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Photo-stabilisation mechanism under natural weathering and accelerated photo-oxidative conditions of LDPE films for agricultural applications

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Abstract

Spectroscopic methods, ultraviolet (UV) and Fourier transform infrared (FTIR) were used to determine the concentrations of the two components of hindered amine light stabilisers (HALS) in low density polyethylene (LDPE) films exposed to natural weathering up to 650 days. The used HALS is a Ciba-Geigy commercial mixture of Chimassorb 944 and Tinuvin 622 with same percentage in weight (50/50% (wt/wt)). The spectroscopic measurements were carried out on the LDPE films having some different HALS contents of 0.1, 0.2, 0.4, and 0.6% (wt/wt). The Chimassorb 944 concentration was determined by means of the absorption band area centred at 225 nm in UV spectra for the absorption of 1,3,5-triazine group, while Tinuvin 622 concentration was measured by the absorption band area at 1734 cm^{-1} in FTIR spectra corresponding to the ester group absorption. The plots describing the loss of the concentration of each component versus time exhibited similar profiles. The results suggest that the two HALS components are involved at the same time in the polymer stabilisation processes. The effect of the HALS concentration on LDPE stabilisation was interpreted applying the well-known operative mechanisms involving piperidinoxyl radicals for natural and accelerated photo-oxidative conditions. Finally electron spin resonance spectroscopy performed on 0.6 and 0.2% under natural exposure formulations are in good agreement with the spectroscopic determination of the HALS contents in the different formulations. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Low density polyethylene; Hindered amine light stabilisers; Photo-stabilisation

1. Introduction

Low density polyethylene (LDPE) is widely used for many outdoor applications, particularly for greenhouses as a covering material. This is mainly due to its flexibility, optical properties coupled with easy handling and low cost [1,2]. However, when exposed to ultraviolet (UV) light, LDPE undergoes structural modifications usually accompanied with dramatic deterioration of the physical and mechanical properties [3]. Thus stabilisers are often included in the polymer to provide stability against photo-oxidation to protect the material from UV light damaging. The effectiveness of a light stabiliser depends on many factors, including its solubility and concentration in the polymer matrix [4]. Physical loss of the stabiliser can occur by diffusion to the polymer surface during exposure [5]. Moreover, a loss of stabiliser can also occur by photochemical reactions and degradation [6] and by evaporation and leaching from the polymer surfaces and the concentration drops [7]. Generally, the physical loss of stabilisers is dependent on the geometry of the polymer samples. The most serious physical losses were observed from articles with high surface to volume ratio, i.e. fibres, thin films, coatings, etc. [5]. The physical loss of stabilisers accelerates the ageing of polymers more than thermal-oxidation or photo-oxidation. This phenomenon involves stabiliser evaporation from polymer surface, i.e. exudation to the polymer surface as precipitate. The limit of the molecular weight of the stabiliser giving persistency against leaching by decreasing the above-mentioned volatility is considered to be approximately 3000 [8]. Furthermore, the solubility of stabilisers decreases dramatically during cooling and an oversaturated metastable state is created at room temperature. A diffusion controlled equilibrium state is slowly formed and is accompanied by stabiliser blooming to the surface [5].

The serious problem to the physical loss of stabilisers can be solved by a chemical modification of the structure of

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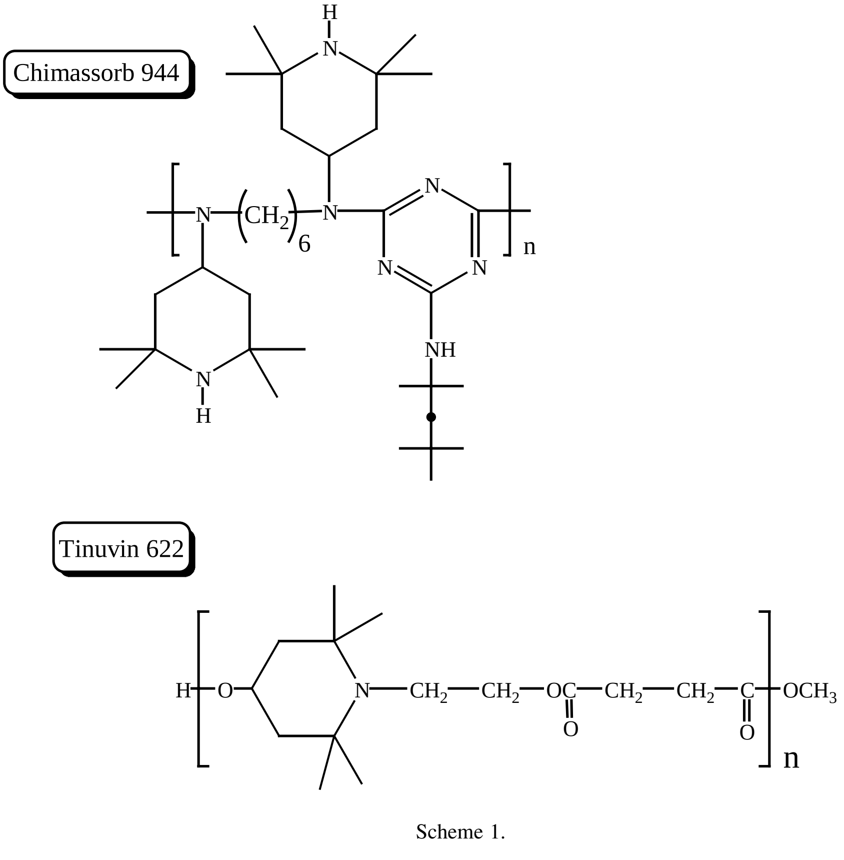
Table 1
HALS concentrations used in LDPE film formulations

Formulations	Chimassorb 944 (g/100 g of PE)	Tinuvin 622 (g/100 g of PE)	Total of HALS (g/100 g of PE)
F1	0.05	0.05	0.1
F2	0.1	0.1	0.2
F4	0.2	0.2	0.4
F6	0.3	0.3	0.6

non-physically persistent stabilisers [9]. A simple approach is that to increase both the molecular weight of stabilisers and its solubility. A great part of more efficient available commercial photo-stabilisers has an oligomeric nature and some suitable substituents improving solubility in the polymer matrix not only in the polymer melt state. Many studies, concerning the photo-stabiliser efficiency with respect to diffusion, have suggested some experimental techniques to measure the stabiliser content in the polymer matrix. Most of the analytical techniques, reported in the literature [10,11], imply a destructive method to determine by extraction of the stabilisers from the polymer (HPLC, GC). Few works were found to deal with the use of direct spectroscopic methods (UV and Fourier transform infrared (FTIR)) for measurements on solid-state films [4,12,13]. The reason of this was attributed to some problems caused by light scattering and reflection, which occur during the measurement of solid materials like polyethylene [12]. In the literature it is reported the feasibility of UV spectroscopy to detect levels of additives ranging from 0.002 to 1.00% in polyethylene [14].

