

Photochemical stability and photostabilizing efficiency of anthracene/hindered amine stabilizers in polymer matrices

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Abstract

Adducts of chromophore (anthracene substituted in position 9) and hindered amine stabilizers (HAS) such as 2,2,6,6-tetramethylpiperidine-4-yl 3-(9-anthracene)propanoate, 1-oxo-2,2,6,6-tetramethylpiperidine-4-yl 3-(9-anthracene)propanoate, [2,2,6,6-tetramethyl-piperidine-4-yl 3-(9-anthracene)propanoate]methyl chloride as well as model compounds 3-(9-anthracene) propanoic acid and methyl 3-(9-anthracene)propanoate were investigated. The photochemical stability of the adducts was determined in photo-decomposition in polystyrene, poly(methyl methacrylate), poly(vinyl chloride), isotactic polypropylene (iPP) and low density polyethylene (LDPE). Their photo-stabilizing efficiency was determined in iPP and in LDPE. The rate of decomposition of adducts on irradiation $\lambda > 310$ nm was very fast in all matrices. Intramolecularly combined chromophore/HAS are more effective stabilizers than 1:1 mixtures of the separated components. The decomposition of anthracene produces free radicals containing HAS. These radicals are able to graft to the polymer chain of iPP and LDPE.

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1. Introduction

Free radicals play a central role in a variety of chemical processes [1,2]. The lack of methods with which to detect and identify very low concentrations of free radicals in condensed phases presents a major obstacle to understanding the impact of these highly reactive species on chemical and biological processes. Direct detection of radicals by electron paramagnetic resonance (EPR) or optical spectroscopies is generally not possible because of high reactivity or low steady-state levels of these species. More often, radicals are detected indirectly by employing radical traps or scavengers which react rapidly with transient radicals to form more stable products.

Spin trapping is one of the most often used indirect methods of radical detection. In polymer research Rånby and Rabek [3] have reviewed this method, in which free radicals are trapped by nitrones or nitroso compounds to produce nitroxyl radicals—spin adducts.

The mechanisms of action and reactivities of free radicals of inhibition are diagnostic parameters for the identification of the radical spin-adduct formed. Spin adduct instability, the inability to resolve mixture of structurally similar spin adducts by EPR and the need for high concentrations of spin traps (due to low rate constants for the trapping reaction) are the main limitations of this technique.

As compared to spin traps, the stable nitroxyl radicals offer some valuable advantages. Reaction of nitroxyl radicals with carbon-centred radicals results in the production of stable diamagnetic alkoxy or aryloxy amines, which can survive isolation and characterisation. Rate constants for the coupling are generally at least one order of magnitude higher than for the reaction of spin traps [4], so that a much lower concentration of nitroxide is needed for the same effect. When the nitroxide contains a chromophore in the same molecule, the radical trapping reaction can be followed by measuring the fluorescence. Fluorescence yield of these nitroxide-fluorophores increases substantially upon conversion of the paramagnetic nitroxyl moiety to a diamagnetic form of nitroxyl [5,6]. Stable nitroxyl radicals are well known quenchers of excited states [7,8].

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In our previous work we have demonstrated the extent of quenching occurring in the bifunctional fluorescence probes containing pyrene [9], naphthalene [10] and 9,10-naphthalene diimide [11]. The type and length of spacer between pyrene and nitroxyl radical were investigated too. As a stable nitroxyl radical 2,2,6,6-tetramethyl-4-hydroxypiperidin-1-oxyl was used. The nitroxyl radical is an active species for the major family of photo- and thermo-stabilizers known as hindered amine stabilizers (HAS). For this reason the stabilizing efficiency of the earlier mentioned fluorescence probes was checked.

In this article we describe the photochemical stability as well as photo-stabilizing efficiency of fluorescence probes based on 9-substituted anthracene. Their preparation and spectral characteristics were described in detail in the first part of this study [12].

2. Experimental part

2.1. Materials

Anthracene (Lachema n.e., Brno, CR) was zone refined, 9-methylanthracene and 9,10-dimethylanthracene were commercial products (Aldrich, Steinheim, Germany), which were used without further purification. Chloroform, dichloromethane and tetrahydrofuran (THF) (Lachema n.e., Brno, CR) were analytical grade reagent. For preparation of polymer films polystyrene [PS, Krasten, Kaučuk Kralupy a.s., CR, SEC (chloroform) $M_n=93,700$ $M_w/M_n=2.7$], poly(methyl methacrylate) (PMMA, Považské Chemické Závody, a.s. Žilina, SR, $M_v=1.01 \times 10^5$), poly(vinyl chloride) (PVC, Neralit 628, Spolana Neratovice, a.s., CR $M_v=1.11 \times 10^5$), low density polyethylene (LDPE, Bralen 2–19, MFI=1.7–2.3 g/10 min, $d=0.916\text{--}0.919$ g cm⁻³, Slovnaft a.s., SR) and isotactic polypropylene (iPP, Daplen, PCD Polymere, Schwechat, Austria) were used.

2.2. Synthesis

The structures of fluorescent probes used in this paper are shown in Scheme 1. The synthesis of **I** was performed according to the described procedure [13] (m.p. 192.5–194 °C, ref. [13] 194–195 °C). Esterification of acid was performed by standard procedure and probe **II** has m.p. 65–66 °C (ref. [14] 64.5–65.5 °C). The 2,2,6,6-tetramethyl-4-hydroxypiperidine 3-(anthracene-9-yl)propanoate (m.p. 91–93 °C) (**III**) was prepared by re-esterification reaction of **II** with 4-hydroxy-2,2,6,6-tetramethylpiperidine [12]. (1-Oxo-2,2,6,6-tetramethyl-4-hydroxypiperidine) 3-(anthracene-9-yl)propanoate (m.p. 125–127 °C) (**IV**) was prepared by oxidation of **III** with *m*-Cl-peroxobenzoic acid [11,12]. The corresponding

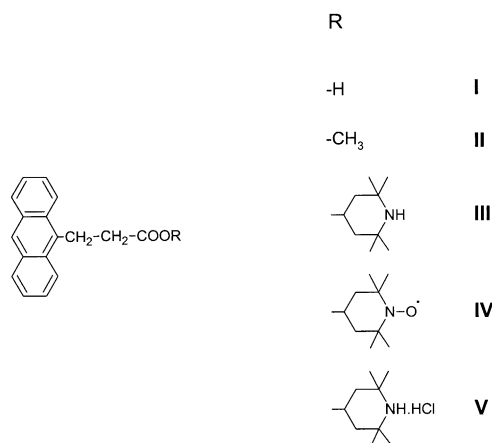
chloride (**V**) (m.p. >265 °C) of **III** was prepared by bubbling of gaseous HCl through an acetone/H₂O (1:1) solution of **III** [11,12]. Details of synthesis as well as spectral characteristics (IR, ¹H NMR, UV) of **III**, **IV**, **V** are described in Ref. [12].

