

Preparation, photochemical stability and photostabilising efficiency of adducts of pyrene and hindered amine stabilisers in iPP matrix

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Abstract

The photostabilising efficiency of compounds containing pyrene as chromophore linked to hindered amine stabiliser (HAS) has been evaluated in photo-oxidation of isotactic polypropylene. Four series of compounds were prepared which have bridges formed either by methylene groups of different length or carbonyl group in α -position to pyrene ring. All derivatives of this type exhibited some efficiency. The most effective was 1-oxo-2,2,6,6-tetramethyl-4-piperidinyl-1-pyrenylacetate (II_d) which exhibited an induction period about half the length at 2×10^{-3} mol kg⁻¹ compared with 2,2,6,6-tetramethyl-4-piperidinol or 1-oxo-2,2,6,6-tetramethyl-4-piperidinol under the similar conditions, monitored by IR spectroscopy. Emission spectroscopy revealed that the chromophore (pyrene) decomposes rapidly when it is used alone or when is linked to HAS in the form of parent amine or *N*-oxyl radicals. The decomposition rate is slower in the case of *N*-oxyl radicals. The increase of emission in the case of *N*-oxyl radicals at the beginning of irradiation indicates the reaction of this radical with other radicals formed during photo-oxidation. These reactions result in non-radical products and consequently in increase of emission due to switching off the intramolecular quenching. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Probes; Pyrene; Hindered amine stabilisers; Fluorescence quenching; Photo-oxidation; Photo-stabilisation; Polypropylene

1. Introduction

Polymers with saturated hydrocarbon main chain, such as polyethylene or isotactic polypropylene in the highly pure state should not absorb above 220 nm and absorption in actinic region of solar radiation above 290 nm should be negligible. In reality, even in the purest polymer of this kind there is some absorption in this region due to irregularly distributed photo-active impurities. Their quantity and sensitivity to photo-oxidation depends on the mode of preparation, thermal history of processing, degree of crystallinity etc. Effective processing and long term stabilisers for this type of polymers are sterically hindered amines (HAS) especially derivatives of 2,2,6,6-tetramethylpiperidines [1–4]. Their stabilisation action is based on the formation and regeneration of *N*-oxyl radical. Paramagnetic *N*-oxyls are also effective quenchers of the excited singlet states of aromatic hydrocarbons as a result of intermolecular electron-exchange interaction between donor–aromatic

hydrocarbon in excited state and *N*-oxyl radical in ground state.

In this paper the photostabilisation efficiency of molecules combining a chromophore with hindered amine stabilisers has been tested. The selected chromophore absorbs the radiation and emits fluorescence. Hindered amine after transformation to *N*-oxyl radical can quench the fluorescence of chromophore by some intramolecular radiationless process due to paramagnetic effect. Reaction of *N*-oxyl radical with other radicals results in formation of diamagnetic product, which is no longer an intra- or intermolecular quencher. Consequently the fluorescence intensity increases [4].

Derivatives of naphthalene as chromophore linked with parent sterically hindered amines were tested as thermo- and photostabilisers for high density polyethylene (HDPE) and isotactic polypropylene (iPP) [5]. Their oxidised form as *N*-oxyl radical was not tested. The course of photooxidation was monitored by UV, IR and emission spectroscopy. The high stabilisation effect in thermo-oxidative degradation of both polymers was ascribed to some specific inhibition reaction of naphthalene. High thermo- and low photostabilisation efficiency was observed by Ortiz et al. [6] for similar derivatives

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where the naphthalene and sterically hindered amine were separated by a long alkyl chain. In thermo-oxidation an autolytic effect is observed. Naphthalene acts in thermostabilisation as a scavenger of oxygen. Spectral characteristics and photostabilisation efficiency have been compared for this type of compound with naphthalene as chromophore and parent and oxidised sterically hindered amine. In all cases the overall stabilisation effect was lower than for the same hindered amine structures but without chromophore. Rather low stabilisation effect was observed for pyrene as chromophore in these combined probes [7].

In this work we extended our previous study on four series of compounds where pyrene is used as chromophore. These compounds have been evaluated in photo-oxidation of iPP. Pyrene is a chromophore with interesting spectral properties; high fluorescence quantum yield and lifetime ($\Phi=0.6$ and $\tau=450$ ns in cyclohexane) and ability to form excimers [8]. In two series of compounds pyrene is linked through a methylene bridge with 2,2,6,6-tetramethyl piperidine. In the other series a carbonyl group situated on pyrene is included in the link between chromophore and 2,2,6,6-tetramethyl piperidine. In this way we have tried to influence the extent of interaction between pyrene and hindered amine.

2. Experimental

2.1. Materials and equipment

1-Pyrenecarboxylic acid, 1-pyreneacetic acid, *m*-chloroperbenzoic acid, titanium(IV) butoxide were obtained from Aldrich and used as received. 2,2,6,6-Tetramethyl-4-piperidinol was from Chemko Strazske Ltd. Slovakia. Silicagel L 100/400 from Lachema, Brno, Czech Republic was used.

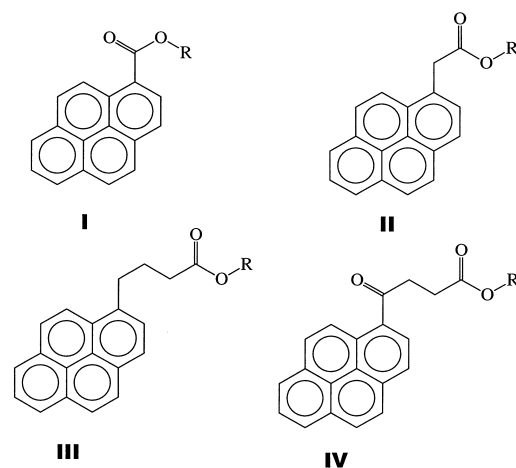
Absorption spectra were measured on M-40 spectrophotometers (Carl Zeiss, Jena, Germany) and on a Shimadzu M-160. ^1H NMR spectra of all diamagnetic compounds were measured on a Tesla 80-MHz (Tesla, Brno, Czech Republic) and on Bruker AC 400 spectrometer. Infrared spectra were recorded with a Nicolet 400 (Nicolet, USA) Fourier Transform Infrared Spectrophotometer. Emission spectra were recorded on Perkin-Elmer MPF-4 (Perkin-Elmer, Norfolk, USA).

2.2. Synthesis

The structures of adducts are given on Scheme 1. They were prepared by standard procedures.

2.2.1. Methyl 1-pyrenecarboxylate (**Ib**)

To the solution of 1 g (4.1 mmol) 1-pyrenecarboxylic acid in methanol three drops of concentrated sulphuric acid were added and the mixture was refluxed for 26 h.



	Ia,IIa, IIIa,IVa	Ib,IIb, IIIb,IVb	Ic,IIc, IIIc,IVc	Id,IIId, IIId,IVd	Ile,IIle,IVe
R	H	—CH ₃			

Scheme 1.