The aim of this work are the concentration determination to study the photo-stabilisation effectiveness as a function of HALS content under natural weathering and accelerated photo-oxidative conditions.

UV and FTIR are used to determine the concentration of the HALS components and the measurements are taken directly from LDPE films without any extraction or refining step. The photostabiliser concentrations in LDPE films as a function of natural weathering and accelerated photo-oxidative conditions are calculated for Chimassorb 944, applying the UV spectrophotometers and for Tinuvin 622 by using FTIR spectroscopy. Finally, ESR spectroscopy, performed on the samples with 0.6 and 0.2% of HALS, was used to measure the piperidinoxyl radical concentration, and hence the HALS content involved in the stabilisation process during the exposure. The comparisons of the spectroscopic results obtained under the two different irradiation



Scheme 1.

conditions indicate different photo-stabilisation efficiency at long irradiation times.

2. Experimental

2.1. Materials

LDPE used is manufactured by the Algerian Company “ENIP” having as trade name B 24/2. The main physical properties of the material are density = 0.923 g/cc and melt flow index (MFI) = 0.3 g/10 min.

The HALS used is mixture of 50% in weight of Tinuvin 622 and 50% of Chimassorb 944, known as Tinuvin 783 and it was provided by Ciba-Geigy. The HALS was added to the LDPE for stabilisation against photo-oxidation at concentrations 0.1, 0.2, 0.4, and 0.6% (w/w) and the stabilised LDPE formulation obtained are coded as F1, F2, F4 and F6, respectively (see Table 1). The chemical structure of the stabilisers, and the molecular weight are given in Scheme 1.

2.2. Preparation of samples

Films 80 μm thick were prepared by blown extrusion process. A Battenfeld SFB 400 extruder with a ratio $L/D = 24$ was adopted. The temperature in the extruder varied from 160 to 180°C along the barrel, while in the die, it decreases from 180 to 160°C. The total residence time was about 20 s. The films were stretched in the air after leaving the die at a pulling speed of 6 m/min. They were cooled by air passing through the die into the bubble. Finally, the films were cooled with a large volume of air upward over the surface of the bubble. WAXS experiments exhibited that the films did not undergo any significant orientation during the preparation. Four concentration levels of the HALS stabiliser were used for the film preparation according to Table 1.

2.3. Natural weathering exposure

Natural weathering of stabilised LDPE films was carried out according to ASTM D 1435. The samples in the form of rectangular bands (30×20 cm^2) were mounted on 45° racks, facing the south direction. The exposure was carried out at Bejaia (Mediterranean town on the eastern coast of Algeria, latitude 36°43′N and longitude 5°4′E). The samples were exposed from December 1996 to October 1998 and removed periodically for analysis. The average radiation in the experimental period was 160 kcal/cm^2 per year. The average temperature varied between 15 (winter) and 25°C (summer). The humidity level varied between 48 (winter) and 94% (summer). The amount of rain was 760 mm/year.

2.4. Photo-oxidation under accelerated conditions

Films were irradiated at 60°C under accelerated photo-oxidative conditions in a Sepap 12.24 apparatus equipped with four mercury medium pressure lamps (400 W) filtered by a borosilicate glass bulbs ($\lambda > 290 \pm 5$ nm) simulating outdoor exposure [15].

2.5. Ultraviolet spectroscopy

UV spectra were recorded with a Perkin–Elmer spectrophotometer Lambda 6, equipped with an integrating sphere preventing the scattered light of LDPE films, with a resolution of 2 nm and sampling range of 0.5 nm. The Chimassorb 944 content in the polymer was determined from the absorption band integration between 213 and 238 nm. The absorption band area centred at 225 nm allows determining the concentration of the stabiliser before and after the natural and accelerated exposure. The contribution of the presence of Tinuvin 622 to the absorption band at 225 nm of Chimassorb 944 was verified to be negligible for all the studied films [16].

2.6. Fourier transform infrared

Infrared spectra were recorded by using a Bruker IFS 88 purged with dry air, with 2 cm^{-1} as resolution and at least 64 scans. The integrated area between 1770 and 1690 cm^{-1} of the absorption band centred at 1734 cm^{-1} was used to determine the Tinuvin 622 concentrations before and after exposure. Tinuvin 622 concentrations for the F1 formulation was influenced by the presence of the growing broad band of the carbonyl oxidation products at long natural and accelerated exposure times. This effect is quite negligible for the formulations having an amount of the photo-stabiliser larger than F1 formulation. The Tinuvin 622 concentrations at the different natural and exposure times were preferably obtained for the F1 formulation by a non-linear curve-fitting by using GRAMS/32 routine software. The second derivative criteria were used to select both the band number and the appropriate bandwidth (12 cm^{-1}) giving a good convergence with the experimental spectra. For long exposure times, these calculations allowed to separate the different contributions to the complex carbonyl envelope band due to the ester groups and the concomitant formation of photo-oxidation products.

The oxidation degree, i.e. carbonyl index, C.I., under the different oxidation conditions were obtained by calculating the carbonyl absorption at 1713 cm^{-1} from the FTIR spectra at the different oxidation times using the spectrum of the unoxidised starting material as a reference. All measured absorbances were normalised by the film thickness by the equation [17]:

$$\text{C.I.} = [A_{1713}/d]100 \qquad (1)$$

where A_{1713} is the measured absorbance at 1713 cm^{-1} from the FTIR spectrum at a certain exposure time and d is the film thickness in microns.

2.7. ESR measurements

ESR spectra were recorded by a Bruker ER200D spectrometer equipped with the X-band cavity and employing

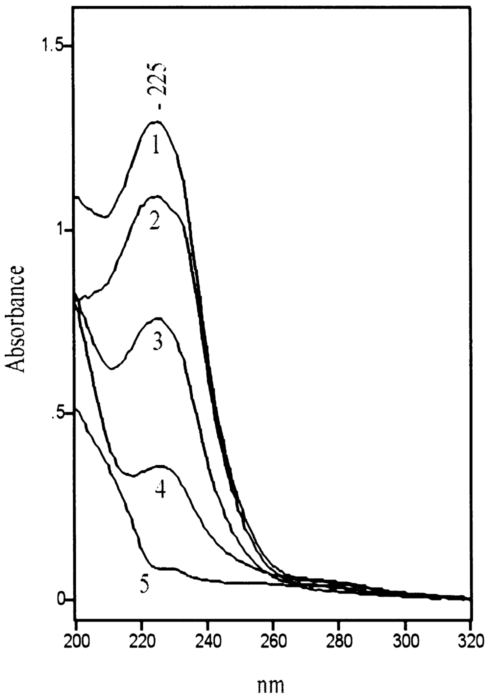


Fig. 1. UV spectral changes of the Chimassorb 944 detected at 225 nm in the UV spectra of the LDPE films with the following formulation: (1) F1; (2) F2; (3) F4; (4) F6 and (5) LDPE reference.