2.3. Preparation of polymer films

Films of PS, PMMA and PVC doped with probes were prepared by casting on a glass plate (28 × 35 mm) a solution of polymer (5 g/100 ml) in 1 ml chloroform or tetrahydrofuran, containing a weighed amount of probe. The final concentration of probe was 0.002 mol kg⁻¹. Films of iPP and PE were prepared in the following way: The additives (6×10^{-3} mol kg⁻¹) dissolved in 20 ml of dichloromethane were added to 25 g of non-stabilized polymer powder. The slurry was kept at room temperature for 18 h until the solvent evaporated. The blends were mixed and homogenized in a Brabender Plastograph at 160 °C for PE and at 190 °C for iPP for 5 min under air and then pressed in a electrically heated laboratory press (Fontune, The Netherlands) at 160 °C for PE and at 200 °C for iPP for 1 min. The thickness of films was 0.08–0.12 mm.

2.4. Techniques

Absorption spectra were taken on a M-40 UV-vis (C. Zeiss, Jena, Germany) and FTIR spectra on Impact 400 (Nicolet, USA). Photo oxidation of iPP and PE films was performed on a merry-go-round type set up. A medium pressure 250 W mercury arc with luminophore envelope (RVL, Tesla Holesovice, CR) was used as the source of radiation with $\lambda > 310$ nm. Photo-decomposition of derivatives **I–V** and anthracene in PS, PMMA, PVC, iPP and PE films was performed on the similar set up, but radiation with $\lambda=366$ nm was isolated from the light of a 125 W medium pressure mercury arc without luminophore with a glass filter and



Scheme 1.

water. The temperature of photo oxidation was 30 °C. The course of photooxidation was followed by FTIR spectroscopy in the carbonyl region 1700–1740 cm^{-1} . Decomposition of the additive in the course of photooxidation was followed by FTIR for ester region at 1735 cm^{-1} and UV spectroscopy for absorption of anthracene at 253 or 390 nm.

Extraction of polymer films was performed twice with 10 ml of chloroform (analytical grade) in sealed glass tube at 25 °C for 24 h. Then the films were washed in pure chloroform and dried under vacuum for 1 h.

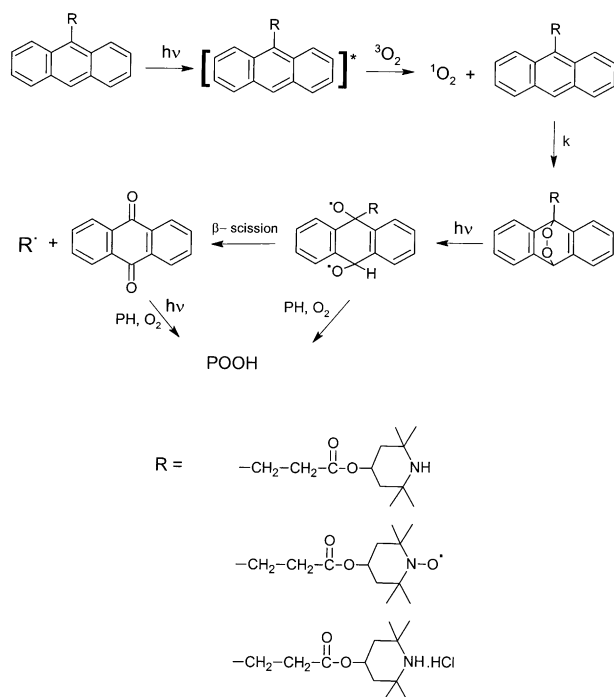
3. Results and discussion

Derivatives I–V containing a carbonyl ester group bound with anthracene in position 9 through ethylene spacer are photochemically active in the presence of air in relatively inert PS, PMMA, PVC, PE, iPP polymer matrices. Photooxidation of the polymer does not occur during the irradiation time needed to photolyse derivatives I–IV. Photodecomposition of these anthracene bifunctional fluorescence derivatives is much faster than the photolysis of other bifunctional fluorescence probes based on pyrene [9] naphthalene [10], and naphthaleneimide [11] and HAS. Under irradiation with light $\lambda > 310$ nm or $\lambda = 366$ nm, the chromophoric part of these derivatives—the anthracene moiety—disappears very fast even in the cases when the anthracene chromophore is linked with structural unit of light stabilizers HAS. The photooxidation of anthracene in presence of the

oxygen is known [15,16] and it results in production of endoperoxide and then anthraquinone (Scheme 2). The typical absorption bands of anthracene at $\lambda = 254$ nm and at the longest wavelength at $\lambda = 310$ –390 nm disappear irreversibly under irradiation with $\lambda > 310$ nm light (Fig. 1A, B). At the wavelength about $\lambda = 240$, 260 and 300 nm there are some indications of isosbestic points which may mean that a simple A to B transformation occurs.

Concerning the influence of polymer matrices on the photooxidation decomposition of probes I–V and anthracene, it is slightly slower in PS when compared with PMMA and PVC matrices. The initial rate of decomposition of methyl ester II in comparison with the ester containing parent amine III and parent amine in the form of stable nitroxyl radical IV is similar in PS, PMMA, PVC (Fig. 2). The initial rate of disappearance of anthracene absorption in the UV spectra is rather high in all matrices. During the first 10 minutes of irradiation the anthracene absorption decreases to about half of its original value. In all matrices, the kinetics follow approximately the first order. The dependence of $\log A/A_0$, where A and A_0 are absorptions at reaction time t and at $t=0$, is linear at beginning but in later stage it is curved, which may indicate some kind of inhibition (Figs. 2–4).

In the case of photodecomposition of III and IV in iPP (Fig. 3) and PE films (Fig. 4) in the presence of air, the rate of photodecomposition of IV is slower than III due to intramolecular quenching of excited anthracene by nitroxyl radical. The rate constant k_A of photooxidation of III in iPP film determined from the slope at beginning of photolysis (Fig. 3) measured at $t = 50$ min. is 0.027 min^{-1} and for IV is 0.021 min^{-1} (Table 1). In PE matrix the rate of decomposition is slower than in iPP for II, III, IV and similarly, the rate constant of decomposition of IV is lower than for III or II. The parent amine III is able to form $>\text{N}-\text{O}^\bullet$ radical in presence of oxygen only after some irradiation time, therefore the rate of decomposition of this derivative in the later stage is slower than the rate of inactive methyl ester derivative II. However decomposition of the anthracene chromophore occurs during several hundreds of minutes.



