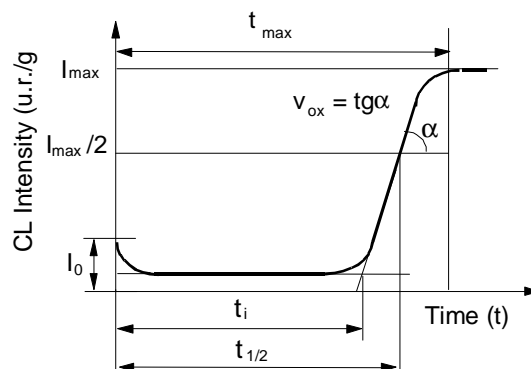


Fig. 1. Chemiluminescence diagram for oxidation of polyolefins,  $t_i$  – oxidation induction time;  $t_{1/2}$  – time required to reach half of maximum CL intensity;  $v_{ox}^{max}$  – oxidation rate on the propagation stage of oxidation;  $t_{max}$  – time elapsed from the beginning of CL determination to the maximum CL intensity;  $I_{max}$  – maximum CL intensity.

## 3. Results and discussion

The efficiency of any stabilizer can be characterized by means of kinetic parameters: time characteristics, oxidation rate and activation energy required by the process. They can be obtained by analysis of time dependencies of chemiluminescence intensities. The protective action of studied antioxidants against thermal oxidation is effective during the first two steps of oxidation: induction and propagation, until the rate of ROO· depletion exceeds its formation rate. On the induction period the stabilization efficiency is effective high and the CL signals are closed to background. During the propagation stage of thermal degradation involves the

depletion of additives, which leads to a sigmoidal dependence of CL intensity on time. Some of chemiluminograms registered for the studied compounds are presented in Figs. 2-4. All these chemiluminograms were registered at three different temperatures (180 °C, 190 °C and 200 °C). They prove that the oxidation process is effectively retarded due to the presence of S1, S2 and S4 compounds.

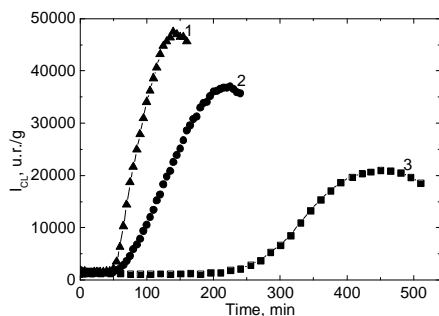


Fig. 2. The isothermal chemiluminescence curves registered at (1) 200 °C, (2) 190 °C and (3) 180 °C for LDPE samples stabilized with diphosphonate S1 at the concentration of 0.25% (w/w).

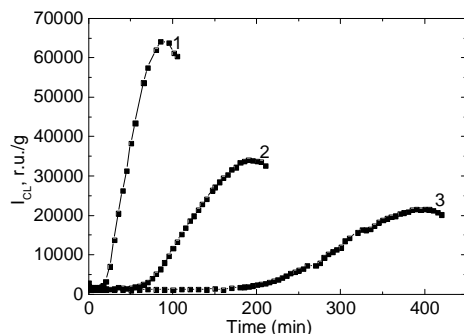


Fig. 3. The isothermal chemiluminescence curves registered at (1) 200 °C, (2) 190 °C and (3) 180 °C for LDPE samples stabilized with diphosphonate S2 at the concentration of 0.25% (w/w).

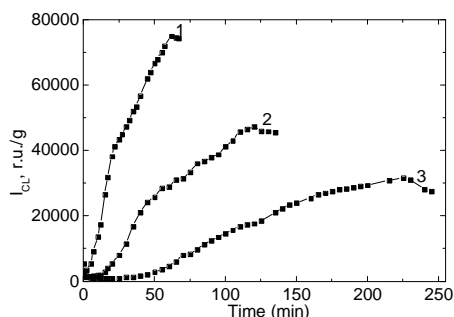


Fig. 4. The isothermal chemiluminescence curves registered at (1) 200 °C, (2) 190 °C and (3) 180 °C for LDPE samples stabilized with diphosphonates S4 at the concentration of 0.25% (w/w).

For comparison, Figs. 5 and 6 present the chemiluminograms obtained for LDPE samples containing

known commercial antioxidants and new synthesized compounds whose efficiency was also tested.

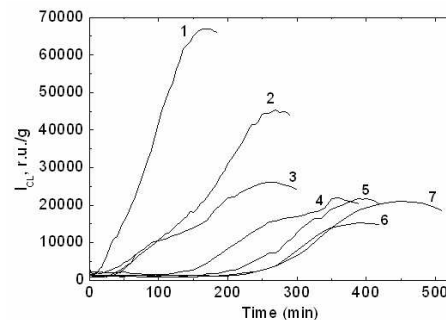


Fig. 5. The isothermal chemiluminescence curves (180 °C, in air) of LDPE samples stabilized (0.25% w/w) with: (1) none; (2) TOPANOL OC; (3) S4; (4) S5; (5) S2; (6) S3; (7) S1.

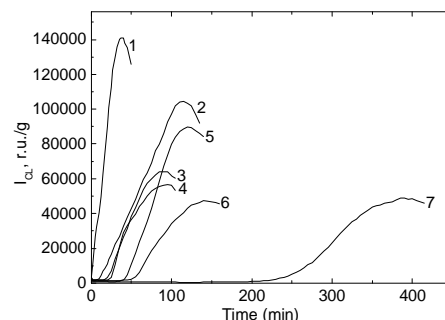


Fig. 6. The isothermal chemiluminescence curves (200 °C, in air) of LDPE samples stabilized (0.25% w/w) with: (1) none; (2) RONOX; (3) S2; (4) S3; (5) TOPANOL OC; (6) S1; (7) FAU 13.