100 kHz modulation. The *g*-values were calculated by comparisons with the spectrum of 2,2-diphenyl-1-picryl-hydrazyl (DPPH), a free radical purchased from Aldrich ($g = 2.0037$). The microwave incident power on the cavity was of the order 5 mW (10 dB), a level at which saturation of the resonance does not occur. ESR spectra of oxidised films under UV accelerated and natural weathering conditions were carried out with a Wilmad quartz flat tissue cell. The immobilised piperinoxyl radical concentration at long exposure times were determined after chloroform extraction for 48 h by using a soxhelet apparatus. All recorded ESR signals carried out were compensated by normalisation with the fixed signal intensity of a ruby chip used as external standard material. Signal intensities were expressed as moles of piperidinyloxy radicals per kg of polymer film by calibration with an accurately prepared polypropylene film containing 0.2% (w/w) of 4-stearoyl-2,2,6,6-piperidinyloxy radical used as standard material [18].

3. Results and discussion

3.1. Spectroscopic determination of the photo-stabiliser concentrations

UV and FTIR spectroscopic techniques have been separately applied to F1, F2, F4 and F6 formulation films to determine the concentrations of Chimassorb 944 and Tinuvin 622 during the exposure time. The absorption band positioned at 225 nm, attributed to n,π^* electronic transition of 1,3,5-triazine moieties [16] in the oligomeric chains of the additive, has been used for the determination of the Chimassorb 944 concentration. The integrated band areas measured in the UV spectra, shown in Fig. 1, give a linear least-square curve fit against the initial photo-stabiliser concentration of four formulations prepared by the blending in a extruder with LDPE. The calibration plot obtained by

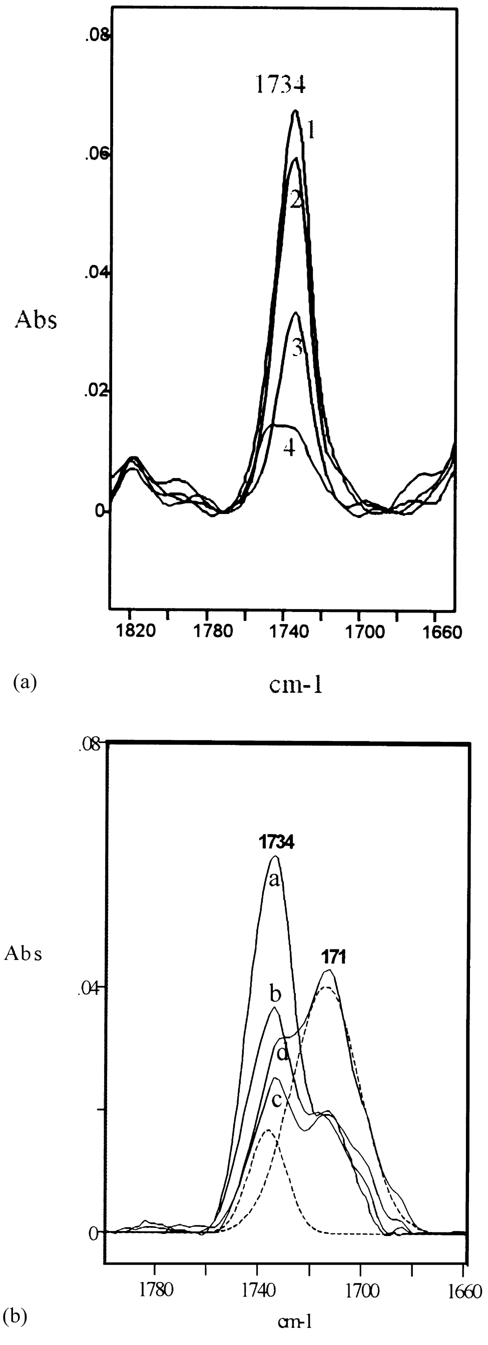


Fig. 2. (a) FTIR spectral changes of the Tinuvin 622 absorption band at 1734 cm^{-1} of LDPE films with the following formulations: (1) F1; (2) F2; (3) F4; (4) F6. (b) FTIR spectra of the natural weathered LDPE films at 650 days for formulation: (a) F6; (b) F4; (c) F2; (d) F1 with the corresponding curve-fitting (dashed lines) simulating the ester and carbonyl bands.

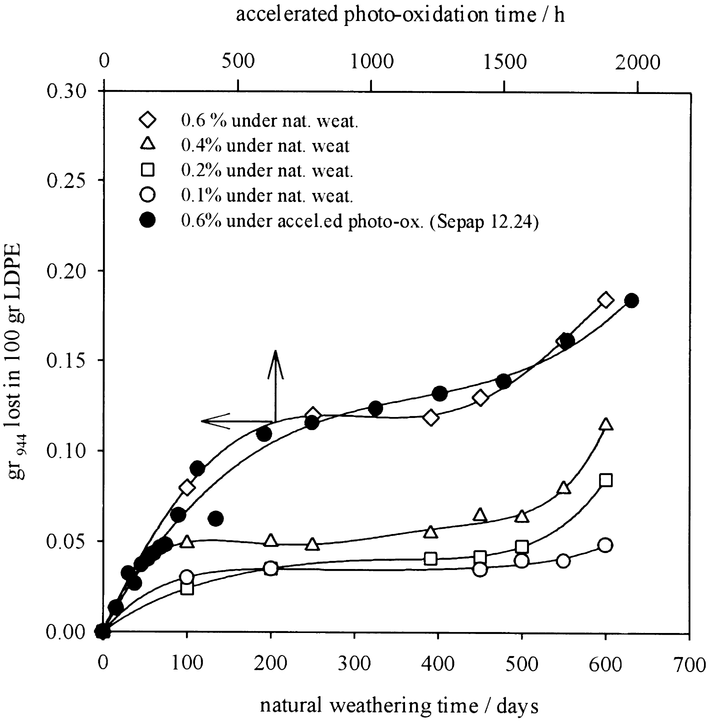


Fig. 3. Chimassorb 944 loss during the natural weathering and accelerated photo-oxidative exposures (see legends).