The crude product obtained by vacuum evaporation of methanol was purified by column chromatography (silica gel). Benzene was used as an eluent. Final product (0.9 g, 85%) was obtained as yellow crystals (*n*-heptane) with mp 81–83°C. ^1H NMR (CDCl_3) δ : 4.10 (s, 3H, CH_3O); 8.057–8.252 (m, 7H, 3–9 pyrene); 8.63 (d, 1H, 2 pyrene); 9.26 (d, 1H, 10 pyrene). FTIR spectrum (CHCl_3) (cm^{-1}): $\nu(\text{C}=\text{O})$ 1722, $\nu(\text{C}-\text{O})$ 1198, $\nu(\text{pyrene})$ 711. UV spectrum ($\lambda[\text{nm}](\log \epsilon)$ in methanol): 236(4.50), 244(4.62), 281(4.43), 352(4.37), 386(3.87).

2.2.2. 2,2,6,6-Tetramethylpiperidin-4-yl 1-pyrenecarboxylate (**Ic**)

A solution of **Ib** (0.3 g, 1.1 mmol), 2,2,6,6-tetramethyl-4-piperidinol (0.4 g, 3 mmol) and one drop of titanium(IV) butoxide in 15 ml of dry toluene was refluxed for 38 h. Toluene was evaporated on vacuum rotary evaporator and crude product was purified on a column of silica gel using benzene, to wash out starting **Ib**, and then a mixture of benzene:methanol=9:1. Eluents were evaporated and the final product was obtained in the form of yellow crystals (0.13 g, 30%) by crystallisation from *n*-heptane; mp = 126–128°C. ^1H NMR (CDCl_3) δ : 1.37 (s, 6H, $2 \times \text{CH}_3$, 2 + 6 axial); 1.45 (s, 6H, $2 \times \text{CH}_3$, 2 + 6 equat); 1.59 (m, 2H, CH_2 , 3 + 5 axial); 2.25 (m, 2H, CH_2 , 3 + 5 equat); 5.66 (m, 1H, $\text{CH}-\text{O}$); 8.07–8.26 (m, 7H, 3–9 pyrene); 8.62 (d, 1H, 2 pyrene); 9.28 (d, 1H, 10 pyrene). FTIR spectrum (CHCl_3) (cm^{-1}): $\nu(\text{C}=\text{O})$ 1713, $\nu(\text{C}-\text{O})$ 1194, $\nu(\text{pyrene})$ 711. UV spectrum ($\lambda[\text{nm}](\log \epsilon)$ in methanol): 244(4.67), 273(4.34), 281(4.43), 352(4.37), 386(3.87).

2.2.3. 1-Oxy-2,2,6,6-tetramethylpiperidin-4-yl 1-pyrene-carboxylate (**Id**)

To a solution of **Ic** (60 mg, 0.155 mmol) in diethyl ether *m*-chloroperbenzoic acid (53 mg, 0.31 mmol) was added in small parts with stirring and cooling (ice). The reaction mixture was stirred with cooling for 1 h and another 1 h at lab temperature. The mixture was washed with 2% Na₂CO₃ water solution, with water and dried with anhydrous sodium sulphate. Ether was evaporated and crude product was crystallised from *n*-heptane giving slightly orange crystals (35 mg, 56%) with mp 174–176°C. FTIR spectrum (CHCl₃) (cm⁻¹): ν(C=O) 1715, ν(C–O) 1198, ν(pyrene) 711. UV spectrum (λ[nm](log ε) in methanol): 244(4.71), 270(4.45), 281(4.53), 352(4.37), 385(3.87).

2.2.4. Methyl 1-pyreneacetate (**Iib**)

Compound **Iib** was prepared and purified by the procedure used in the synthesis of compound **Ib**. Yellow crystals (81%) with mp 90–92°C were obtained. ¹H NMR (CDCl₃) δ: 3.7 (s, 3H, CH₃O) 4.35 (s, 2H, CH₂CO) 7.9–8.3 (m, 9H, pyrene). FTIR spectrum (CHCl₃) (cm⁻¹): ν(C=O) 1733, ν(CH₃ asym) 1436, ν(C–O) 1165, ν(pyrene) 847. UV spectrum (λ[nm](log ε) in methanol): 234(4.67), 242(4.93), 265(4.45), 275(4.74), 311(4.13), 326(4.51), 341(4.68).

2.2.5. 2,2,6,6-Tetramethylpiperidin-4-yl 1-pyreneacetate (**Iic**)

This compound was prepared and purified in a fashion analogous to compound **Ic**. Yellow oil (50%) was obtained which gradually solidified to crystals with mp 132–136°C. ¹H NMR (CDCl₃) δ: 1.2 (s, 6H, 2×CH₃, 2+6 axial) 1.25 (s, 6H, 2×CH₃, 2+6 equat) 1.3 (m, 2H, CH₂, 3+5 axial) 1.9 (m, 2H, CH₂, 3+5 equat) 4.3 (s, 2H, CH₂CO) 5.2(m, 1H, CH–O) 7.95–8.3 (m, 9H, pyrene). FTIR spectrum (CHCl₃) (cm⁻¹): ν(C=O) 1724, ν(C–N) 1370, ν(C–O) 1165, ν(pyrene) 847. UV spectrum (λ[nm](log ε) in methanol): 233(4.64), 243(4.81), 255(4.02), 265(4.36), 276(4.62), 312(4.00), 325(4.39), 341(4.56).

2.2.6. 1-Oxy-2,2,6,6-tetramethylpiperidin-4-yl 1-pyreneacetate (**Iid**)

The same procedure was used as for **Id**. However the crude product was purified by column chromatography (silica gel, benzene:methanol=9:1). Orange oil (53%) which did not crystalize was obtained after solvent evaporation. FTIR spectrum (CHCl₃) (cm⁻¹): ν(C=O) 1727, ν(C–N) 1366, ν(C–O) 1163, ν(pyrene) 847. UV spectrum (λ[nm](log ε) in methanol): 234(4.52), 243(4.75), 255(4.00), 265(4.29), 276(4.55), 311(3.95), 325(4.32), 341(4.49).

2.2.7. 2,2,6,6-Tetramethylpiperidin-4-yl 1-pyreneacetate hydrochloride (**Iie**)

To a solution of **Iic** (57 mg, 0.1 mmol) in chloroform, methanol saturated with hydrogen chloride was added

dropwise. A precipitate was formed gradually. Yellow powder (85%) with mp 264–266°C was obtained by filtration. UV spectrum (λ[nm](log ε) in methanol): 234(4.57), 243(4.80), 255(4.16), 265(4.43), 276(4.66), 311(4.01), 325(4.38), 341(4.54).

2.2.8. Methyl-4-oxo-4-(1-pyrenyl) butyrate (**Ivb**)

4-Oxo-4-(1-pyrenyl) butyric acid (4 g, 13.3 mmol) in methanol (50 ml) saturated with hydrochloric acid was heated under reflux for 1 h. Yellow needles were obtained by crystallisation from methanol mp 105–108°C (Ref. [9] 108–108.5°C). Yield: 3.3 g (82%). ¹H NMR (CDCl₃) δ: 2.95 (t, 2H, –CH₂–CO); 3.55 (t, 2H, CH₂–CO–O); 3.75 (s, 3H, CH₃–O–CO); 8.0–8.95 (m, 9H, pyrene). UV spectrum (λ[nm](log ε) in methanol): 234(4.56), 242(4.61), 278(4.57), 353(4.26).