Scheme 2.

Table 1

The rate constants of photooxidation of anthracene derivatives doped in iPP and PE films

Probe	k_A in iPP film ^a (min^{-1})	k_A in PE film ^a (min^{-1})
II	–	0.027
III	0.027	0.019
IV	0.021	0.012

^a The slopes were determined from the beginning of photolysis at time $t = 50$ min.

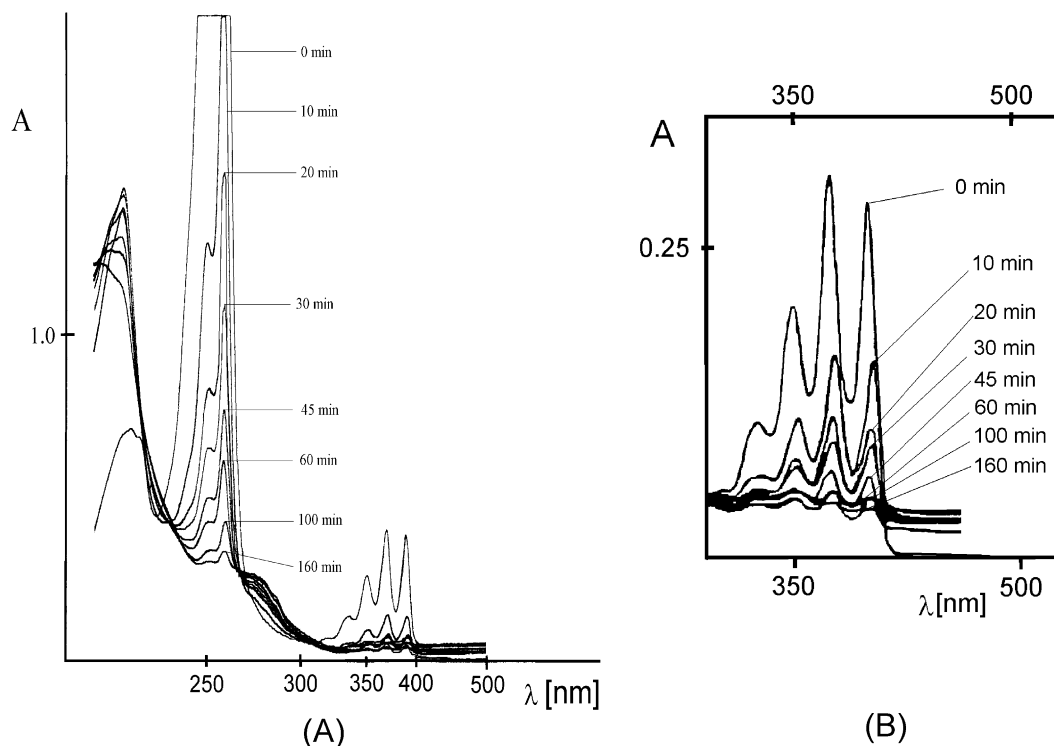


Fig. 1. Photolysis of III (A) and IV (B) in iPP films irradiated with > 310 nm, measured at 254 nm (A) and 310–390 nm (B) respectively.

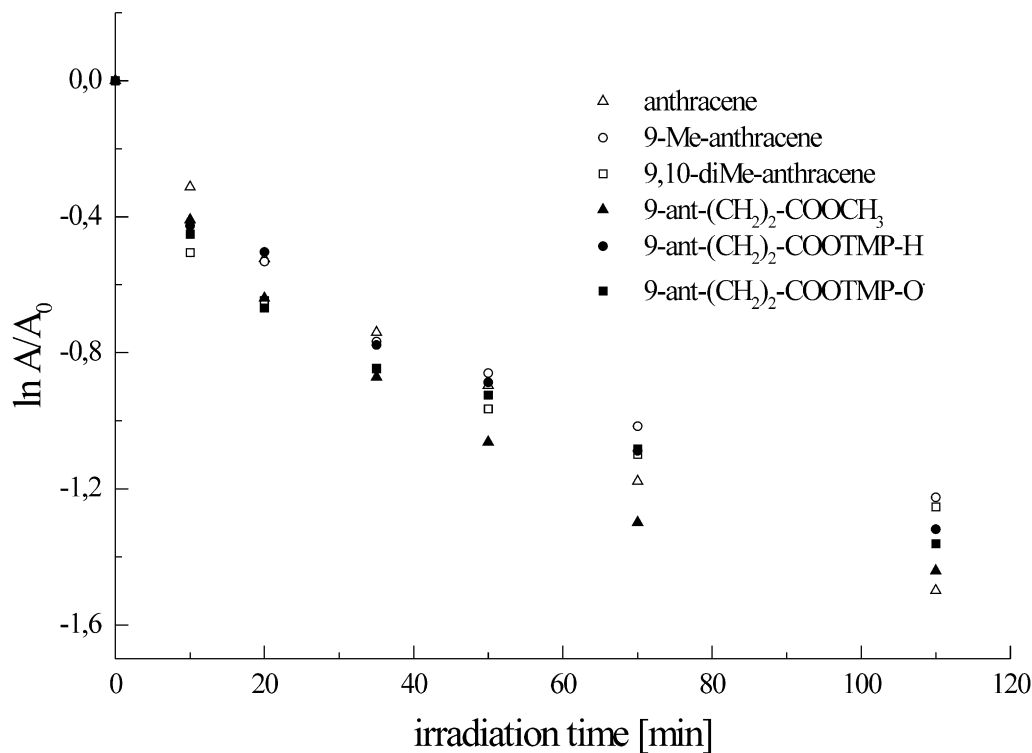


Fig. 2. Kinetics of photooxidation of anthracene derivatives doped in PS film irradiated in the presence of air at $\lambda = 366$ nm.