the linear fit gives the following equation:

$$A_{225} = 19.6[\text{Chimassorb 944}] \qquad r^2 = 0.987 \qquad (2)$$

where A_{225} and [Chimassorb 944] are the absorbance area of the band centred at 225 nm for each formulation and the concentration of Chimassorb 944 expressed as gram per 100 g of LDPE, respectively. Similarly, the calibration plot for Tinuvin 622 concentration was obtained by the absorption area measured in the FTIR spectra of the band centred at 1734 cm^{-1}, shown in Fig. 2(a). This band is attributed to ester groups in the oligomeric chains of the additive. The integrated areas against the Tinuvin 622 concentration gives a good linear correlation with a linear least-square curve fit having the following equation:

$$A_{1734} = 3[\text{Tinuvin 622}] \qquad r^2 = 0.982 \qquad (3)$$

where A_{1734} and [Tinuvin 622] are the integrated absorbance area for each formulation of the band centred at 1734 cm^{-1} and the Tinuvin 622 concentration expressed as grams per 100 g of LDPE, respectively.

The great advantage of this spectroscopic method is the non-destructive analytical procedure to determine the photo-stabiliser concentration in comparison with other analytical methods using gas-chromatographic techniques. Since the presence of the other component, i.e. Tinuvin 622 and LDPE polyolefin cannot impart any additional absorption contribution at the same wavelengths, the above reported analytical method can be widely applied for UV spectra determined at the different natural and accelerated exposure times without any restriction. The method applied for the determination of the Tinuvin 622 concentration, based on the absorbance measurements at 1734 cm^{-1}, gives good results for all the formulations of unexposed films (see Fig. 2(a)). At long exposure times, the natural and accelerated photo-oxidised films show the formation of a growing band positioned at 1713 cm^{-1} attributed to the formation of carbonyl groups, as shown in Fig. 2(b). The ester group absorbances at 1734 cm^{-1} can be easily determined for those films containing a Tinuvin 622 concentration higher than 0.1% (w/w) as a function of the exposure time, but those relative to F1 formulation are conveniently estimated by the non-linear curve fitting after 350 days. Fig. 2(b) shows that the band at 1734 cm^{-1} for the F1 formulation (*spectrum d*), is strongly influenced by the presence of a dominant growing absorption band of carbonyl groups by non-linear curve fitting procedure as reported for the dashed line spectra. Under accelerated photo-oxidation conditions the same experimental evidences have been observed for F1 formulation at long exposure times. Thus the curve fitting procedure seems to be a best solution for the ester content determination in F1 formulation after 350 and 800 h for the natural and accelerated exposure times, respectively.

3.2. Natural weathering exposure

The above-reported methods based on the UV and FTIR spectroscopies have been applied to the photostabiliser concentration changes as a function of natural exposure time. Fig. 3 exhibits the trends of the loss of Chimassorb

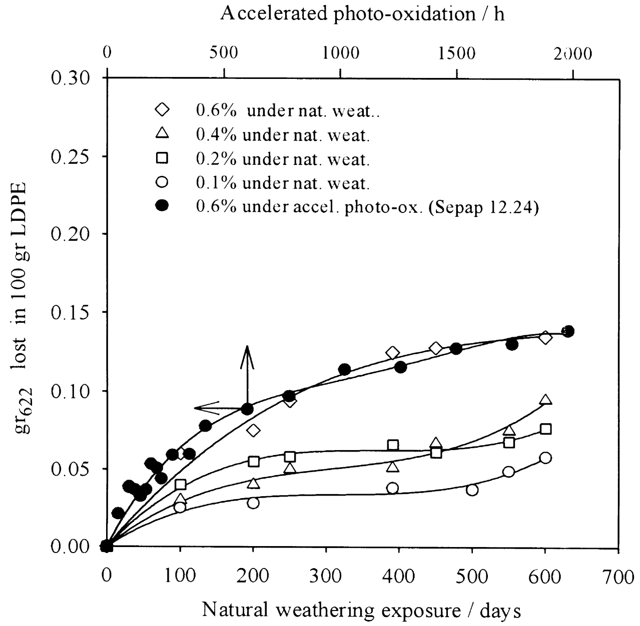


Fig. 4. Tinuvin 622 loss during the natural weathering exposure (see legends).

944 in the four formulations during the exposure time as determined by UV. Similar kinetic profile of the loss is observed for all formulations. At the initial stage of exposure, i.e. up to the first 150 days, a pronounced loss of the stabiliser in the samples is observed, followed by a plateau for almost 300–350 days and a final loss increase after 500 days of exposure. After 600 days of exposure only the F1 formulation shows a complete disappearance of the stabiliser.

Moreover, it is worth noting that the F1 and F2 samples loose almost the same amount of the Chimassorb 944 up to 500 days. In fact, after 100 days of natural weathering exposure, the amount lost in the F1 and F2 samples are 24 and 17 mg per 100 g of PE, respectively, and at 500 days the values become 36 and 45 mg, respectively. The lost of Chimassorb 944 of the F4 formulation is up 500 days not very different from that of the two films with F1 and F2 formulations (see Fig. 3). The similar trends of the F1, F2 and F4 indicate that the consumption of the stabiliser during the exposure is almost independent of the initial concentration. In contrast, the loss of the stabiliser of the film with the F6 formulation is very large. The different behaviour between the stabiliser loss of the F6 formulation and the other three formulations is very likely due to the consumption of the additives involved in the stabilisation process. Fig. 4 exhibits the loss of Tinuvin 622 concentration as a function of the exposure time. In this figure F1, F2 and F4 formulations show a continuous increase of the loss of the Tinuvin 622 up to 200 days, but a quasi plateau is observed during the successive 300 days of exposure indicating a quite constant concentration of the photostabiliser.

The comparison between Fig. 3 (Chimassorb 944) and Fig. 4 (Tinuvin 622) for the F1, F2, and F4 formulations show that the loss of the two components of the HALS mixture occurs simultaneously with the same extent. This result suggests that the two HALS components are likely involved simultaneously in the stabilisation process and physical loss. For the F6 formulation, the two trends of the loss are different. This could be due to a phenomenon of migration and volatilisation of stabilisers' molecules involved in the photostabilisation processes.