2.2.9. 2,2,6,6-Tetramethylpiperidin-4-yl-4-oxo-4-(1-pyrenyl)butyrate (**Ivc**)

Procedure the same as for **Ic**. Yield of product after chromatography (silicagel, chloroform acetone) was 0.87 g (62%) mp 117–122°C. ¹H NMR (CDCl₃) δ: 1.15 (s, 6H, CH₃, 2+6 axial); 1.25 (s, 6H, CH₃, 2+6 equat); 1.1–1.3 (m, 3H, CH₂, 3+5 axial + NH); 1.97 (m, 2H, CH₂, 3+5 equat); 2.9 (t, 2H, CH₂CH₂–CO–); 3.55 (t, 2H, CH₂, CH₂–CO–O); 5.27 (m, 1H, >CH–O); 8.0–8.9 (m, 9H, pyrene). IR (KBr) cm⁻¹: ν(C–H) 3042–2900, ν(C=O) 1733, ν(C=O)1674, ν(C–O) 1261, ν(pyrene) 852. UV spectrum (λ[nm](log ε) in methanol): 234(4.52), 242(4.56), 281(4.44), 354(4.13).

2.2.10. 1-Oxy-2,2,6,6-tetramethylpiperidin-4-yl-4-oxo-4-(1-pyrenyl)butyrate (**Ivd**)

Procedure same as in **Ic**. Product (0.6 g, 58%) was obtained after chromatography (silicagel, benzene, acetone) and crystallisation from diethylether with mp 95–99°C. IR (KBr) cm⁻¹: ν(C=O) 1733, ν(C=O) 1672, ν(NO⁺) 1363, ν(C–O) 1155, ν(pyrene) 849. UV spectrum (λ[nm](log ε) in methanol):234(4.60), 242(4.62), 281(4.46), 353(4.19).

2.2.11. 2,2,6,6-Tetramethylpiperidin-4-yl-4-oxo-4-(1-pyrenyl)butyrate hydrochloride (**Ive**)

Procedure the same as with **Iie** yielded yellow crystalline compound mp 117–125°C. UV spectrum (λ[nm](log ε) in methanol): 235(4.57), 243(4.66), 280(4.67), 354(4.18).

Preparation of 2,2,6,6-tetramethylpiperidin-4-yl-4-(1-pyrenyl)butyrate (**IIIc**), 1-oxo-2,2,6,6-tetramethyl piperidin-4-yl-4-(1-pyrenyl)butyrate (**IIIb**) and 2,2,6,6-tetramethyl-piperidin-4-yl-4-oxo-4-(1-pyrenyl)butyrate hydrochloride (**IIIe**) was described previously [10,11].

2.3. Polymer preparation

Additives were incorporated into unstabilised PP powder (Daplen, Borealis, Linz, Austria) in two

concentrations 2×10^{-2} and 2×10^{-3} mol kg⁻¹, respectively. The required amount of additive was dissolved in methanol and this solution was added to 1 g of PP powder. The methanol was evaporated with continuous mixing at room temperature. The PP films (0.1 mm) were pressed in an electrically heated laboratory press (Fontune, The Netherlands) at 200°C for 1 min.

2.4. Photo-oxidation

Photo-oxidation was performed on the merry-go-round type set up. Medium pressure 400 W or 250 W mercury arc (RVC or RVL, Tesla Holesovice, Czech Republic) was used as the source of radiation ($\lambda > 310$ nm). The temperature of photo-oxidation was 30°C. The course of photo-oxidation was followed by FTIR spectroscopy in the carbonyl region (1700–1740 cm⁻¹). Decomposition of the additives in the course of photo-oxidation was followed by FTIR and UV spectroscopy.

3. Results and discussion

The kinetics of decay of probes based on pyrene was monitored by UV spectroscopy. Absorption spectra of pyrene derivatives linked with 2,2,6,6-tetramethylpiperidine structural unit in the form of parent amine with methylene bridge exhibit well-resolved vibrational structure as like unsubstituted pyrene. On the other hand, carbonyl group directly linked on the pyrene strongly

influences the absorption spectrum. Absorption bands are broader and exhibit less resolved vibrational structure (Fig. 1). Spectral bands are gradually shifted to longer wavelengths. The same behaviour was observed for the set of methyl esters and 1-oxy-2,2,6,6-tetramethylpiperidin-4-yl esters.

Irradiation with $\lambda > 310$ nm leads to gradual decomposition of all samples to products, which do not absorb in region of pyrene absorption. Consequently, a decrease of absorption is observed although the samples contain a structural unit effective in light stabilisation. Absorption spectra of 2,2,6,6-tetramethyl-4-piperidyl 1-pyrenyl acetate (**IIc**) in iPP matrix for different time of irradiation are shown in Fig. 2. The extent of decomposition can be expressed as the decrease of the area in absorption spectrum after irradiation assuming 100% before irradiation. In Fig. 3, the courses of degradation of pyrene and derivatives of 4-(1-pyrenyl) butanoic acid (**IIIa–IIIc**) are depicted. The decomposition of parent pyrene is very rapid at irradiation with 400 W mercury arc. It completely disappears after two hours of exposure. The decomposition of acid (**IIIa**) and methylester (**IIIb**) is rapid, being complete after 3 h of irradiation. Parent amine (**IIIc**) is more stable — about 4 h. The most stable is *N*-oxyl derivatives (**IIIc**). Its decomposition required three times longer irradiation time under the same condition as parent amine.

In all cases, pyrene was decomposed most rapidly. Other pyrene derivatives (**I–IVa,b,c**) besides *N*-oxyl (**I–IVd**) decomposed in similar way. Basically, no big difference among them was observed. The decay of these

