

COMPARATIVE STUDY OF SOME CALIX [n] ARENES AND OTHER PHENOLIC COMPOUNDS INFLUENCE ON THE THERMAL STABILITY OF LDPE

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Abstract The calix [n] arenes are cyclic oligomers, which are obtained by p-alkyl-phenols with formaldehyde condensation. One of the most important applications of this class of compounds is their antioxidative capacity used in polymers stabilization.

The paper presents a comparative study of p-t-butyl-calix [n] arenes (n = 4; 6; 8) and other phenolic compounds influence on the thermal stability of LDPE by chemiluminescence method. Relative properties namely the activity and stability of additives were also calculated.

The experimental results proved that the antioxidant feature of p-t-butyl-calix [4] arene is higher than the same feature of p-t-butyl-calix[6]arene and p-t-butyl-calix-[8]-arene for all sorts of LDPE. A thermostabilisation activity order of calix [n] arenes and other phenolic compounds is proposed.

Keywords: calix [n] arenes, chemiluminescence, LDPE (low density polyethylene), thermal stability

1. INTRODUCTION

Calixarenes are cyclic oligomers obtained by condensation of formaldehyde with p-alkyl-phenols in the basic environment [1, 2]. Their general structure is presented in figure no. 1. Apart from the mentioned substituents, other groups can replace the phenolic proton offering a high solubility in water.

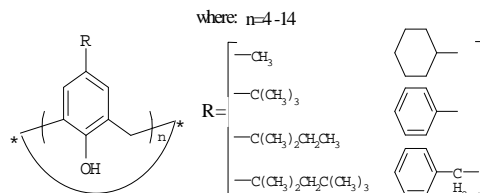


Fig. 1 - General structure of calixarenes

Some studies on antioxidant features of calixarenes were already reported [3-7]. Seiffarth et al. [5] pointed out the stabilizing role of calixarenes in photo-oxidation of polyolefins and Yuan [6] has demonstrated the improvement effect of p-t-butyl-calix[4]arene on oxidative radiolysis of polypropylene. Jipa et al. [8] investigated the stabilization effect of p-t-butyl-calix[n]arene (n = 4, 6) on thermal degradation of polypropylene. Zaharescu et al. [9] studied the main kinetic features of radiolysis of polypropylene in the calixarenes presence confirming the precedents reports.

The present paper presents the contribution of p-t-butyl-calix[n]arene (n = 4, 6, 8) in thermal stability of different sorts of LDPE. Other phenolic antioxidants were also investigated in order to compare the oxidation prevention efficiency of calixarenes with commercially available antioxidants.

2. Experimental

In the developed experiments we have used two sorts of low density polyethylene (LDPE – K322 and A23FB/035P). Their main characteristics are listed in Table 1. Raw polymers were purified by dissolution in hot o-xylene and precipitation into cool methanol. After complete cooling, the supernatant was removed by filtration. The solid was allowed to dry, obtaining coalescent powder. The powders were rinsed many times with acetone and dried at room temperature.



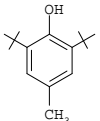
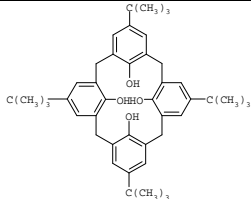
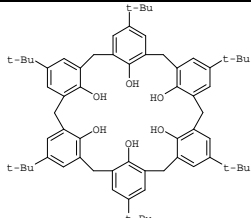
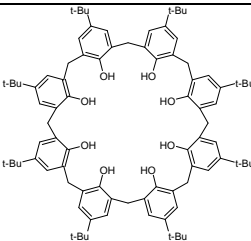
Table 1
Some characteristics of studied polyethylenes

Type	Sort	Density (g/cm ³)	Cristallinity (%)	Melt flow index (g/10 min)	Provenience
LDPE	K322	0,920	52	0,5	PETRO Brazi
LDPE	A-23FB035P	0,921	53	1,83	ARPECHIM Pitesti

Two types of calixarenes, p-t-butyl-calix[4]arene and p-t-butyl-calix[6]arene were investigated as antioxidants. For comparison p-t-butyl-phenol and 2,4,6-tri-t-butyl-phenol and 2,6-di-t-butyl-4-methyl-phenol (TOPANOL OC) were also studied. Molecular structures of these additives are presented in Table 2.