This hypothesis is confirmed by the ESR spectroscopy,

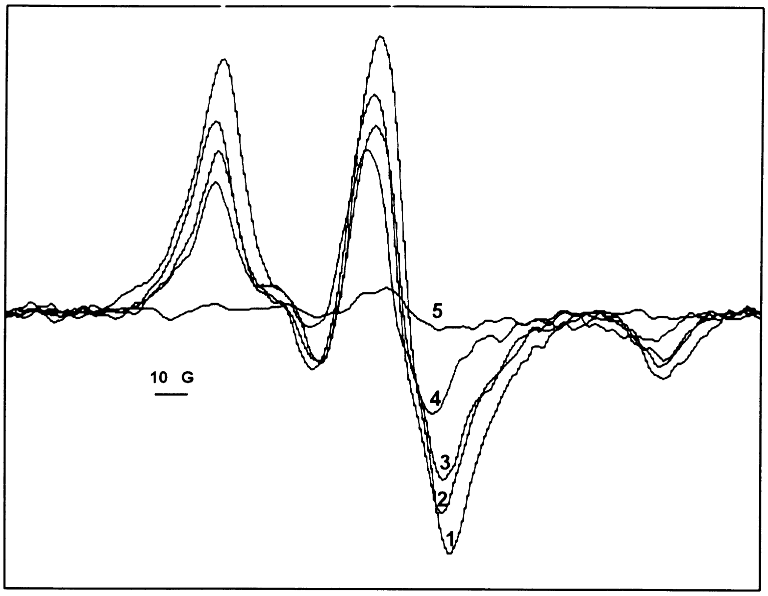
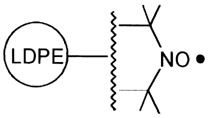
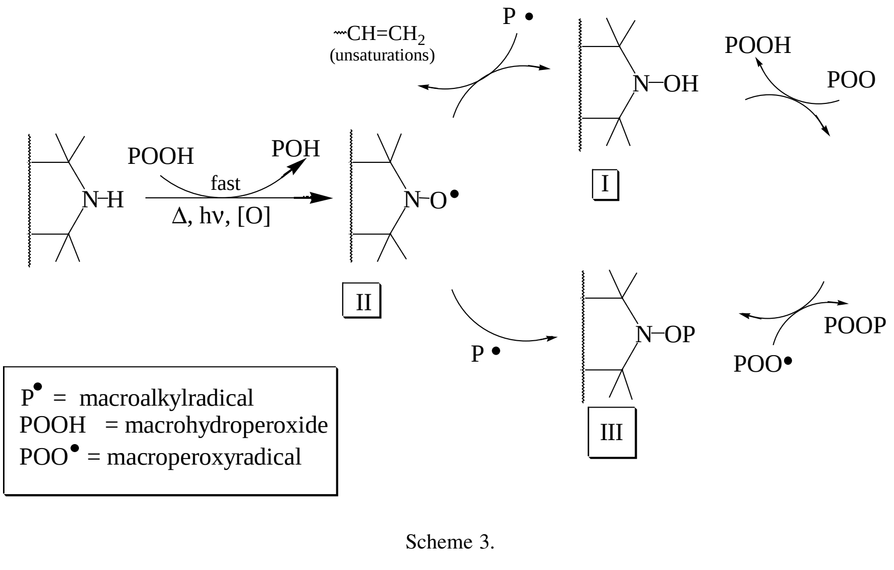


Fig. 5. ESR signals of immobilised piperinoxyl radical for a LDPE film with the F6 formulation recorded at several natural weathering times (in days): (1) 170; (2) 280; (3) 391; (4) 450; (5) unoxidised starting film.



Scheme 2.

which gives the piperidinoxyl spectral changes in the sample films with the F6 and F2 formulations. Fig. 5 shows the increase of piperidinoxyl radical concentration with the exposure time for the F6 formulation. The observed broad spectroscopic pattern is characteristic piperidinoxyl radicals into the polymer matrix. However, some previous studies have suggested the generation of polymer-bound piperidinoxyl radicals as shown in Scheme 2. This means that a certain amount of non-extractable compounds can be formed during polymer photo-oxidation [19–21]. These polymer-bound radicals have been widely proposed to explain both the efficient free radical traps and the formation of *N*-alkoxypiperidine (III), which have been accepted to be effective photostabiliser mechanism [22,23] as shown in Scheme 3. An experimental evidence of the piperidinoxyl immobilisation in LDPE matrix has been demonstrated by the persistency of the piperidinoxyl radicals in LDPE films at long natural weathering exposure times after repeated chloroform extractions. Since the spectroscopic pattern observed by ESR spectroscopy remain unchanged after solvent extraction, the piperidinoxyl radical concentrations have been determined in the same manner of those unextracted films. For the films of the F6 and F2 formulations under natural weathering, the piperidinoxyl concentration loss after the extraction is reported in Table 2. This table shows a low percentage loss after solvent extraction, i.e. a high concentration of the immobilised piperidinoxyl radical, at long natural weathering times and that it is dependent both on the initial photostabiliser concentration and on the exposure time. In fact, the F6 formulation shows a greater immobilised piperidinoxyl radical concentration than F2 one at the same natural weathering exposure time. It is worth noting that the amount of non-extractable piperidinoxyl radicals ranging from 11 to 19% at long natural long exposure times higher than 650 days for F2 and F6 formulations, respectively. These results are in agreement with previous findings indicating the similar immobilised piperidinoxyl concentrations after solvent extraction [20,21]. Furthermore, the piperidinoxyl radical concentration can be used to determine the kinetic behaviour both for the formation and the disappearance of these radicals during the natural weathering. It has been observed for the F6 formulation that the piperidinoxyl radical concentration rapidly increases during the first 100 days and subsequently decreases up to a stationary final value as reported in Fig. 6. A very similar behaviour is observed for the sample with F2 formulation. This kinetic behaviour can be related to the initial fast loss of the Chimassorb 944 as reported in Fig. 3. As shown in Scheme 3, the fast conversion from piperidine moieties to piperidinoxyl radicals (II) can readily occur in the presence of hydroperoxides. Since the frequently formulated piperidinoxyl regeneration is mainly due to *N*-alkoxypiperidine (III) [19], it seems that a moderate concentration of piperidinoxyl radical is necessary in polymer matrix to be effective under natural conditions. Thus, the initial loss of Tinuvin 622 and Chimassorb 944, simultaneously occurring during the stabilisation processes, can be ascribed both to the radical attack of the peroxy radicals or hydroperoxides inducing several chain scission of these oligomeric stabilisers with a subsequent diffusion and volatilisation of the additive fragments. Furthermore, the piperidinoxyl radicals concentration in F6 formulation after 100 days is quite similar to that found by Gugumus [24] in PE plaques with 0.2% (w/w) of Tinuvin 770 corresponding to about 200 kLy under Florida desert exposure conditions. Accordingly, these previous results have suggested that above 0.3% (w/w) of HALS, the volatilisation



Scheme 3.