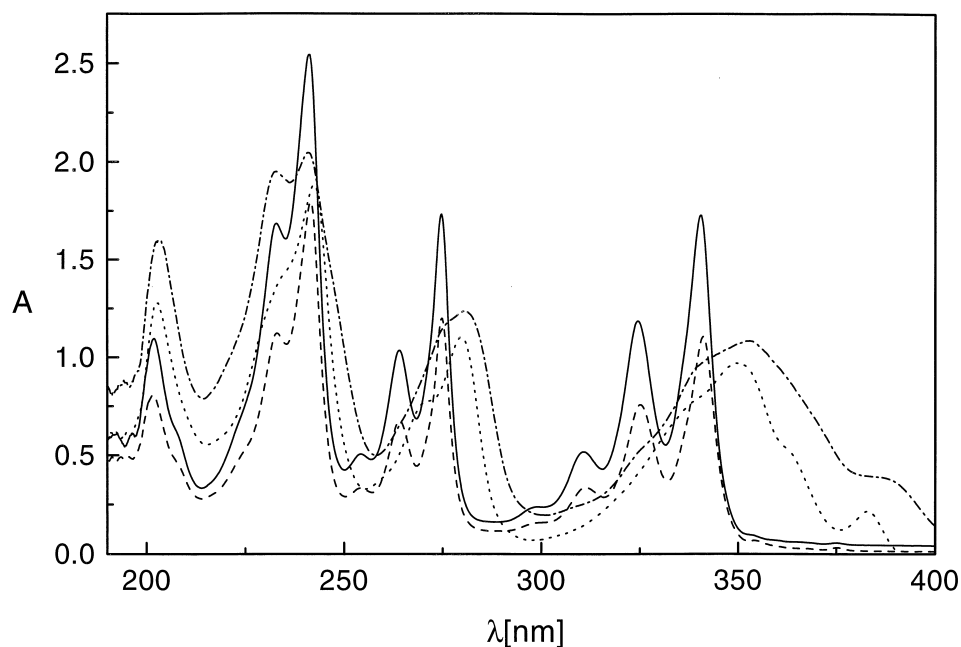


Fig. 1. Absorption spectra of 2,2,6,6-tetramethylpiperidin-4-yl 1-pyrenecarboxylate (**Ic**) ····; 2,2,6,6-tetramethylpiperidin-4-yl 1-pyreneacetate (**IIc**) —; 2,2,6,6-tetramethylpiperidin-4-yl-4-(1-pyrenyl)butyrate (**IIIc**) - - -; and 1-oxy-2,2,6,6-tetramethylpiperidin-4-yl-4-oxo-4-(1-pyrenyl)butyrate (**IVc**) - · - · in methanol.

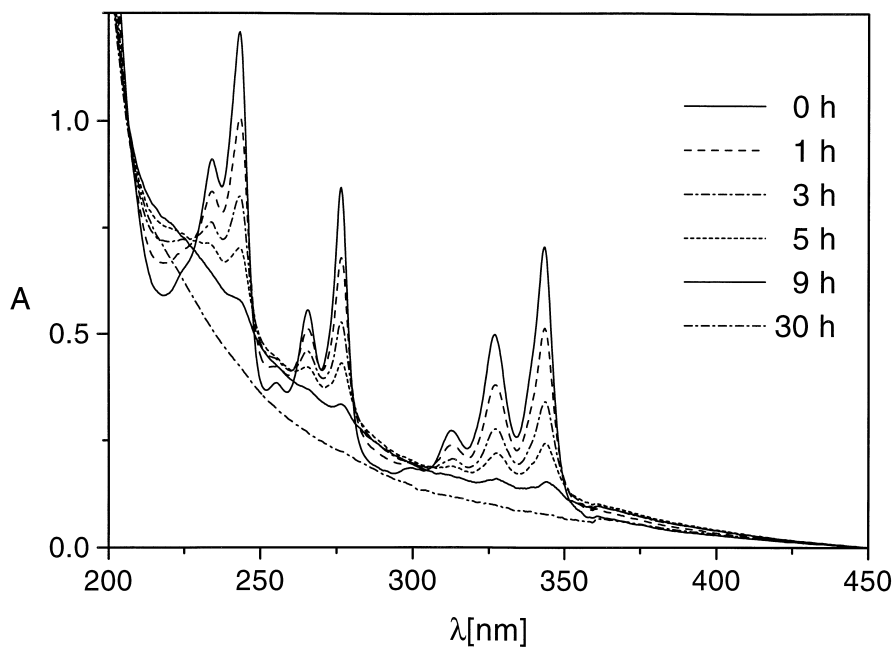


Fig. 2. Changes of absorption spectra of 2,2,6,6-tetramethylpiperidin-4-yl 1-pyreneacetate (**IIc**), $c = 2 \times 10^{-3} \text{ mol kg}^{-1}$ in PP film during irradiation (400 W, $\lambda > 310 \text{ nm}$).

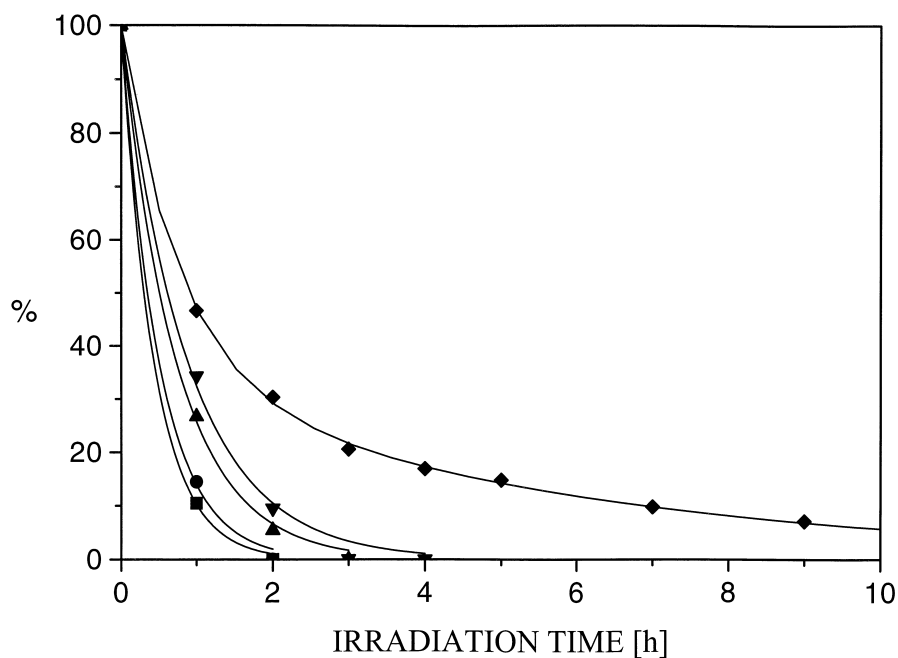


Fig. 3. Kinetics of photolysis ($\lambda > 310 \text{ nm}$) of adducts ($c = 2 \times 10^{-3} \text{ mol kg}^{-1}$) in PP films: ■, pyrene; ●, 1-pyrene butyric acid (**IIIa**); ▲, methyl-(1-pyrenyl)butyrate (**IIIb**); ▼, 2,2,6,6-tetramethyl piperidin-4-yl-4-(1-pyrenyl)butyrate (**IIIc**), ◆, 1-oxo-2,2,6,6-tetramethylpiperidin-4-yl-4-(1-pyrenyl)butyrate (**IIId**).

additives was well fitted by a single exponential indicating that simple decomposition reaction occurs. The decomposition of additive containing *N*-oxyl structural unit was the slowest. The course of decomposition is fitted by a biexponential function. It indicates that par-

allel reactions occur. It is known that *N*-oxyls can inhibit decomposition either by quenching or by reaction with other radicals forming diamagnetic products, such as alkoxyamines and hydroxyamines. Quenching is not sufficiently effective and the concentration of *N*-oxyls

was not high enough for scavenging of all radicals and simultaneously the photolytic decomposition of chromophore occurred.