Chemiluminescence measurements were performed using an OL-94 unit [10, 11]. Isothermal determinations were carried out at 180, 190 and mainly 200^oC because of high thermal stability of the organic support.

Table 2
Molecular structures of the additives

Additive	Molecular structure	Code
p-t-butyl-phenol		(1)
2,4,6-tri-t-butyl-phenol		(2)
2,6-bi-t-butyl-4-methyl-phenol (Topanol OC)		(3)
p-t-butyl-calix-[4]-arene		(4)
p-t-butyl-calix-[6]-arene		(5)
p-t-butyl-calix-[8]-arene		(6)

3. Results and discussion

Chemiluminescence curves drawn for unstabilized LDPE sorts present a shoulder in the starting period of thermal degradation [11]. This thing proves the existence of two consecutive processes that may differentiate the oxidation rates of various classes of radicals.

The chemiluminescence curves for LDPE (K322 and A-23 FB/035P) in the presence of different compounds containing phenolic groups are presented in figures no. 2 and 3.

The addition of stabilizers causes an increase of oxidation induction time and lower oxidation rate in accordance with specific inhibition activities (Fig. 2, Fig. 3, Table 3, and Table 4).

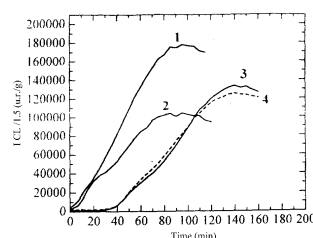


Fig. 2 - CL curves drawn for stabilized LDPE (K322) at 200⁰C. Additive concentration: 0.25% (w/w). (1) Free; (2) *p-t*-butyl-calix[8]arene; (3) *p-t*-butyl-calix[4]arene; (4) *p-t*-butyl-calix[6]arene

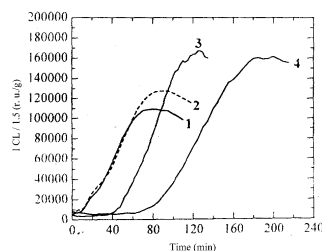


Fig. 3 - CL curves drawn for stabilized LDPE (A-23 FB/035P) at 200⁰C. Additive concentration: 0.25% (w/w). (1) Free; (2) *p-t*-butyl-calix[8]arene; (3) *p-t*-butyl-calix[4]arene; (4) *p-t*-butyl-calix[6]arene

Table 3

Kinetic parameters of thermal oxidation of stabilized LDPE (K322). Additive concentration: 0.25% (w/w). Degradation temperature: 200⁰C

Additive	Induction period t_i (min)	Half period of oxidation $t_{1/2}$ (min)	Maximum oxidation rate, v_{max}^{ox} (u.r./g/min)	Maximum CL intensity I_{CL} (u.r/g)	Maximum oxidation time, t_{max} (min)	Relative activity A_{rel}	Relative stability S_{rel}
-	15	54	1675	125792	112	-	-
(1)*	16	38	2495	118168	76	1.00	1.49
(2)	24	57	1958	130297	110	9.00	1.17
(4)	40	83	1532	122935	145	25.00	0.91
(5)	31	68	1663	103960	115	16.00	0.99

*Standard

Table 4
Kinetic parameters of thermal oxidation of stabilized LDPE (A-23 FB/035P). Additive concentration: 0.25% (w/w). Degradation temperature: 200°C

Additive	Induction period t_i (min)	Half period of oxidation $t_{1/2}$ (min)	Maximum oxidation rate, v_{\max}^{ox} (u.r./g/min)	Maximum CL intensity I_{CL} (u.r/g)	Maximum oxidation time, t_{\max} (min)	Relative activity A_{rel}	Relative stability S_{rel}
-	12	32	4140	163131	61	-	-
(1)*	46	72	3080	161700	108	1.00	0.74
(2)	46	71	3431	161832	115	1.00	0.83
(4)	78	121	1914	159493	195	1.94	0.46
(5)	58	85	3399	180990	131	1.35	0.82

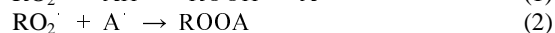
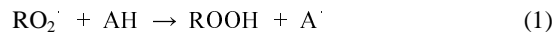
*Standard

The antioxidant effect of the studied calix[n]arenes ($n = 4, 6$) becomes relevant in the first period of oxidation. The values of induction time and half-period of oxidation are higher than the similar parameters exhibited by unstabilized polymer.