Table 2
Percentage loss of the piperidinoxyl concentration in LDPE films after chloroform extraction under natural weathering and accelerated photo-oxidation exposure

Under natural weathering		
Days	Loss (%)	
	F6	F2
391	68	35
450	55	25
550	30	21
650	19	11
Under accelerated photo-oxidation		
Time (h)	Loss (%)	
	F6	
1500	44	
1750	29	
1900	20	
2000	15	

and blooming of the photo-stabilisers was the prevailing effect without having a corresponding increase of piperidinoxyl radical concentration [24].

The FTIR spectra exhibit also the expected formation both of carbonyl at 1713 cm^{-1} and vinyl groups at 909 cm^{-1}. Simultaneously the disappearance of some bands at 1734, 1532, 1040 and 870 cm^{-1} are reasonably attributed to some vibrations of two photo-stabilisers.

Fig. 7 shows that the C.I. degree calculated at 1713 cm^{-1} smoothly increases after 300 days under natural weathering exposure. This effect can be attribute to the disappearance of piperidinoxyl radical concentration as suggested in Fig. 6.

Fig. 7 indicates that the best formulation for the natural weathering exposure should have a HALS content at least 0.4% (w/w), although diffusion or volatilisation induce the loss of the major part of the photo-stabilisers. The vinyl group formation at 909 cm^{-1} (see Fig. 8), usually due to Norrish II photochemical reactions in the unstabilised PE films, is also detected after 100 days under natural weathering exposure. No induction time is observed for the generation of these groups for all formulations under natural conditions. As expected, the vinyl formation rates increases with decreasing the HALS content in the films observed at long exposure times. The F4 and F6 formulations show the same kinetic behaviour, but the remaining formulations give origin at an enhancement of the vinyl concentration at long exposure times. These results suggest that the vinyl group growth in LDPE films can be mainly ascribed to the regeneration of piperidinoxyl radicals (II) as shown in the well-accepted photostabilisation mechanism of Scheme 3. This suggestion is in great accordance with the low carbonyl content shown in Fig. 7.

3.3. Accelerated photo-oxidation

The F6 formulation was also investigated under accelerated photo-oxidative conditions in Sepap 12.24 to determine the acceleration factor by comparison with the natural weathering results. Under accelerated photo-oxidative conditions both the oxidation product formation and

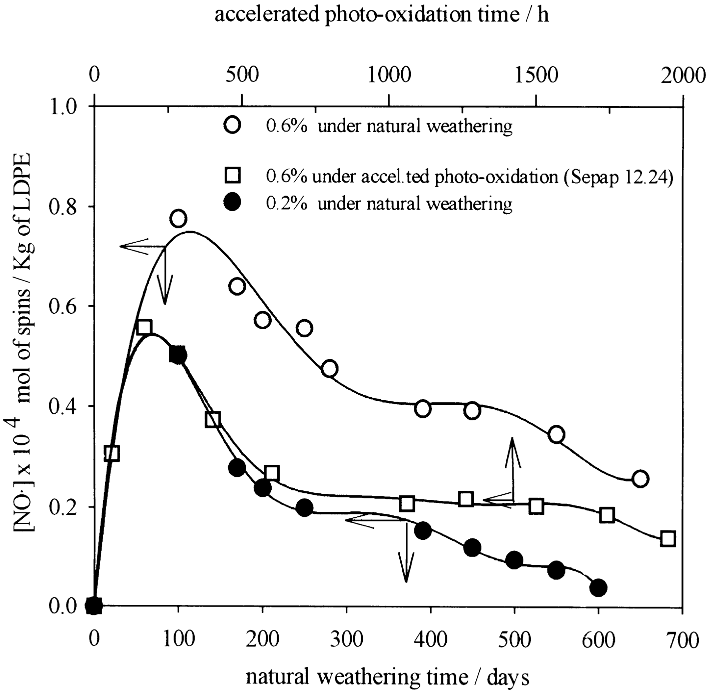


Fig. 6. Piperidinoxyl radical concentrations for F6 and F2 formulations as a function of both the accelerated photo-oxidation and natural weathering times.

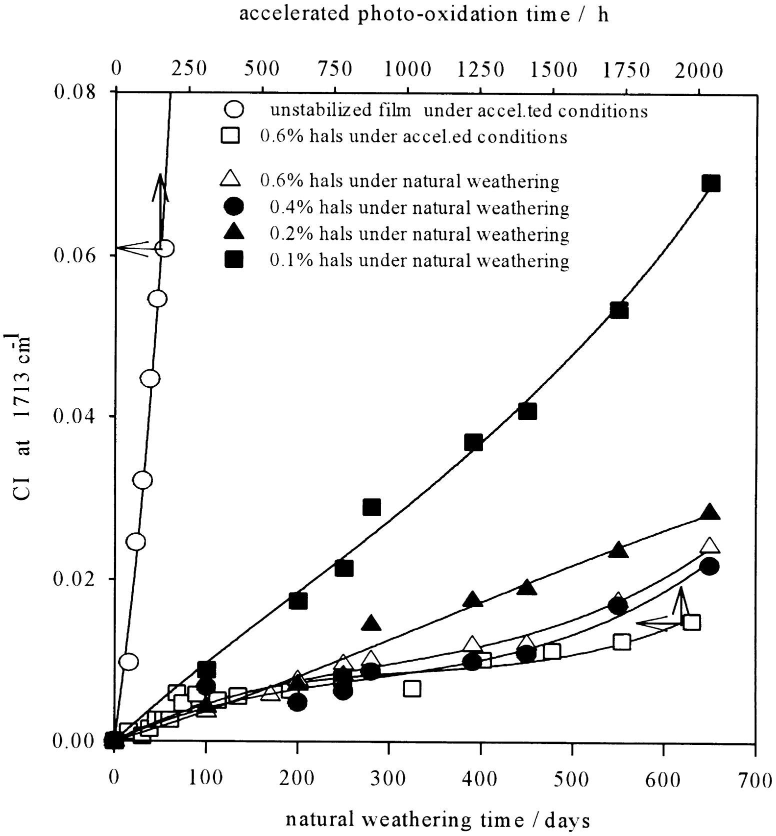


Fig. 7. Comparisons between Carbonyl Index (C.I.) found under natural weathering and accelerated photo-oxidative condition (see legends).