The influence of decomposition products on the course of photooxidation of iPP and PE is discussed in the next part. The period to reach carbonyl absorption 0.2 (this value roughly corresponds to the 50% loss of

impact strength) is ca. 180 h for pure iPP and ca. 600 h for PE under the given conditions. The courses of photooxidation of iPP and PE films containing pure anthracene, carboxylic acid (I) and methyl ester (II)

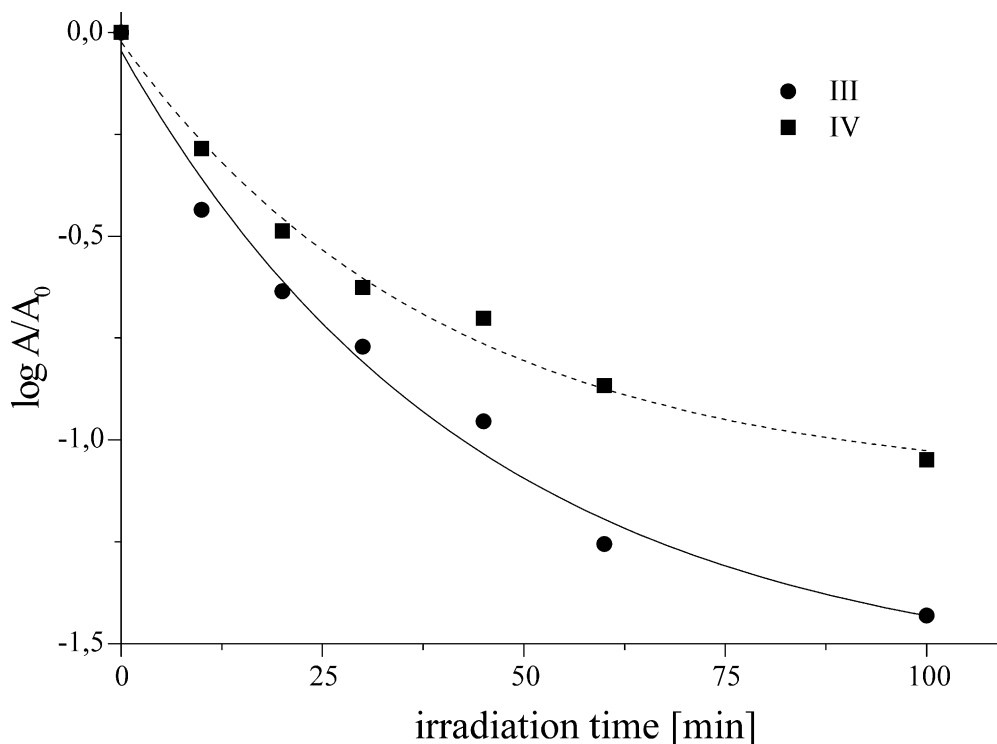


Fig. 3. Kinetics of photooxidation of **III** and **IV** in iPP film irradiated in the presence of air at $\lambda > 310$ nm.

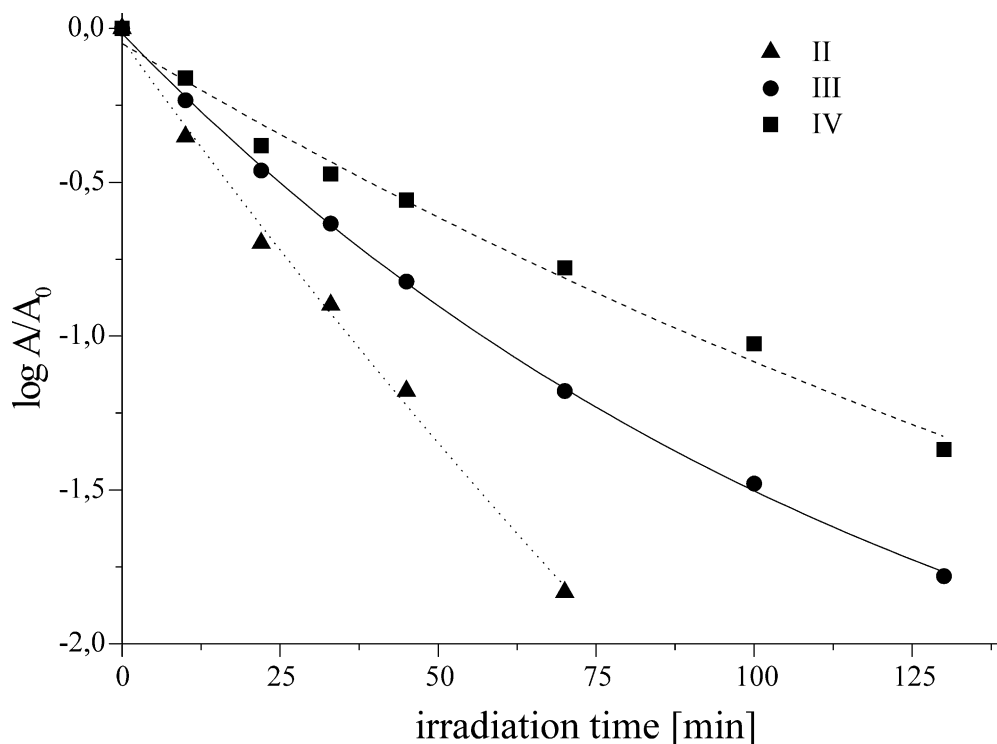


Fig. 4. Kinetics of photooxidation of **II**, **III** and **IV** in PE film irradiated in the presence of air at $\lambda > 310$ nm.

without active HAS moieties and hydrochloride **V** are shown on Figs. 5 and 6. Because PE is more resistant to photooxidation than iPP (induction period of PE is about three times longer than for iPP) the PE is more suitable to differentiate small variations of the sensitisation

and stabilisation of probes **I–V** than is iPP. The starting molar concentration was the same for all derivatives $6 \times 10^{-3} \text{ mol kg}^{-1}$. This value is equivalent to 0.2 wt.% of (2,2,6,6-tetramethylpiperidine-4-yl)-3-(anthracene-9-yl)propionate (**III**) in the polymer. This is the most