The course of photo-oxidation was followed by emission spectroscopy for films of iPP doped with samples **Ia–Ie** and **IIa–IIe** at concentration 2×10^{-2} mol kg $^{-1}$. The fluorescence spectra of all samples before irradiation exhibited vibrational structure. The ratio between

bands of fluorescence spectrum changed during irradiation. The vibrational structure of the fluorescence spectrum of **IIa** completely disappeared (Fig. 4). The fluorescence intensity decreased during irradiation for all samples except **Id** and **IId** indicating decomposition of pyrene chromophore during photo-oxidation (Fig. 5). Additives **Id** and **IId** showed an increase of emission as result of scavenging. Non-radical products are formed

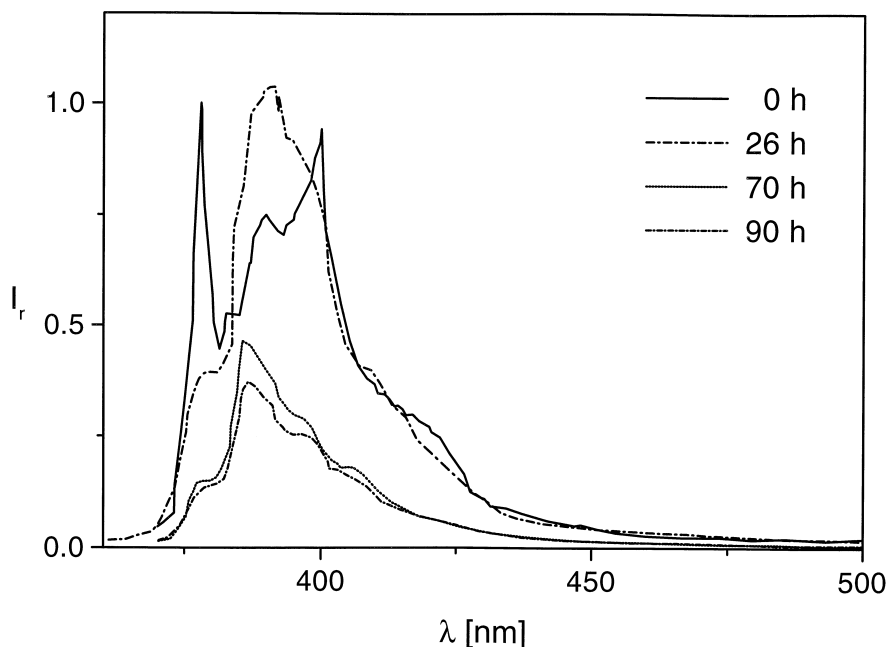


Fig. 4. Influence of irradiation on emission spectra of 1-pyreneacetic acid (**IIa**) ($c = 2 \times 10^{-2}$ mol kg $^{-1}$) in PP film (excitation at 367 nm).

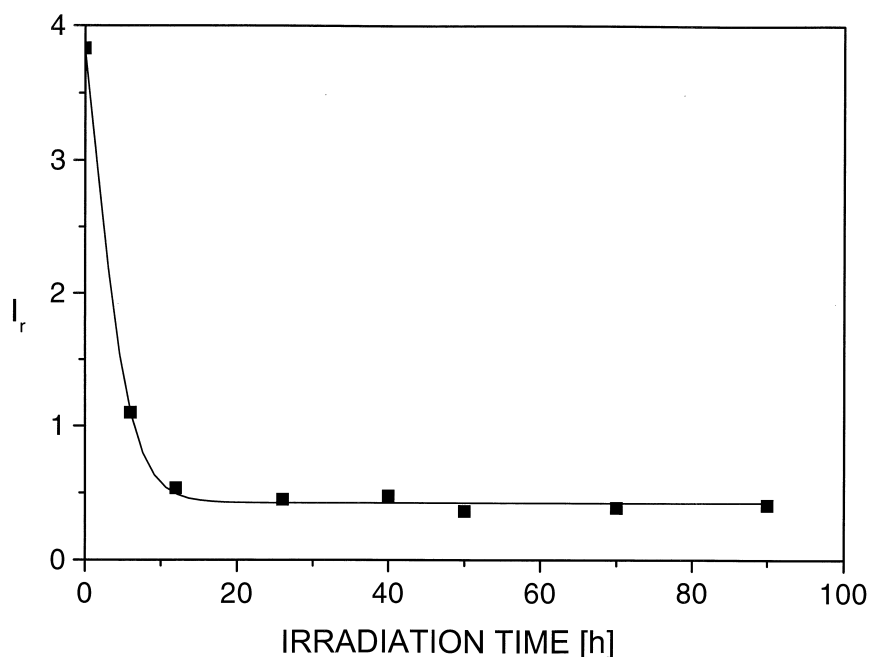


Fig. 5. Influence of emission intensity on irradiation time for 2,2,6,6-tetramethylpiperidin-4-yl 1-pyreneacetate hydrochloride (**IIe**) ($c = 2 \times 10^{-2}$ mol kg $^{-1}$) in PP film (excitation at 367 nm).

which exhibit higher fluorescence because intramolecular quenching is switched off [4]. For **Id** the fluorescence intensity increased, decreased and after 90 h of irradiation was still higher than at the beginning. The band ratio was changed (Fig. 6). For **IIId** the intensity of fluorescence was 2.5 times higher for irradiation 12 h and after 90 h it was as intense as before irradiation.

The fluorescence spectrum was hypsochromically shifted (Figs. 7 and 8).

The course of the photo-oxidation of the polypropylene films was measured by monitoring the growth in the non-volatile carbonyl oxidation products using FTIR spectroscopy. Fig. 9. shows the rate of photo-oxidation of PP films containing pyrene and derivatives

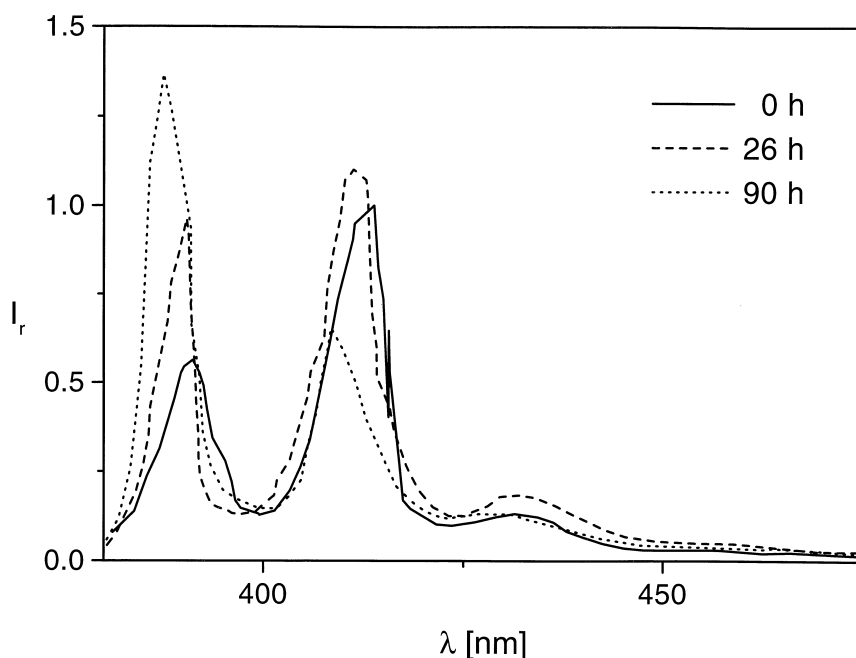


Fig. 6. Influence of irradiation on fluorescence emission of 1-oxy-2,2,6,6-tetra methylpiperidin-4-yl 1-pyrenecarboxylate (**Id**) in PP film (excitation at 367 nm).

