Chemiluminescence of Isotactic Polypropylene Induced by Photo-Oxidative Degradation and Natural Weathering

Silviu Jipa,[1,2] Radu Setnescu,[1,2] Traian Zaharescu,[2] Tanta Setnescu,[1,2] Mustapha Kaci,[3] Naima Touati[3]

[1]*Valahia University of Targoviste, Faculty of Sciences, Dept. of Chemistry, Bd. Regele Carol nr. 2, Targoviste, Romania*
[2]*National Institute for Advanced Research in Electrical Engineering (INCDIE ICPE–CA), Splaiul Unirii 313, sector 3, Bucharest, Romania*
[3]*Laboratoire des Matériaux Organiques, Département de Génie des Procédés, Université Abderrahmane Mira, Route de Targa–Ouzemmour, Bejaia 06000, Algeria*

ABSTRACT: The analysis of the chemiluminescence (CL) kinetic parameters (induction time, oxidation rate, and activation energy) after the UV irradiation and outdoor exposure of isotactic polypropylene (i-PP) films have been studied. The initial CL emission intensity increased with increasing photodegradation time of i-PP films. On photodegradation, the activation energies were found to decrease linearly with time of UV-irradiation and outdoor exposure. The slopes of these linear dependences were used to indicate the degree of photodegradation of the polymer and also for the characterization of the stabilizing effect of the additive. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4623–4629, 2006

Key words: chemiluminescence; photodegradation; isotactic polypropylene; Sanduvor PR 31 stabilizing effect
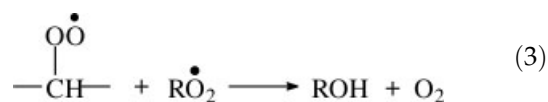
INTRODUCTION

The degradation of polymeric materials is determined by various factors such as heat, UV light, ozone, and mechanical stress, resulting in brittleness, cracks, color change, etc. Degradation is promoted by oxygen, humidity, and strain. The degradation rates are extrapolated to predict the service life of a material under different conditions.

The greatest damage to polymers exposed under natural conditions is caused by the UV portion of sunlight, even though this portion represents up to 10% (depending on the atmospherical conditions and latitude) of the total energy reaching the earth from the sun, with about 50% being visible and about 40% IR light.[1]

The photo-oxidation of polypropylene has been recognized to involve the initiation of a free radical chain reaction by the photolysis of hydroperoxide groups. The homolysis of the hydroperoxide by UV irradiation is the primary initiation step (reaction 1). The photolysis of hydrogen-bonded peroxides (reaction 2) produces a peroxy radical as well as alcoxy radical:[2]

$$\text{ROOH} \xrightarrow{\text{h}\nu} \text{R}\overset{\bullet}{\text{O}} + \overset{\bullet}{\text{O}}\text{H} \tag{1}$$

$$\begin{array}{c} \text{ROOH} \\ \vdots \\ \text{ROOH} \end{array} \xrightarrow{\text{h}\nu} \text{R}\overset{\bullet}{\text{O}} + \text{R}\overset{\bullet}{\text{O}}_2 + \text{H}_2\overset{\bullet}{\text{O}} \tag{2}$$

The most significant reaction is the β-scission of the alcoxy radical to produce a chain scission, a ketone and an alkyl radical. The chain breaking may also occur due to the reaction of the hydroxyl radical formed in reaction (1) with a carbonyl group to produce an acid end group. The carbonyl groups necessary for this reaction are formed by the termination reaction of peroxy radicals (reaction 3):

$$\begin{array}{c} \overset{\bullet}{\text{OO}} \\ | \\ -\text{CH}- \end{array} + \text{R}\overset{\bullet}{\text{O}}_2 \longrightarrow \text{ROH} + \text{O}_2 \tag{3}$$
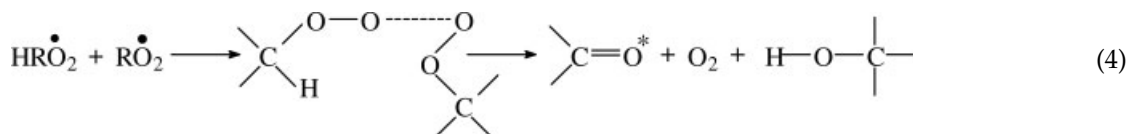
The resultant carbonyl group may also undergo a Norrish II reaction to produce a chain scission.