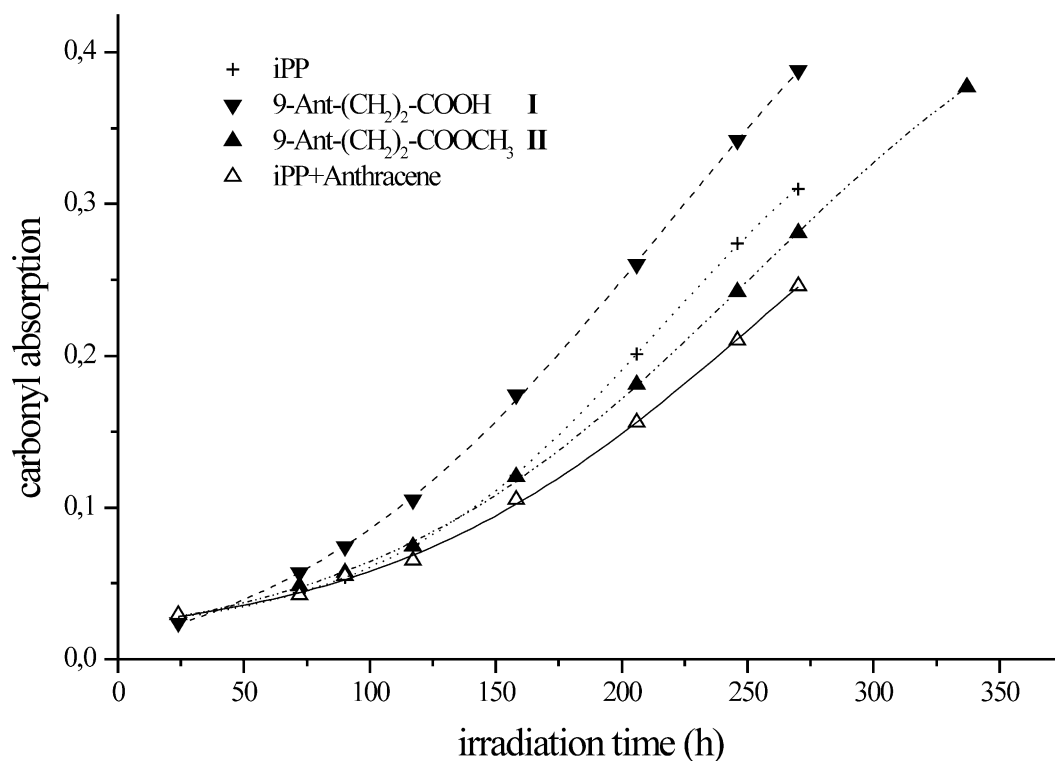


Fig. 5. Rate of photooxidation ($\lambda > 310$ nm) of iPP films (ca. 0.1 mm) containing anthracene and anthracene derivatives.

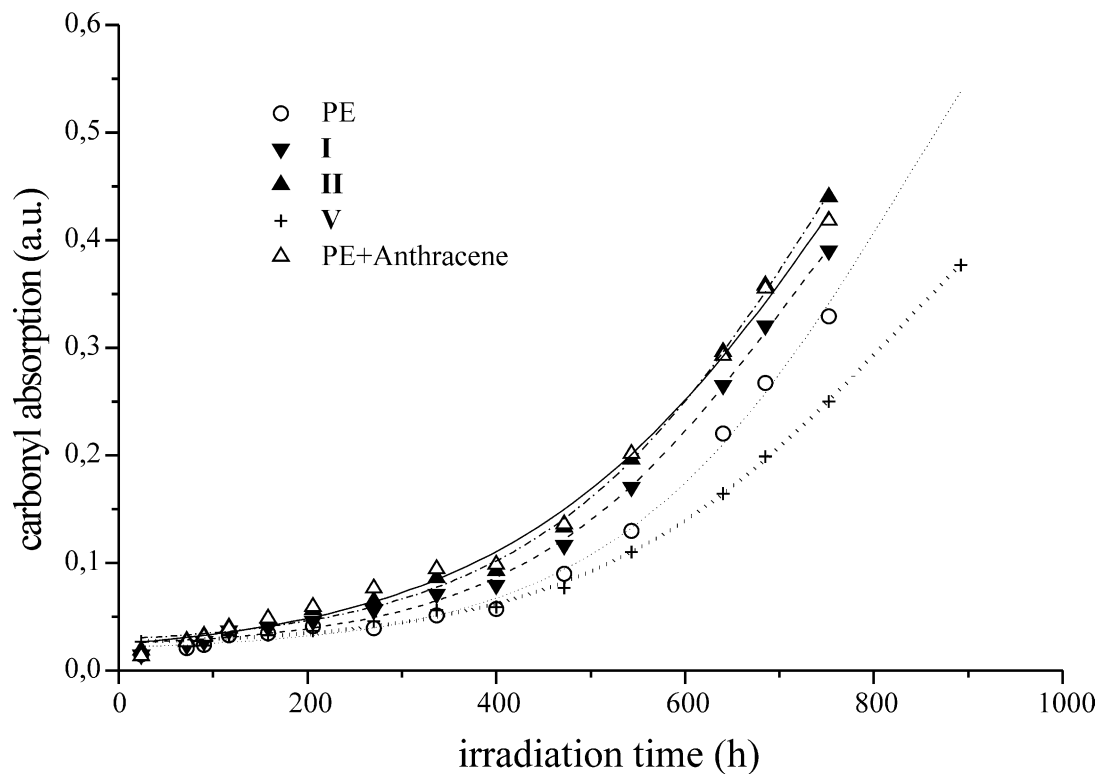


Fig. 6. Rate of photooxidation ($\lambda > 310$ nm) of PE films (ca. 0.1 mm) containing anthracene and anthracene derivatives.

common concentration used for testing stabilizing efficiency of HAS. Processing of additives into iPP and PE in the Plastograph Brabender chamber is the best way to reach homogeneity of the additive dispersion despite

the possibility of thermal decomposition or partial evaporation of the additive due to the high temperature, 190 °C for iPP and 150 °C for PE. The real additive concentrations in the pressed films after these thermal

treatment depend on the structure of the additives. The following values were calculated from UV spectra of iPP films. For pure anthracene the starting concentration $6 \times 10^{-3} \text{ mol kg}^{-1}$ dropped down to $1.6 \times 10^{-3} \text{ mol kg}^{-1}$. Higher concentration persists for acid (**I**)— $3.5 \times 10^{-3} \text{ mol kg}^{-1}$ as well as for methyl ester (**II**)— $4.4 \times 10^{-3} \text{ mol kg}^{-1}$. For anthracene it is only 27 wt.% from the original value for acid 58 wt.% and methyl ester 73 wt.%. The higher resistance against thermal decomposition as well as evaporation due to the higher temperature was reached for piperidyl ester (**III**)—93 wt.% and for nitroxyl radical (**IV**) 99 wt.%. The resistance against decomposition and physical loss increases with increasing molecular mass. As shown earlier, the time of complete photo-decomposition of all derivatives is approx. 2 h. In this time, according to Figs. 1–4 anthracene as well as anthraquinone (which has a similar UV spectrum to anthracene) produced from anthracene according to the Scheme 2, disappeared from the polymer matrix. Decomposition products, which do not absorb UV light do not influence the course of iPP photooxidation at the beginning of this process—ca. 75 h (Fig. 5). Only after this time one can see possible sensitisation in the case of acid **I** and almost negligible stabilizing effect of anthracene and methyl ester **II**. Similar effects are seen in the case of PE films shown on Fig. 6. In this case only slight sensitisation effect can be seen for all derivatives without structural unit of HAS.