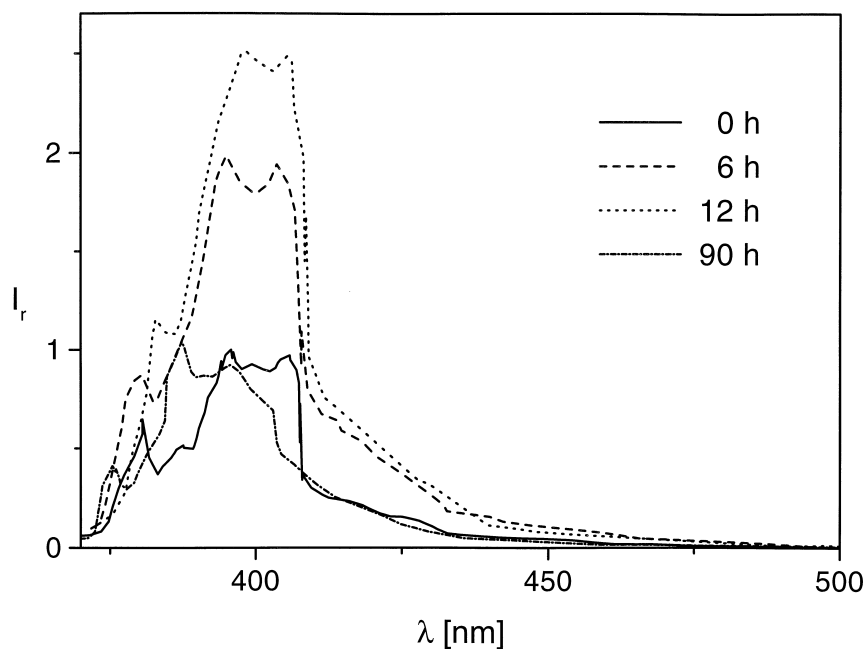


Fig. 7. Changes of emission spectra of 1-oxy-2,2,6,6-tetramethylpiperidin-4-yl 1-pyreneacetate (**IIId**) in PP film during irradiation (excitation at 345 nm). Concentration of additive $c = 2 \times 10^{-2} \text{ mol kg}^{-1}$.

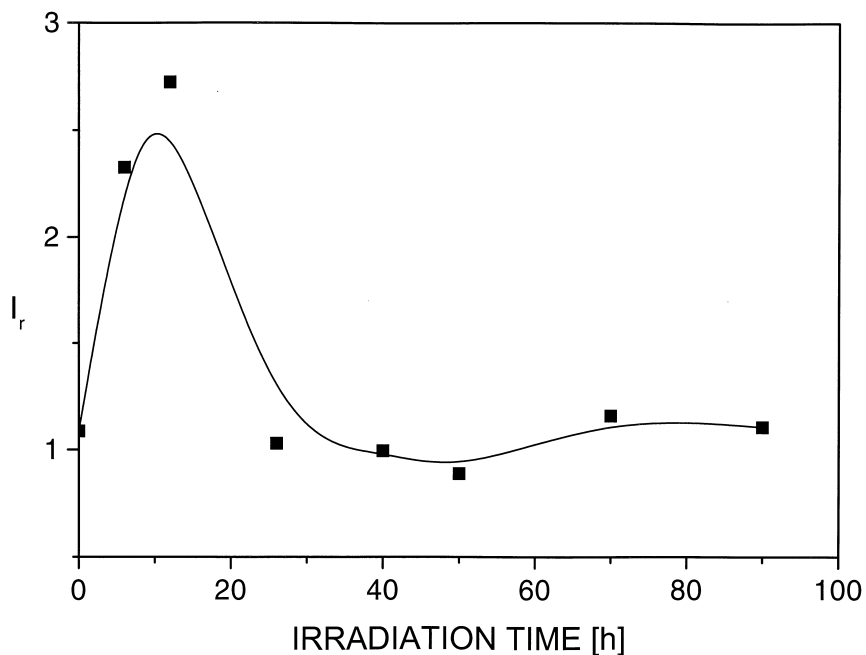


Fig. 8. Influence of emission intensity on time of irradiation for 1-oxy-2,2,6,6-tetramethylpiperidin-4-yl 1-pyreneacetate (**IIId**) in PP film during irradiation (excitation at 345 nm). Concentration of additive $c = 2 \times 10^{-2} \text{ mol kg}^{-1}$.

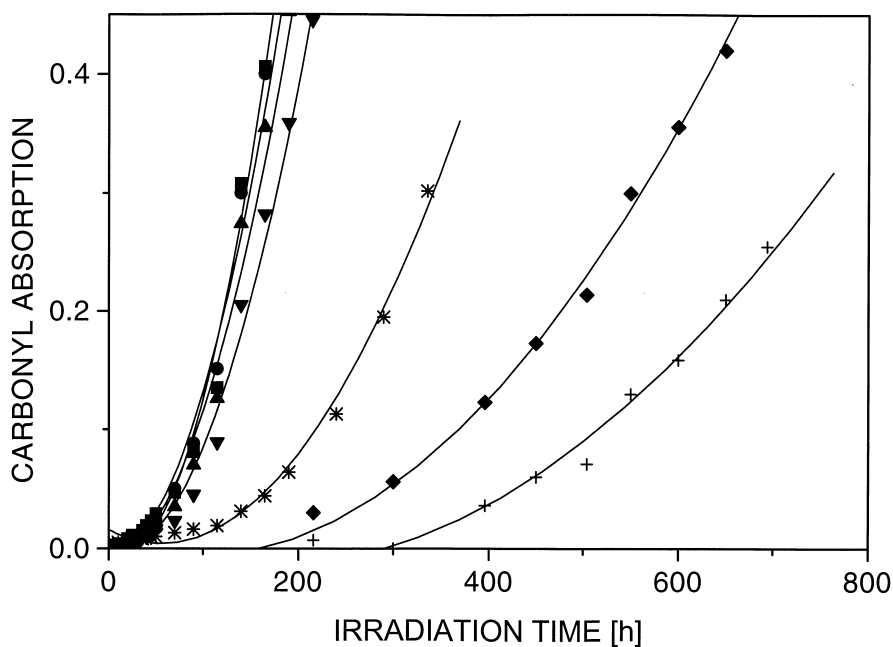


Fig. 9. Rates of photo-oxidation ($\lambda > 310 \text{ nm}$) of PP films (ca. 0.1 mm) containing: \blacksquare , no additive; \bullet , pyrene; \blacktriangle , 1-pyreneacetic acid (**IIa**); \blacktriangledown , methyl 1-pyreneacetate (**IIb**); \blacklozenge , 2,2,6,6-tetramethylpiperidin-4-yl 1-pyreneacetate (**IIc**); $+$, 1-oxy-2,2,6,6-tetramethyl piperidin-4-yl 1-pyreneacetate (**IIId**) and $*$, 2,2,6,6-tetramethylpiperidin-4-yl 1-pyreneacetate hydrochlorid (**IIe**). Additives concentration was $2 \times 10^{-3} \text{ mol kg}^{-1}$. 250 W mercury arc was used.