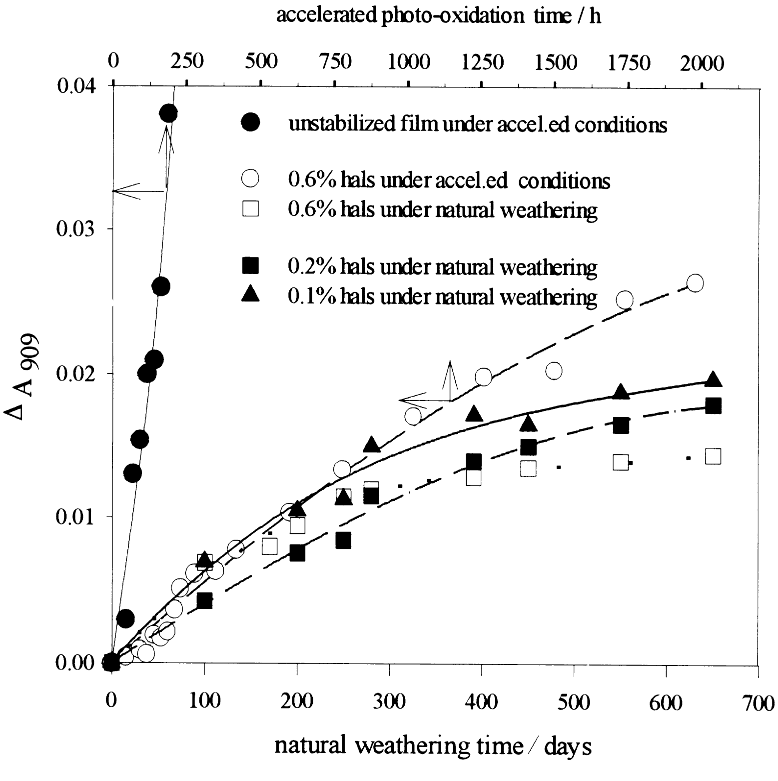


Fig. 8. Vinyl group generation rates, as followed by the FTIR spectral changes with the band at 909 cm^{-1}, for the different formulations under natural weathering and accelerated photo-oxidative condition (see legends).

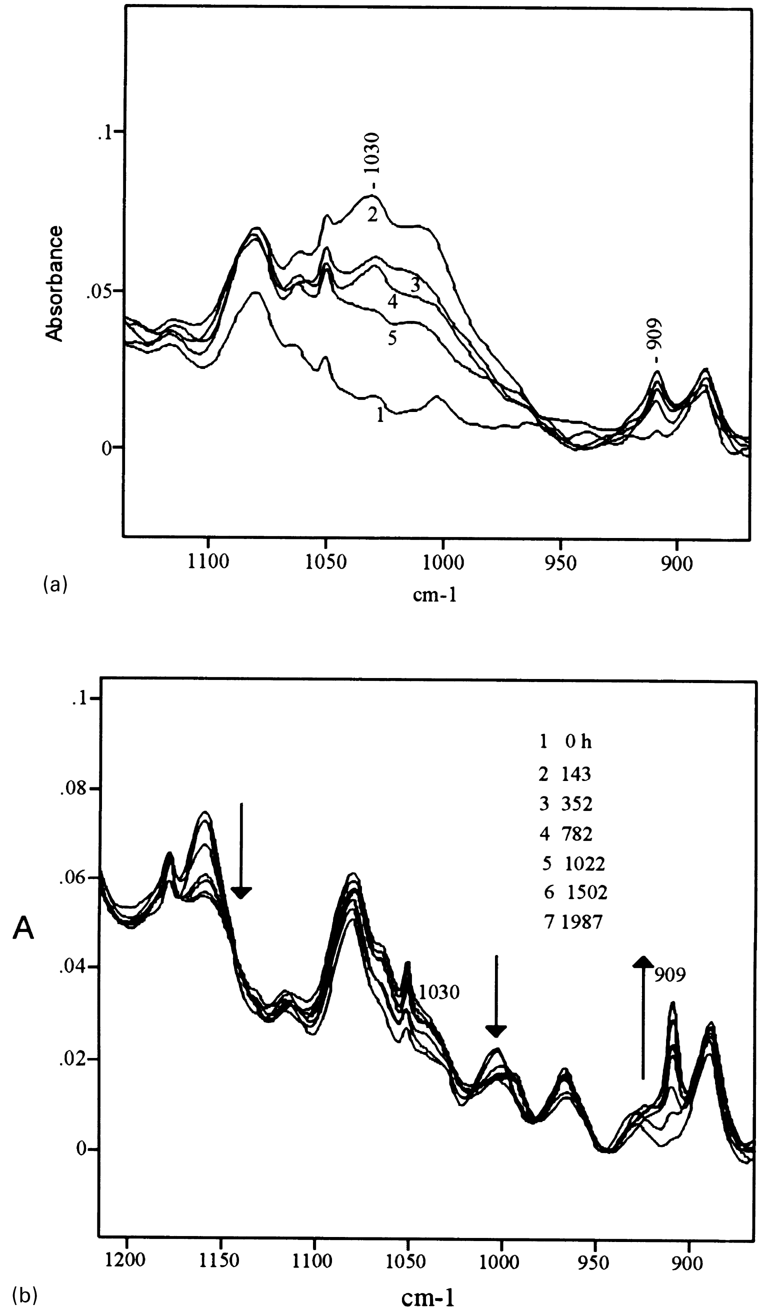


Fig. 9. FTIR spectral changes in the region between 1300 and 850 cm^{-1} for LDPE films with F6 formulation under: (a) natural weathering exposure; and (b) accelerated photo-oxidative condition (Sepap 12.14).

photo-stabiliser losses are compared with the formation rate of carbonyl, vinyl unsaturation and piperidinoxyl radical concentration obtained by FTIR, UV and ESR spectroscopies, respectively. The losses of Chimassorb 944 and Tinuvin 622, determined for the F6 sample film under accelerated photo-oxidative conditions, are shown in Figs. 3 and 4. It is found that loss of Chimassorb 944 at 600 days is about 180 mg per 100 g of LDPE and that of the Tinuvin 622 about 130 mg. This behaviour is similar to that found under natural weathering exposure.

The major losses of two photo-stabilisers in LDPE films occur during the first 500 h of the exposure, where about 30% of both the additives are lost. Then the loss rate decreases significantly at long accelerated photo-oxidation times, indicating much less consumption of the two stabilisers. Both the photo-stabilisers have the same percentage loss behaviour without showing any induction time in the initial stage of photo-oxidation. The results are in good agreement with the kinetic profile of the piperidinoxyl radical disappearance after 200 h, as reported in Fig. 6, induced by a concomitant oligomer chain scission and radical scavenging occurring in LDPE film for two photostabilisers.