Various types of hindered amines are largely used to protect polymers against photooxidation. Among them, hindered tertiary amines containing α-H at the nitrogen atom are very effective in hydroperoxide decomposition.

Correspondence to: R. Setnescu (rsetnescu@yahoo.com).

The process of degradation is accompanied by chemiluminescence emission. The origin of this emission is bimolecular termination of peroxy radicals (Russell

mechanism[3]), as it is generally accepted that the CL is in fact a phosphorescence from an excited ketone molecule:

$$HR\overset{\bullet}{O_2} + R\overset{\bullet}{O_2} \longrightarrow \quad \text{[structure]} \quad \longrightarrow \quad \text{C}=\text{O}^* + O_2 + H{-}O{-}\overset{|}{\underset{|}{C}}{-} \tag{4}$$

Chemiluminescence measurement has been used as a tool for the investigation of the oxidation of various polymers or polymer materials at elevated temperatures,[4–11] solar or UV light,[12–15] cold helium plasma,[16] electrical stress,[17] electron beam[18] and γ-ray irradiation.[19,20] Many attempts have been made to use chemiluminescence for estimation the efficiency of stabilizers.[21–28]

The chemiluminescence method can be used to measure quantities which are properties of the reactions (induction periods, oxidation rates, and activation energies) and which do not depend on the particular equipment used. In this article we intend to show that apparent values of activation energy as they are calculated from isotherm CL parameters are sensitive to degradation state of the polymer. As we know, such a way to use CL method in characterization of degradation level of polymer materials has not been reported up to date. We investigated the occurrence of these effects on PP films stabilized by Sanduvor PR 31, a (tertiary) hindered amine light stabilizer (HALS) containing α-H (see Scheme 1). Previous work on these films provided data regarding the photo-induced grafting of this HALS on PE and PP[29,30] and its stabilization effect towards radiation induced oxidation of PE.[31]

EXPERIMENTAL PART

Materials

The isotactic PP used was manufactured by Exxon Mobil Chemical (Dahran, Saudi Arabia) and is com-

mercialized under the trade name BK-160-4102. The melt flow index of the polymer is 3 g/10 min according to ASTM D 1238L.

The HALS used was produced by Clariant company (Huningue, France) under the trade name Sanduvor PR31. The additive was added to the polymer against photooxidation at a concentration of 0.3% (w/w). The Sanduvor PR31 is a new class of HALSs which is characterized by its capacity to be grafted to polymer chains by photochemical reactions. This modified stabilizer has one single structure that combines HALS acting as free radical scavenger and a UV absorbing unit based on a benzylidene malonate structure which provides an absorption maximum at 308 nm. This absorption band is observed to decrease in intensity with exposure time in polypropylene and disappears completely up to almost 15 days in natural weathering and 20 h in accelerated UV conditions.[30] This result was attributed to the occurrence of a rapid photoreaction between the Sanduvor PR31 and the polymer matrix through the methylenic double bond scission.[29–34] The chemical structure of Sanduvor PR 31 is given in Scheme 1.

Sample preparation

Polypropylene pellets and Sanduvor PR 31 powder were intimately mixed during extrusion. Thus, films of 130 ± 5 μm thickness were prepared by using a Barmag Aktiengesellschaft D-42895 extruder (Remscheid, Germany) with a length/diameter ratio of 24. The temperature in the barrel of the extruder, as well as in the die was maintained at 230°C. The film was stretched in the air after leaving the die at a pulling speed of 5 m/min. Before use, the films were washed by ethanol at room temperature.