of 1-pyreneacetic acid at concentration $2 \times 10^{-3} \text{ mol kg}^{-1}$. Additives like pyrene, 1-pyreneacetic acid and its methyl ester at this concentration showed either no or extremely low stabilising effect. Derivatives containing covalently bonded structural unit of HAS exhibited

performance inhibiting the photo-oxidation. The best efficiency was reached with adequate nitroxyl radical — **IIId**, followed by parent amine — **IIc**. Naturally the lowest effect was exhibited by the parent amine in the form of hydrochloride — **IIe**. In this form the oxidation

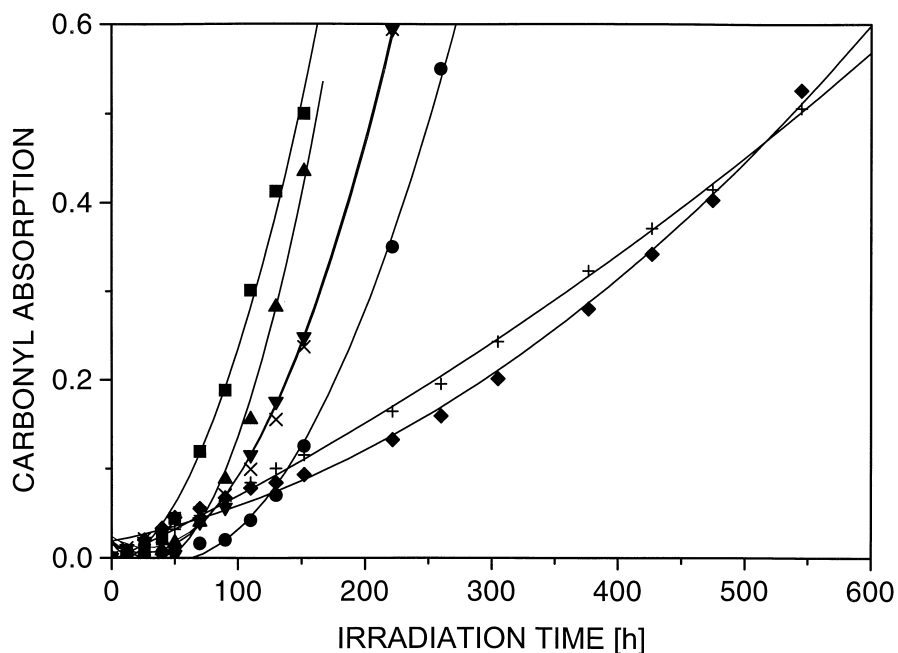


Fig. 10. Rates of photo-oxidation ($\lambda > 310$ nm) of PP films (ca. 0.1 mm) containing: ■, no additive; ●, pyrene; ▲, 1-pyreneacetic acid (**IIa**); ▼, methyl 1-pyreneacetate (**IIb**); ◆, 2,2,6,6-tetramethylpiperidin-4-yl 1-pyreneacetate (**IIc**); +, 1-oxy-2,2,6,6-tetramethyl piperidin-4-yl 1-pyreneacetate (**II d**) and *, 2,2,6,6-tetramethylpiperidin-4-yl 1-pyreneacetate hydrochlorid (**IIe**). Additives concentration was 2×10^{-2} mol kg^{-1} . 250 W mercury arc was used.

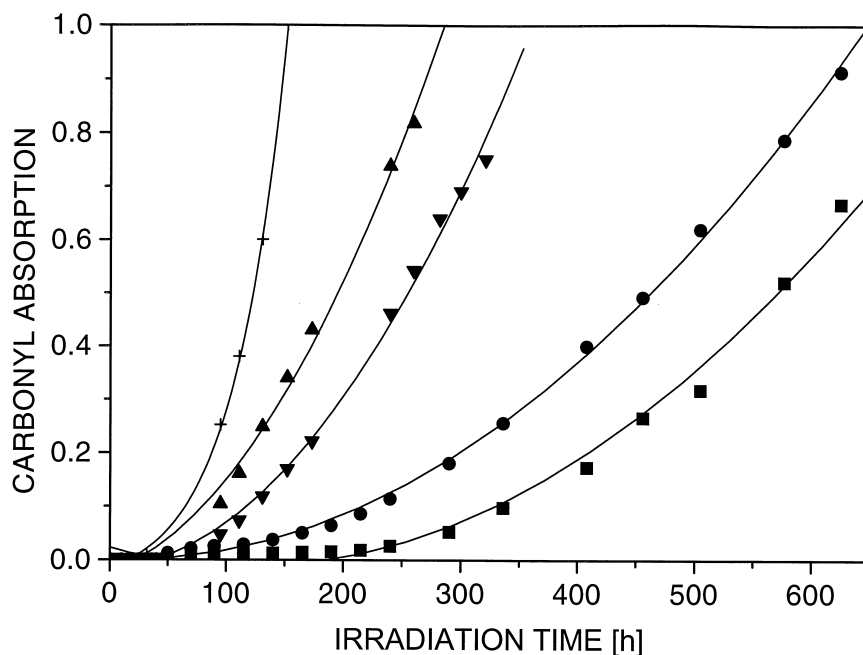


Fig. 11. Rates of photo-oxidation ($\lambda > 310$ nm) of PP films (ca. 0.1 mm) containing: +, no additive; ■, 2,2,6,6-tetramethylpiperidin-4-yl 1-pyr-enecarboxylate (**Ic**); ●, 2,2,6,6-tetramethyl piperidin-4-yl 1-pyreneacetate (**IIc**); ▲, 2,2,6,6-tetramethylpiperidin-4-yl-4-(1-pyrenyl)butyrate (**IIIc**); and ▼, 2,2,6,6-tetramethylpiperidin-4-yl-4-oxo-4-(1-pyrenyl)butyrate (**IVc**). Additives concentration was 2×10^{-3} mol kg^{-1} . 250 W mercury arc.

of parent amine $> \text{NH}$ to active stabilising form of nitroxyl radical $> \text{NO} \cdot$ is inhibited.