As it can be observed from these chemiluminograms, the S1 diphosphonate is the most efficient antioxidant through the new synthesized compound series. Its antioxidant activity is closed to TOPANOL OC activity at 180 °C. On the other hand, it can be also observed that, at 200 °C, S1 diphosphonate presents a high efficiency in the thermal stabilization process, even greater than TOPANOL OC, RONOX and SANDOSTAB P-EPO antioxidants (as Table 3 illustrates).

Table 3. Kinetic parameters of thermal oxidation of stabilized LDPE (K322). Additive concentration: 0.25% (w/w). Degradation temperature: 200 °C.

Additive	$t_i$ (min)	$t_{1/2}$ (min)	$v_{max}^{ox}$ (u.r./g/min)	$I_{CL, max}$ (u.r/g)	$t_{max}$ (min)	$A_{rel}$	$S_{rel}$
-	8	41	2533	17733	95	-	-
FAU 13	250	300	630	6512	390	6.54	0.25
RONOX	10	58	2033	20915	115	0.05	0.80
SANDOSTAB P-EPO	30	68	1464	11177	125	0.59	0.58
TOPANOL OC	45	77	2065	11971	120	1.00	1.00
S1	52	83	800	47450	140	1.19	0.32
S2	19	45	1201	65678	90	0.30	0.47
S3	23	39	2120	56550	95	0.41	0.84
S4	6	19	2600	75050	60	-	1.03
S5	9	19	3650	69500	62	-	1.70

where antioxidant activity (A) expressed by the relation:

$$A = \frac{t_x - t_0}{t_s - t_0}$$

( $t_0$ ,  $t_x$  and  $t_s$  are, respectively, the induction periods, grafically deduced from chemiluminograms for pure LDPE, LDPE with the particular additive and with TOPANOL OC, which was taken as a standard).

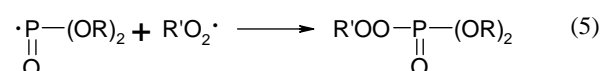
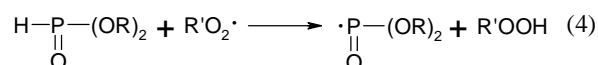
Table 3 shows also the relative stability (S) on the propagation period. This parameter was calculated by the following relation:

$$S = \frac{(v_{ox})_x}{(v_{ox})_0}$$

where  $(v_{ox})_0$  and  $(v_{ox})_x$  are the maximum oxidation rates for pure and antioxidant-protected LDPE, respectively.

The **S1**, **S2** and **S3** - based compounds present a remarkable relative stability at 200 °C. This means that their antioxidant activity is present in the propagation stage of thermal oxidation process.

The antioxidant activity of these new synthesized diphosphonates can be explained by the mechanism reported by equations (4) and (5).



The oxidation process occurring by reaction of oxygen with free radicals needs certain activation energy. The accumulation of oxygenated intermediates progresses on time as a result of oxidation chain and by additional bond scission providing new reactive sites. In the first stage, when the concentration of chain initiators is very low, the energy required for oxidative degradation is high [14]. As the degradation creates new reaction centers, the energy necessity is diminished (as it may be seen in Table 4 for unprocessed polyethylene). The presence of stabilizers increases the activation energy values (as Table 5 presents). Higher values of energy are corellated with greater additive concentration. In the same time, the stabilization efficiency may be expressed by the activation energy that depicts the ability of oxidation prevention to the chain breaking. Due to the impossibility of real discrimination between various intermediate reactions with characteristic activation energies, only global values are available depicting thermal stability of polymer substrate.

Table 4. Activation energy of thermooxidation process for unstabilized LDPE (K322).

Parameters	From oxidation induction period ( $t_i$ )	From maximum oxidation period ( $t_{max}$ )
$E_a$ (KJ/mol)	113.8	71.5
$\ln A$	-26.6	-13.9
Correlation coefficient	0.99	0.92

Table 5. Activation energy of thermooxidation process for stabilized LDPE (K322) with **S1** (0.25% w/w).

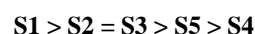
Parameters	From oxidation induction period ( $t_i$ )	From maximum oxidation period ( $t_{max}$ )
$E_a$ (KJ/mol)	136.2	99.4
$\ln A$	-30.8	-20.3
Correlation coefficient	0.93	0.99

#### 4. Conclusions

The oxidation of the low density polyethylene in the presence of diphosphonates derivatives reveals the stabilization activity of this type of compounds. Some of them are efficient, the thermal resistance being comparable with the effect of commercial hindered phenols (TOPANOL OC) and greater than the effect of other commercial antioxidants with phosphor atoms in molecule (RONOX and SANDOSTAB P-EPQ).

Relative activity and relative stability prove that some of these new synthesized compounds have a satisfactory activity (especially at low temperatures), which may be taken into consideration for industrial practice.

The antioxidative efficiency of the diphosphonates derivatives at 180 °C decreases in the following order:



The activation energies required for thermal oxidation are much higher in the presence of diphosphonates derivatives in comparison with purified polymer. The good values obtained for activation energy confirm the possibility of using these new synthesized compounds as thermal protectors.

Chemiluminescence provides a way for quickly determining the reactivity or stability of polymer materials.

Some promising applications for chemiluminescence are connected to industrial and academic applications: mechanisms of polymer reactions, ageing, degradation; environmental effects against polymer materials; effects of

process, fabrication, and formulation variable on polymer reactions and stability; quality control in polymer manufacture and treatment and control of processing.

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\* Corresponding author: jipasilviu@yahoo.com