UV-irradiation and natural weathering

PP films were irradiated in air at 20°C for various times. UV irradiation was carried out at University A. Mira of Bejaia, using a middle pressure Hg lamp. The distribution of the temperature and the radiation in the sample was optimized to better simulate the solar spectrum in external conditions. In this direction, the lamp has been equipped with a special filter which cut all the radiations bellow 290 nm. The natural exposure
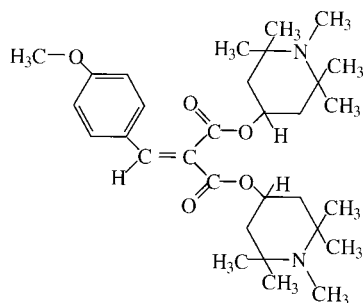
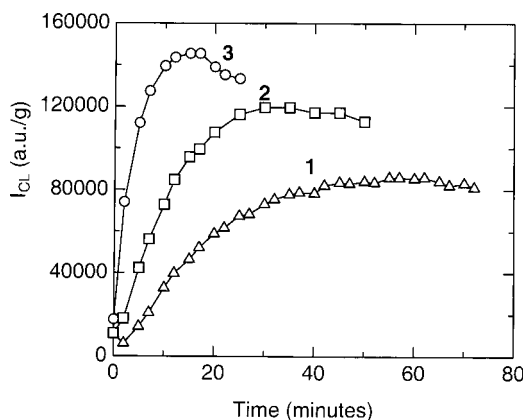**Scheme 1** The chemical structure of Sanduvor PR 31.

Figure 1 The isothermal CL curves at different temperatures from unstabilized i-PP film, UV irradiated for 20 h: 160°C (1); 170°C (2); 180°C (3).

Figure 3 The isothermal CL curves at different temperatures from PR 31 stabilized i-PP film, unexposed: 180°C (1); 190°C (2); 200°C (3).

was carried out at Bejaia on the East coast of Algeria according to ASTM D 1435. The samples were in the form of rectangular bands (30 × 20 cm) and were mounted on racks facing southward.

Chemiluminescence analysis

Chemiluminescence emission of film samples were obtained in an OL-94 Oxyluminograph analyzer developed by ICPE-CA (Bucharest, Romania).[35] The measurements were performed in isothermal mode and the kinetic parameters of oxidation were calculated from chemiluminescence curves in the same manner as it has been shown in the literature.[13,20]

Activation energy has been calculated on the basis of the following Arrhenius-type equation, using the values of some CL parameters at various temperatures:

$$\ln t_j = A \cdot e^{-E_{a_j}/kT} \tag{5}$$

In the above equation, t_j is one of the time parameters derived from CL measurements, namely $t_{1/2}$ (time to reach half of maximum of CL intensity) or t_{max} (time to reach maximum of CL intensity).

RESULTS AND DISCUSSION

Chemiluminescence records from the UV degradation and weathering of both unstabilized and stabilized polypropylene films are shown in Figures 1–4. As can be seen, the chemiluminescence intensity increases gradually with increasing measurement temperature. The chemiluminescence intensity also increases with UV irradiation time or outdoor-exposing duration. Both effects could be caused by an increase in the oxidation susceptibility of the material either at elevated temperatures or as a result of the action of a previous stress. As can be seen, the oxidation process is considerably suppressed in the presence of HALS (the oxida-
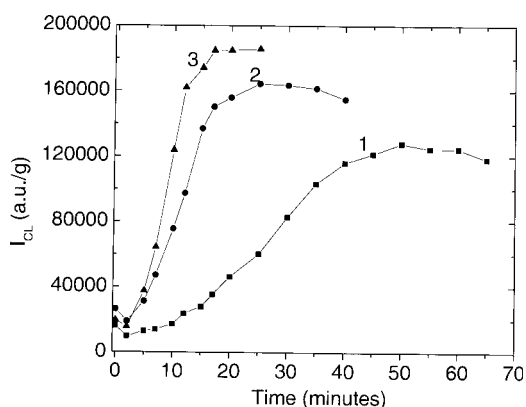