The same set of additives at 10 times higher concentration — 2×10^{-2} mol kg^{-1} showed different

behaviour — Fig. 10. All inhibited photo-oxidation of PP-films. Among the additives which do not contain HAS structure in their molecule pyrene was the best followed by methyl 1-pyreneacetate and 1-pyreneacetic

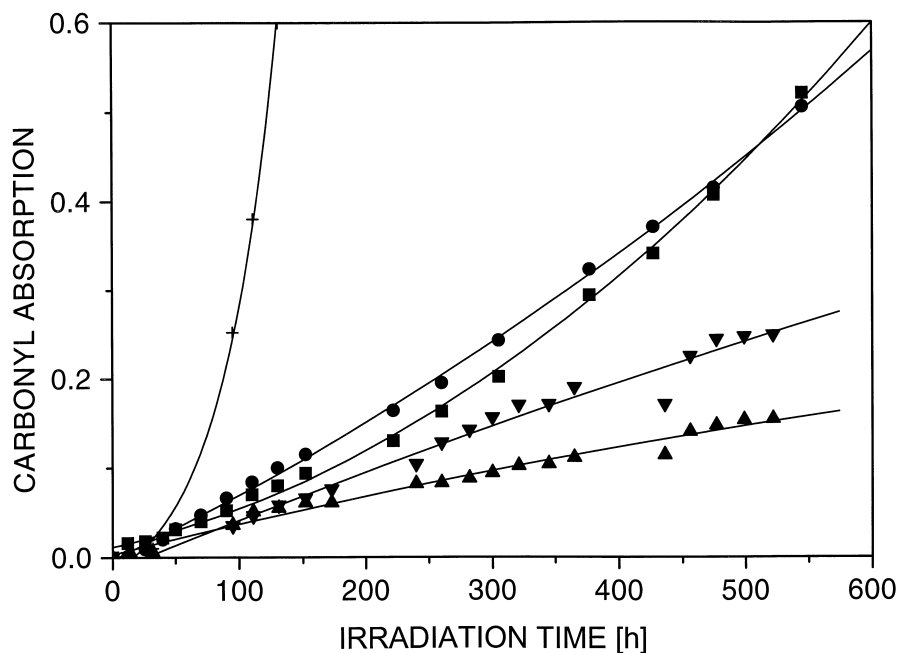


Fig. 12. Rates of photo-oxidation ($\lambda > 310$ nm) of PP films (ca. 0.1 mm) containing: +, no additive; ■, 1-oxy-2,2,6,6-tetramethylpiperidin-4-yl 1-pyrenecarboxylate (IId); ●, 1-oxy-2,2,6,6-tetramethylpiperidin-4-yl 1-pyreneacetate (IIId); ▲, 1-oxo-2,2,6,6-tetramethyl piperidin-4-yl-4-(1-pyrenyl)butyrate (IIId) and ▼, 1-oxy-2,2,6,6-tetramethylpiperidin-4-yl-4-oxo-4-(1-pyrenyl)butyrate (IVd). Additives concentration was 2×10^{-3} mol kg^{-1} . 250 W mercury arc.

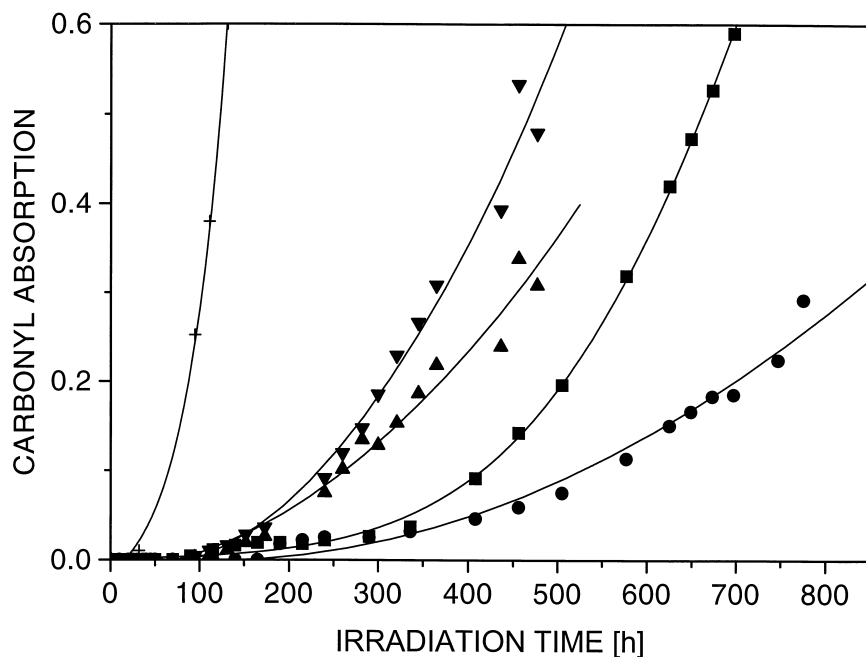


Fig. 13. Rates of photo-oxidation ($\lambda > 310$ nm) of PP films (ca. 0.1 mm) containing: +, no additive; ■, 1-oxy-2,2,6,6-tetramethylpiperidin-4-yl 1-pyrenecarboxylate (IId); ●, 1-oxy-2,2,6,6-tetramethylpiperidin-4-yl 1-pyreneacetate (IIId); ▲, 1-oxo-2,2,6,6-tetramethyl piperidin-4-yl-4-(1-pyrenyl)butyrate (IIId) and ▼, 1-oxy-2,2,6,6-tetramethylpiperidin-4-yl-4-oxo-4-(1-pyrenyl)butyrate (IVd). Additives concentration was 2×10^{-2} mol kg^{-1} . 250 W mercury arc.

acid. It has been stated [12] that pyrene was able to stabilise PP. Comparison of ESR spectra of irradiated pure PP and PP with pyrene showed that pyrene is able to inhibit production of alkyl-type radicals and this way

stabilise the polymer. Surprisingly the efficiency of additives containing unit with HAS in their structure **IIc**, **IIId** and **IIe** dropped to roughly one half of their efficiency at the lower concentration. There is no simple

explanation of this behaviour. Photo-oxidation is a complex process. In the presence of complex additives containing structural units acting as an initiator and stabilisers at the same time the overall effect depends on the ratio of these units as well as on the concentration. In our case at lower concentration prevails more stabilisation effect and at higher concentration antagonistic effect of pyrene chromophore and HAS unit seems to be more important.

Fig. 11 shows the effect of the length of link between pyrene and HAS in the form of parent amine $>NH$. The best efficiency has been reached with the shortest link, just carboxylic unit. Increasing the length of the bridge resulted in the drop of stabilising efficiency. Derivatives with carbonyl group next to pyrene are better than equivalent derivatives with methylene group directly linked to pyrene.

Efficiency of *N*-oxyls was higher in comparison with equivalent parent amines in all structures under the study. This is quite common behaviour for the stabilisers of HAS type [2,3]. At lower concentration ($c = 2 \times 10^{-3}$ mol kg $^{-1}$) the length of the link had the same effect on the efficiency of *N*-oxyls of used compound as for the parent amines. But in this case the derivatives with carbonyl group on pyrene are slightly less effective — Fig. 12. At higher concentration there is a change in overall performance. Derivatives with longer link showed better efficiency but those with shorter link worsened their performance — Fig. 12. It seems that the overall picture is the balance of positive and negative influence of the length of link, position of carbonyl group and concentration. Intramolecular quenching is more effective in the case of short link derivatives and for derivatives with methylene group attached to pyrene.

Finally it might be concluded that all derivatives prepared in this work containing in one molecule pyrene as a chromophore and structural unit of HAS exhibited some degree of photostabilising efficiency. Induction period of HAS part itself in the form of 2,2,6,6-tetramethyl-4-piperidinol is ca. 600 h and for equivalent *N*-oxyl, i.e. 1-oxy-2,2,6,6-tetramethyl-4-piperidinol is ca. 700 h at the similar concentration and irradiation conditions [13]. These values are much higher than the best ones reached by using additives prepared in this work. It seems that

some intramolecular antagonistic effect prevails in all combinations of pyrene and HAS (Fig. 13).

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