Derivative **V** containing parent amine structure, but in the form of hydrochloride salt, is also ineffective. The real stabilizing species of HAS is the stable nitroxyl radical $>\text{NO}\cdot$ arising from the original parent amine $>\text{NH}$. This transformation is substantially blocked when the parent amine is in the form of $>\text{NH}_2^+ \text{Cl}^-$ [17,18]. The dependencies in Figs. 7 and 8 show more effective stabilisation of iPP and PE in the presence of the parent amine (**III**) and N-oxyl (**IV**) with a relatively long induction period mainly for iPP. Induction periods of these derivatives in iPP matrices are much longer compared with induction periods of other similar bifunctional adducts where the chromophores were pyrene [9] naphthalene [10], or naphthaleneimide [11]. In PE films N-oxyl is substantially more effective in photo-oxidation processes than is the parent amine. Photooxidation of iPP films doped with additives **III** and **IV** is inhibited effectively in comparison with the mixture of inactive methyl ester 3-(9-anthracene)propanoate **II** and HAS in the form of 4-hydroxy-2,2,6,6-tetramethylpiperidine or stable nitroxyl radical (4-hydroxy-2,2,6,6-tetramethylpiperidine-N-oxyl) although the molar concentration of **III** and **IV** and molar concentration of the mixture **II** and HAS are the same in all cases (Fig. 7). These higher efficiencies are probably due to the partial grafting of the active part of adduct molecules **III** and **IV** to iPP. Because of this fact their disappearance from matrices by physical processes is

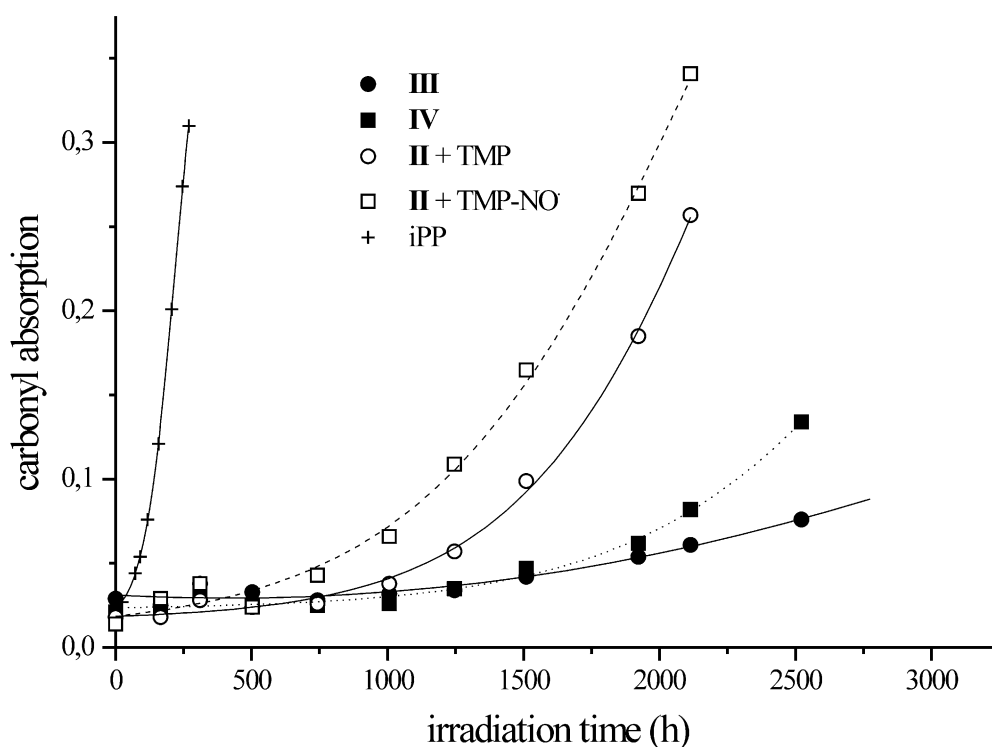


Fig. 7. Rate of photooxidation ($\lambda > 310 \text{ nm}$) of iPP films (ca. 0.1 mm) containing **III**, **IV** and mixture of methyl 3-(9-anthracene)propanoate (**II**) and 4-hydroxy-2,2,6,6-tetramethylpiperidine and 4-hydroxy-2,2,6,6-tetramethylpiperidine-N-oxyl.

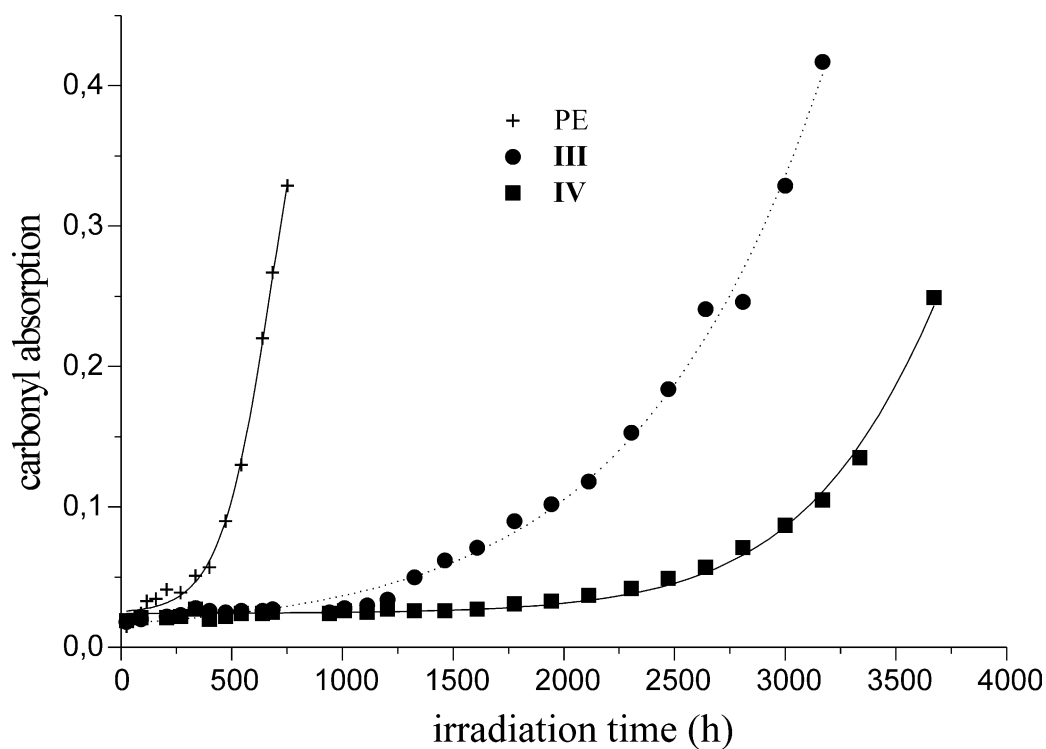


Fig. 8. Rate of photooxidation ($\lambda > 310$ nm) of PE films (ca. 0.1 mm) containing anthracene derivatives.