Figure 2 The isothermal CL curves at different temperatures from PR 31 stabilized i-PP film, UV irradiated for 400 h: 180°C (1); 190°C (2); 200°C (3).
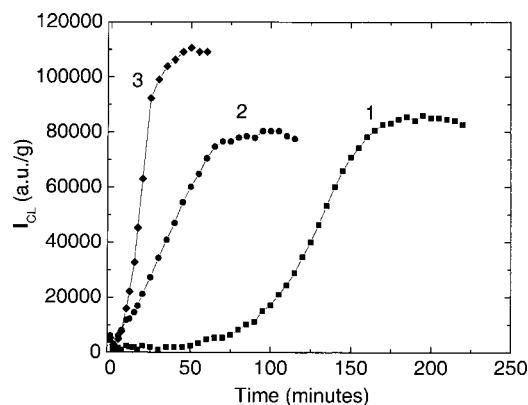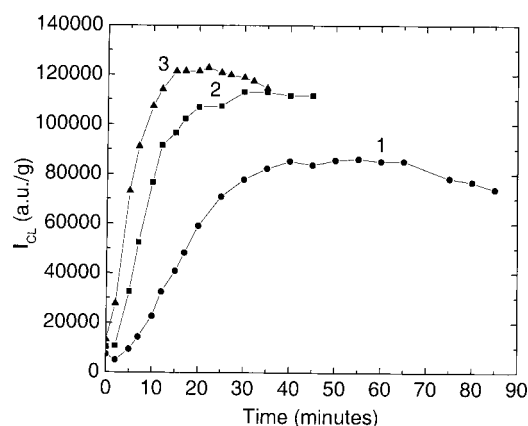

Figure 4 The isothermal CL curves at different temperatures from unstabilized i-PP film, outdoor exposed for 45 days: 170°C (1); 180°C (2); 190°C (3).

TABLE I
CL Parameters for Photodegradation of i-PP under Different Conditions

Sample	Treatment conditions	I_0 (a.u./g)	v_{ox}^{max} (a.u./g.min.)	I_{max} (a.u./g)
Unstabilized	Outdoor exposure 72 days	20 952	6 905	100 619
PR 31 stabilized	Outdoor exposure 72 days	4 500	1 150	70 318
Unstabilized	UV irradiation 70 h	28 900	9 163	118 531
PR 31 stabilized	UV irradiation 70 h	8 738	3 277	85 500

tion rate is lower, the $t_{1/2}$ and t_{max} values are higher) and this observation allow us to use the CL isotherm method to characterize the effect of this compound in photo-stabilization of i-PP.

The kinetic oxidation parameters (180°C) for UV and outdoor exposures are summarized in Table I, which presents the maximum oxidation rate (v_{ox}^{max}), the initial CL emission (I_0), and the CL maximum intensity (I_{max}). The initial CL parameter (I_0) is proportional with a concentration of peroxy radicals. As can be seen, the degradation of the stabilized i-PP sample slows down perceptibility in the case of weathering. The effect of the photostabilizer in decreasing the kinetic oxidation CL parameters is beyond doubt. This effect is clearly demonstrated in Figures 5 and 6 and can be related to the abovementioned mechanism. Thus, the polymer containing Sanduvor PR31 is less degraded upon photo-oxidation as compared to free of additive sample. As a result, the thermal stability observed upon CL measurement will be higher in the former case, as compared with the latter one.

The activation energies values calculated from chemiluminescence data obtained for i-PP exposed under accelerated and natural conditions were summarized in Tables II and III, respectively. Jones et al.[36] pointed out that the critical hydroperoxide concentration is reached

when 50% of a substance is oxidized. Using this assumption, the time ($t_{1/2}$) corresponding to $I = 0.5 I_{max}$ was determined. The activation energy obtained from $t_{1/2}$ describes the induction period, while that resulted from t_{max} corresponds to maximum oxidation time.

Theoretically, the activation energy must be constant but some polymer change this kinetic parameter with degree of stabilization[37] or degradation;[38,39] the greater the polymer degradation, the lower the value of activation energy.

The change in activation energy values for i-PP with UV irradiation time and outdoor exposure time are shown in Figures 7 and 8.