The decreased percentage loss of two additives after 600 h is probably due to the generation of immobilised piperidinoxyl, preventing the photostabiliser diffusion into the polymer matrix. The presence of these immobilised piperidinoxyl radicals can be confirmed after solvent extraction as reported in Table 2. As postulated by some authors [25,26], these results can be explained by piperidinoxyl radical regeneration and immobilisation maintaining a radical scavenging efficiency also at long photo-oxidation times. In contrast, some differences in the formation rate of carbonyl and vinyl unsaturations in comparison with the natural weathering exposure are shown in Figs. 7 and 8. Fig. 7 shows that, under accelerated photo-oxidative conditions, the carbonyl index degree rapidly increases during the first 500 h. At long accelerated photo-oxidation exposure times, a lower C.I. degree is observed than that found under natural weathering conditions. In contrast, the formation rate of unsaturation groups under accelerated photo-oxidative conditions is faster than that under natural weathering at long exposure times. It is ruled out that the Norrish II photochemical reactions are much involved in the unsaturation generation because of both the low carbonyl concentration and the absence of the induction time. We believe that the observed behaviour reported in Fig. 8 can be attributed to a different photo-stabilising efficiency of HALS under two photo-oxidative conditions. Furthermore, the region between 1300 and 1000 cm^{-1} in the FTIR spectra recorded under natural weathering conditions shows the formation of a broad band centred about 1030 cm^{-1} as shown in Fig. 9(a). This broad band is not observed under accelerated photo-oxidative conditions as shown in Fig. 9(b). According to the widely accepted photo-stabilisation mechanism shown in Scheme 3, the regenerative efficiency of piperidinoxyl radicals (II) is based on both the conversion from *N*-alkoxypiperidine (III) and *N*-hydroxylpiperidine (I) by means of radical scavenging of macroalkyl radicals and macroperoxyradicals, respectively. These reactions are very important both to regenerate and to maintain stationary piperidinoxyl concentration in the polymer film. The lack of regeneration of radical (II) from *N*-alkoxypiperidine moieties (III) can explain both the low vinyl unsaturations and the high C.I. degree under natural weathering. This hypothesis is in good agreement with the findings of the broad band formation centred at 1030 cm^{-1}. Probably the reason of this difference in the regeneration efficiency could be attributed to the thermal- and photo-stability under accelerated exposure which can play an important role in the conversion of *N*-alkoxypiperidine moieties to produce piperidinoxyl radicals as suggested by some authors [24,25].

4. Conclusions

This paper discusses the application of UV and FTIR spectroscopic techniques to determine the HALS concentration in LDPE films before and after exposure to natural weathering and accelerated photo-oxidative conditions. The UV and FTIR analyses suggest that the photostabiliser disappearance for HALS content above 0.4% (w/w) up to 600 days is mostly probably due to its physical loss at long photo-oxidation times under both photo-oxidative conditions. On the contrary, the photostabiliser disappearance at the initial stage is due to the chain scission with a consequent volatilisation and diffusion of these fragments on the surface. The additive persistency strongly influences the photo-stabilisation efficiency, but the presence of the “immobilised” piperidinoxyl radicals bound to polyethylene chains by radical recombination can prevent the photo-stabiliser loss. The polymer-bound piperidinoxyl radicals can be regenerated for a quite long exposure time under both oxidative conditions. It is suggested that the kinetic profile of polymer bound-piperidinoxyl radicals is dependent on the thermo- and photo-lability of *N*-alkoxypiperidine moieties.

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References

[1] Doak KW. In: Mark HF, Bikales NM, editors. Encyclopaedia of polymer science and engineering, vol. 6. New York: Wiley, 1986. p. 383–429.
[2] Hamid SH, Amin MB, Khan JH, Maadhah AG, Al-Jarallah AM. Polym Mater Sci Engng 1991;64:165.
[3] Lamantia FP. Eur Polym J 1984;20:993.
[4] Bonekamp JE, Maecker NL. J Appl Polym Sci 1994;54:1593.
[5] Billingham NC. In: Pospisil J, Klemchuk PP, editors. Oxidation inhibition in organic materials, vol. 2. Boca Raton, FL: CRC Press, 1990. p. 249.
[6] Bell B, Beyer DE, Maecker NL, Papenfus RP, Priddy DB. J Appl Polym Sci 1994;54:1605.
[7] Moisan JY. In: Comyn J, editor. Polymer permeability, London: Elsevier, 1992. p. 119.
[8] Tichalek J, Sedlar J. Polym Degrad Stab 1989;24:1.
[9] Scoponi M, Ghiglione C. Die Angew MakromolChem 1997;252:237.
[10] Gijsman P, Hennekens J, Tummers D. Polym Degrad Stab 1993;39:225.
[11] Macko T, Furtner B, Lederer K. J Appl Polym Sci 1996;62:2201.
[12] Moller K, Gevert T. J Appl Polym Sci 1996;61:1149.
[13] Kaci M, Rezgui F, Sadoun T. Macromol Symp 1998;127:123.
[14] Luongo JP. Appl Spectrosc 1965;19:117.
[15] Scoponi M, Pradella F, Carassiti V, Tartari D. Macromol Chem Phys 1994;195:985.
[16] Scoponi M, Polo E, Pradella F, Bertolasi V, Carassiti V. J Chem Soc Perkin Trans II 1992:1127.
[17] Scoponi M, Pradella F, Kaczmarek H, Amadelli R, Carassiti V. Polymer 1996;37:903.
[18] Gerlock JL. Anal Chem 1983;55:1520.
[19] Hodgeman DKC. In: Grassie N, editor. Developments in polymer degradation-4, London: Applied Science, 1982. p. 189.
[20] Hodgeman DKC. J Polym Sci: Polym Chem Ed 1980;18:533.

[21] Hodgeman DKC. J Polym Sci Polym Chem Ed 1981;19:807.
[22] Howard JA, Tait JC. J Org Chem 1978;43:4279.
[23] Grattan DW, Carlsson DJ, Howard JA, Wiles DM. Can J Chem 1979;57:2834.
[24] Gugumus F. Polym Degrad Stab 1993;40:167.
[25] Allen NS, Edge M. Fundamentals of polymer degradation and stabilisation. London: Elsevier, 1992 (chap. 5).
[26] Rabek JF. Photostabilisation of polymer. London: Elsevier, 1990 (chap. 6).