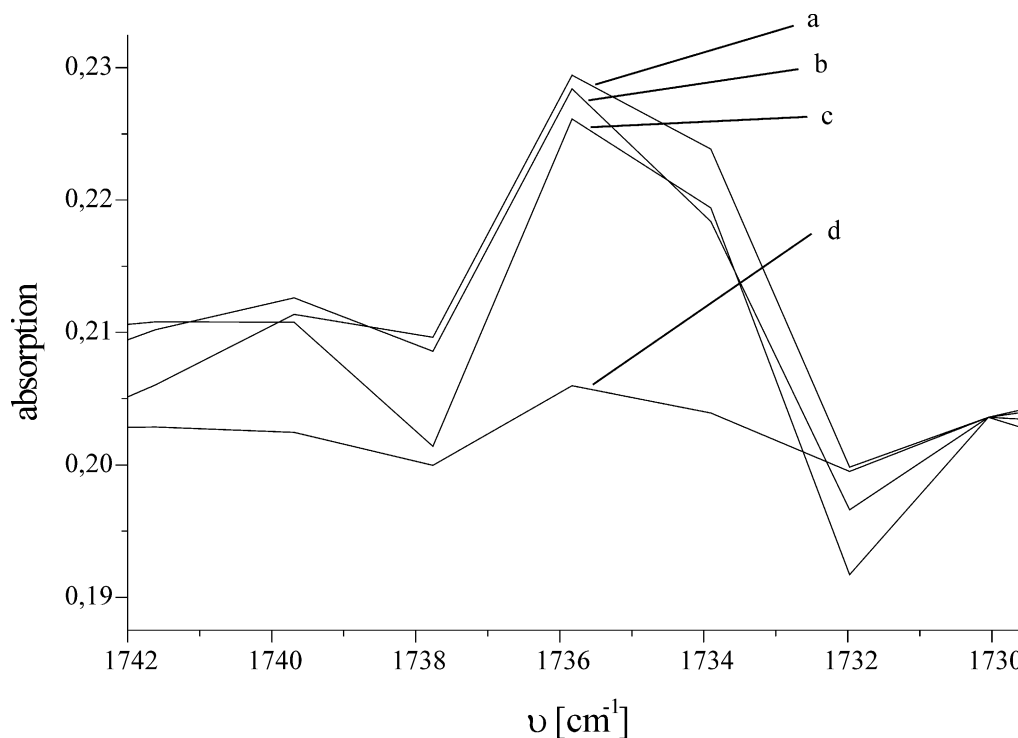


Fig. 9. FTIR spectra of iPP films doped with **III**: (a) original, (b) irradiated 100 min., (c) irradiated and extracted in chloroform, (d) extracted without irradiation.

lower. The evidence for this conclusion is supported by the results of influence of extraction on the stabilizing efficiency. According to Scheme 2 the last step of photodecomposition of 9- or 9,10- substituted anthracenes

in the presence of air resulted in the production of endoperoxide and free radicals. In our case radicals $\cdot\text{CH}_2\text{-CH}_2\text{-CO-O-HAS}$ are produced and they should be able to bond to iPP or PE chains by grafting. We

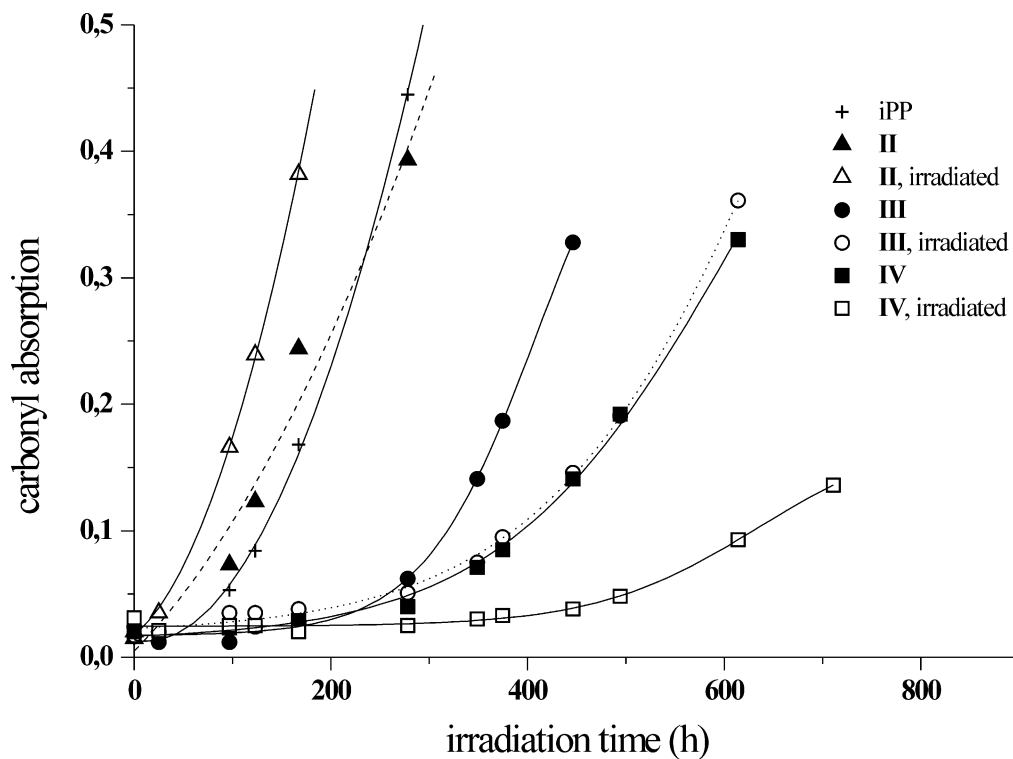


Fig. 10. Courses of photooxidation of iPP films containing anthracene derivatives. Three of them were irradiated for 100 min with $\lambda > 310$ nm before extraction. All films were extracted in CHCl_3 at 25 °C for 24 h.