As can be seen in Tables II and III, $E_{t_{1/2}} > E_{t_{max}}$. This difference could be due to the existence of different processes; $E_{t_{1/2}}$ corresponds for induction period, while $E_{t_{max}}$ corresponds to overall process (induction and acceleration). Anyway, all stabilized samples present higher values for $E_{t_{1/2}}$ and $E_{t_{max}}$ in comparison with unstabilized ones. It is generally accepted that higher values of activation energy correspond to higher stability of a material. In our case, we can clearly observe that Sanduvor PR 31 induces higher values of activation energy of thermal oxidation as compared to unstabilized samples. This effect can be related to an antioxidative effect of the HALS which can occur even
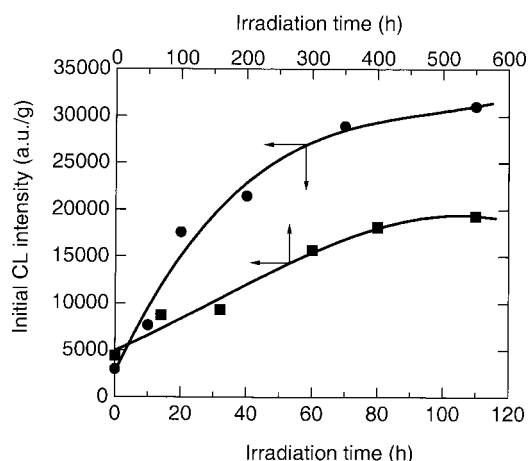
Figure 5 Dependence of the initial CL intensity (at 180°C) on the UV-irradiation time for unstabilized (●) and PR 31 stabilized (■) i-PP.
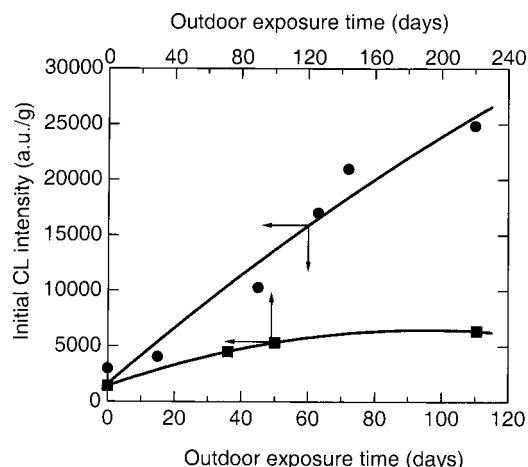
Figure 6 Dependence of the initial CL intensity (at 180°C) on the outdoor exposure time for unstabilized (●) and PR 31 stabilized (■) i-PP.

TABLE II
Activation Energy Values from CL Data for the UV-Irradiated Isotactic Polypropylene

Irradiation time (h)	Induction time ($t_{1/2}$)			Maximum oxidation time (t_{max})		
	$E_{t_{1/2}}$ kJ/mol	lnA	Correl. coef.	$E_{t_{max}}$ kJ/mol	lnA	Correl. coef.
Unstabilized sample						
0	164.1	−39.5	0.98	117.1	−26.3	0.96
20	152.6	−39.6	0.96	106.3	−25.5	0.99
70	113.4	−28.9	0.99	89.9	−21.2	0.99
110	98.2	−24.9	0.97	58.9	−12.7	0.95
Stabilized sample						
0	167.6	−39.7	0.98	116.1	−25.5	0.99
160	105.2	−24.4	0.99	112.2	−25.6	0.93
400	98.1	−22.9	0.96	91.8	−20.5	0.98

TABLE III
Activation Energy Values from CL Data for the Outdoor
Exposed Isotactic Polypropylene

Irradiation time (days)	Induction time ($t_{1/2}$)			Maximum oxidation time (t_{max})		
	$E_{t_{1/2}}$ kJ/mol	lnA	Correl. coef.	$E_{t_{max}}$ kJ/mol	lnA	Correl. coef.
Unstabilized sample						
0	164.1	−39.5	0.98	117.1	−26.3	0.96
15	159.9	−38.8	0.98	—	—	—
45	116.9	−28.9	0.99	99.4	−22.8	0.97
63	111.9	−27.8	0.99	73.2	−16.2	0.99
100	51.6	−12.1	0.99	—	—	—
Stabilized sample						
0	167.6	−39.7	0.98	116.1	−25.5	0.99
15	165.6	−39.6	0.97	116.6	−25.9	0.99
160	143.9	−34.5	0.93	115.2	−25.7	0.99
221	—	—	—	99.7	−21.7	0.96
281	126.1	−29.6	0.91	64.1	−12.5	0.94

at elevated temperatures, as previously reported in the literature[19,20] in the case of polyethylene. In fact, the occurrence of this effect allows us to apply CL in characterization of the HALS effectiveness and in evaluation of the extent of degradation effects.