The oxidation protective effect of calix[4]arenes and calyx[6]arenes is more efficient than the similar effect induced by p-t-butyl-phenol which is generally considered as a weak antioxidant. However, calyx[6]arene is more able to inhibit oxidative degradation than 2,4,6-tri-t-butyl-phenol which is a medium activity additive.

It may be noticed that p-t-butyl-calix[4]arene presents more satisfactory kinetic parameters than p-t-butyl-calix[6]arene. The rates of oxidation measured in the calix[n]arenes presence have satisfactory values, even at 200°C when the low relative stability takes values between 0.46 and 0.99. Relative activity and relative stability for both calix[n]arenes show adequate values for an antioxidant (Table 3, and Table 4). Analogous results were obtained for all the tested temperatures, this effect increasing at low temperature. It means that protective effect of calix[n]arenes is maintained at high temperature.

It may be stated that calix[n]arenes play the role of chain breaking antioxidant according with the following reactions:



where AH is calyx[n]arene, RO_2^\cdot is peroxy radical and A^\cdot is phenoxy radical.

This mechanism is suggested by the analogy to general theory of antioxidant action [12] and by the coupling ability of phenolic configurations in scavenging free radicals.

The influence of calix[4]arene concentration on kinetic parameters of thermo-oxidative degradation of LDPE (K322) is presented in figure no. 4. Linear changes may be explained by constant efficiency for all concentrations based on the trapping of radicals in the central hole of the molecular geometry.

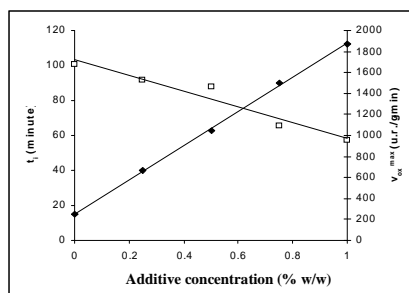


Fig. 4 - Influence of additive (p-tpbutylcalix[4]arene) concentration on oxidation parameters of LDPE (K322). Temperature: 200°C

Table 4 lists the kinetic parameters obtained for the thermal degradation of the other sort of LDPE, A23FB/035. Analogous behavior of studied antioxidants in both sorts of LDPE can be remarked. It may be observed that both of studied calixarenes are more active than 2,4,6-tri-*t*-butyl-phenol. Moreover, the *p*-*t*-butylcalix[4]arene exhibits more satisfactory effects in oxidative protection of LDPE than the *p*-*t*-butylcalix[6]arene.

The high ability of calixarenes in improving thermal resistance of LDPE can be explained by the influence of crystallinity on the movement of RO_2^{\cdot} radicals. The radical size plays also an important role in oxidation progress by blocking peroxy radicals. Calixarenes have circular arrangement of phenolic functions and the retention of radicals is more successful if the fragment is a linear configuration rather than a branched structure.

The antioxidative effect of studied calixarenes in the two sorts of polyethylene can be explained by participation of hydroxy units in the process of chain breaking and formation of aryl-oxy radicals according with the purposed scheme (Fig. 5).

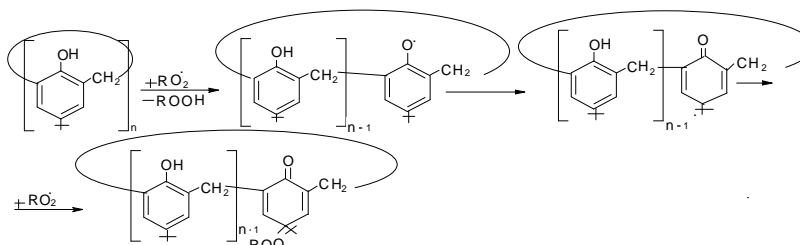


Fig. 5 - Proposed mechanism of antioxidant action of calixarenes

4. Conclusions

Due to proper values of kinetic parameters of thermal degradation of polymers calixarenes may be considered like antioxidants. Their prevention action over the whole duration of degradation is confirmed by the linear dependence of all kinetic parameters on additive concentration.

Measurements of chemiluminescence emission in polyethylene with different antioxidant compounds - p-t-butylphenol, 2,4,6-tri-t-butyl-phenol, p-t-butyl-calix[4]arene and p-t-butyl-calix[6]arene – confirms the behavior of calixarenes as stabilizers of medium to good activity acting as chain breaking antioxidants.

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