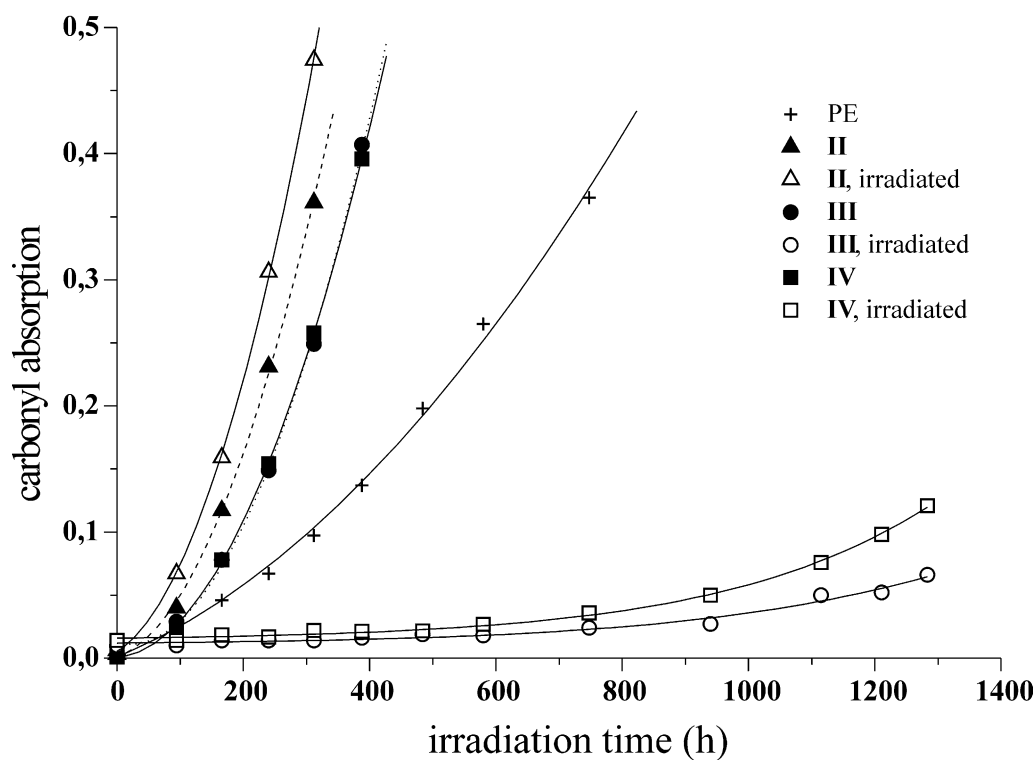


Fig. 11. Rate of photooxidation of PE films containing anthracene derivatives. Three of them were irradiated before extraction for 100 min with $\lambda > 310$ nm. All films were extracted in CHCl_3 at 25 °C for 24 h.

tried to prove grafting in the following way. Three iPP films with probes **II**, **III** and **IV** were irradiated and three were not. The samples were irradiated up to 90% of anthracene UV absorption disappearance (100 min). Irradiated and non-irradiated samples were extracted in chloroform. Chloroform is able to wash out low molecular additives under used conditions. This has been checked by using photochemically inactive 2,2,6,6-tetramethyl-4-piperidyl octadecanoate. FTIR spectra showed complete disappearance of the ester band at 1740 cm^{-1} of this additive from iPP film. In the case of three irradiated films we should extract decomposition products which are not grafted on polymer. In the case of non-irradiated films additives should be extracted in the form they were incorporated into iPP powder. This is correct hypothesis in the case when additive is not partially grafted during processing. The compositions of both sets of films were checked by FTIR and UV spectroscopy. Fig. 9 shows the FTIR spectra of irradiated and non-irradiated films containing additive **III** before and after chloroform extraction showing the region of ester band. Irradiated sample (Fig. 9b) shows the same absorption as original film (Fig. 9a). This means that the ester link survived this process of irradiation. Irradiated film after extraction showed approx. 25% lower intensity of this band. It means that the most of the $\cdot\text{CH}_2\text{-CH}_2\text{-CO-O-HAS}$ radicals are grafted on iPP. One quarter of radicals probably abstracted a proton from polymer and was converted to extractable $\text{CH}_3\text{-CH}_2\text{-CO-O-HAS}$. The ester band of the original non-irradiated sample after extraction did not disappear completely. Grafting reactions had to take place to some extent at the processing of iPP films as well. The courses of photooxidation of extracted iPP and PE films are shown in Figs. 10 and 11. In the case of non-irradiated iPP films as well as irradiated samples containing derivative **II** which does not contain stabilizing unit of HAS extraction has very small effect on photooxidation. Additive **III** (HAS in the form of parent amine) as well as additive **IV** (HAS in the form of stable nitroxyl radical) showed some stabilizing efficiency for both nonirradiated/extracted and irradiated/extracted iPP films. The first case is the result of partial decomposition and grafting in processing. Stabilizing efficiency of **III** in irradiated/extracted film is two times larger because of the earlier mentioned photolysis and subsequent grafting of HAS on the iPP chain. A similar effect with slightly higher efficiencies was observed for derivative **IV**. A different situation arose in the case of PE films (Fig. 11) The rate of photooxidation of non-irradiated/extracted films containing derivatives **II**, **III** and **IV** was higher than pure PE film. At the moment we do not have a reasonable explanation for this effect. PE films irradiated/extracted containing derivatives **III** and **IV** showed very high resistance against photooxidation.

This relates to a high extent of grafting of active HAS on PE chain.

4. Conclusions

This study shows quite clearly that adducts of anthracene substituted in position 9- and hindered amine stabilizers bound through a spacer with two methylenes and an ester group (**III** and **IV**), methyl 3-(9-anthracene)propanoate, 3-(9-anthracene)propanoic acid are extremely photochemically labile. The anthracene moiety decomposed on photolysis in all polymer matrices under investigation. The photo-decomposition in the presence of air produces besides other radicals, free radicals with HAS. Part of them is able to graft on polymer chain of iPP and PE. The rest can abstract protons from the polymer to produce $\text{CH}_3\text{-CH}_2\text{-CO-O-HAS}$. Partial grafting on iPP, PE and persistence in polymer matrix is the reason for quite high photo-stabilizing efficiency even for extracted samples.

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