In the case of the exposed samples, the activation energy would decrease because of higher oxidation susceptibility of the photo-oxidized polymer, caused by the occurrence of active oxygen containing species (peroxy radicals and hydroperoxides) induced during
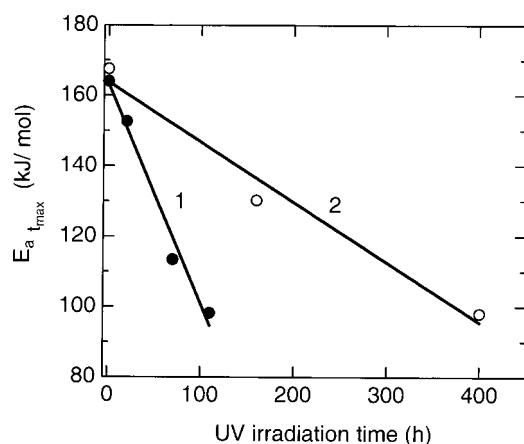

Figure 7 Activation energy dependence on UV irradiation time for unstabilized (1) and PR 31 stabilized (2) i-PP films.
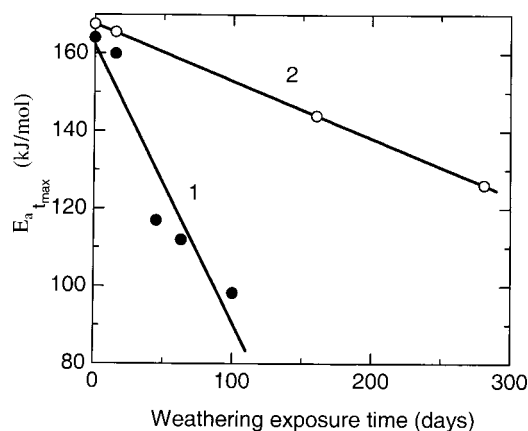

Figure 8 Activation energy dependence on weathering exposure time for unstabilized (1) and PR 31 stabilized (2) i-PP films.

TABLE IV
Slope from the Plots of Activation Energy vs. Time

Sample	Slope from the plots $E_{t_{1/2}}$ vs. time (h^{-1})	Slope from the plots $E_{t_{max}}$ vs. time (h^{-1})
Unstabilized i-PP film, outdoor exposed	0.03	0.0267
PR 31 stabilized i-PP film, outdoor exposed	0.00625	0.00625
Unstabilized i-PP film, UV irradiated	0.62	0.50
PR 31 stabilized i-PP film, UV irradiated	0.16	0.06

the photo-oxidation step. It can be expected that lower concentration of such species will be found in HALS containing samples. Therefore, a decrease in the activation energy of the oxidation of these samples will be lower than in the case of unstabilized counterparts. Now, if we represent activation-energy values as a function of the exposure time, we can observe that straight lines are obtained, suggesting a quasi-linear decrease in activation energy. The slopes of these straight lines, as shown in Figures 7 and 8, can indicate for the degree of photodegradation of the polymer and/or the stabilizing effect of the additive (Table IV).

The smaller the slope, the higher the sample stability. The examination of the efficiency of polypropylene photostabilizers from CL measurements may lead to a better understanding of the photoprocesses involved and optimum photostabilization.

CONCLUSIONS

The susceptibility of the i-PP samples towards UV and outdoor induced degradation was studied using the isothermal CL method. The values of apparent activation energy were found to be sensitive to both the antioxidative effect of the HALS and degradation level of the material. The decrease in the values of activation energy as a function of exposure time seems to be linear in the investigated ranges. The slope of such straight lines was higher as the oxidation susceptibility was increased. Thus, the samples were found to be most affected by UV-irradiation as compared to weathering exposure. However, in both cases, the presence of Sanduvor PR 31 in the i-PP samples provides more stability in comparison with unstabilized ones, as is suggested by the slope values of activation energy as a function of exposure time.

The proposed procedure, based on apparent activation energy values, seems to be adequate in evaluation the degradation level of the polymeric materials exposed under various conditions and in assessment of stabilizers effectiveness as well. The main advantage seems to be that it allows avoiding the experimental errors because it is based on a relative great number of determinations.

As it was evidenced, activation energy from CL data would be considered as a valuable parameter in evaluation of the degradation state of different materials.

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