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Preparation, photochemical stability and photostabilizing efficiency of adducts of 1,8-naphthaleneimide and hindered amine stabilizers in polymer matrices

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Abstract

Adducts of 1,8-naphthaleneimide and hindered amine stabilizer (HAS) such as 1-R-substituted-2,2,6,6-tetramethyl-4-aminopiperidine were prepared where R is –H, –O·, –OH, –$COCH_3$ and –$OCOCH_3$. The photochemical stability of adducts was determined at photolysis in isotactic polypropylene, polystyrene and polyvinylchloride. Their photostabilizing efficiency was determined at photooxidation of isotactic polypropylene. The photochemical stability of the adducts is low in all matrices. The *N*-oxy derivative was the most stable in all matrices. The photolysis of all derivatives is the slowest in polystyrene. Intramolecularly combined chromophore/HAS are less effective stabilizers than in 1:1 mixture of separated components. The 1,8-naphthaleneimide chromophore decreases the stabilization efficiency of hindered amine structural units as compared to its absence. © 1998 Elsevier Science Ltd. All rights reserved.

1. Introduction

Photostabilizing efficiency of sterically hindered amines (HAS) such as 2,2,6,6-tetramethylpiperidine is well established for most comodity polymers mainly for polyolefines [1–3]. These polymers usually do not exhibit any or weak absorption in the UV region of solar radiation. Therefore, the photodegradation and photostabilization is associated with photochemical behaviour of adventitious often ill-defined impurities.

By the advent of special polymers with complex chromophores, the photodegradation origins in chromophores and photostabilization is decisevely influenced by them. At the same time, the long term persistence of organic compounds such as dyes, filters, stabilizers, photochromic substances, fluorescence brigtheners and probes, optically active units is important for their proper function in the solid state matrices. Their disappearence from matrices is due to physical processes like volatility, extraction, washability blooming etc. and photochemical decomposition. A simple route to stabilise even the system of complex chromophores is to apply HAS as well. Recently, it has been demonstrated that photolysis of spironaphthoxazines in toluene solution was inhibited by HAS [4].

In a previous paper [5] the photostabilizing efficiency of combined molecules containing chromophore/HAS and their mixtures have been evaluated. In this case chromophores were aromatic hydrocarbons such as naphothalene and pyrene. The photostabilizing efficiency of HAS is decreased more when the chromophore was intramolecularly bound to HAS than in mixture of individual components. In the case of naphthalene, the photostabilizing efficiency was partially preserved. For pyrene, the photostabilizing efficiency was completely lost.

In this paper the photochemical stability and photostabilizing efficiency of HAS in the presence of bound and free 1,8-naphthaleneimide chromophore is evaluated. The aim of the study is to elucidate the mechanism of action of HAS in the presence of this simple but photophysically interesting chromophore [6].

2. Experimental

The synthesis of the derivatives **I** to **VI** was performed according to Scheme 1 modifying some described procedures [7].

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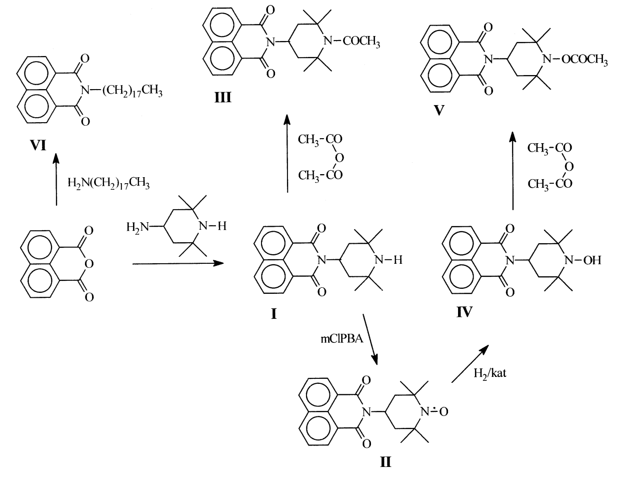

Scheme 1.

2.1. N-*(2,2,6,6-Tetramethylpiperidin-4-yl)-1,8-naphthaleneimide* (***I***)

1,8-Naphthalenedicarboxylic acid anhydride (3.2 g, 16 mmol) suspended in 30 ml of *N*,*N*-dimethylformamide (DMF) was added dropwise over 45 min to a solution of 2.8 g (18 mmol) of 4-amino-2,2,6,6-tetramethylpiperidine in 30 ml DMF. Acetic acid (1 ml) was added and the resulting solution was stirred at 100°C for 3.5 h. The crude product which precipitated on cooling with addition of ether was chromatographed on a column of silica gel with $CHCl_3$:MeOH = 2:1 as an eluent giving after crystallisation 3.9 g (73%) of white crystals, m.t. 168–170°C. ^{1}H NMR ($CDCl_3$) δ: 1.26 (s, 6H, 2× CH_3 2 + 6 axial.), 1.4 (s, 6H, 2× CH_3 2 + 6 equat.) 1.66 (m, 2H, CH_2 5 + 3 axial.), 2.55 (m, 2H, CH_2 5 + 3 equat.), 5.69 (m, 1H, N–CH) 7.75–8.63 (m, 6H, napht.). FTIR ($CHCl_3$): ν(CO sym.) 1699 cm^{-1}, ν(CO asym.) 1657 cm^{-1}, ν(C–N) 1348 cm^{-1}, ν(O–C–N) 1248 cm^{-1}, ν(napht.) 780 cm^{-1} (from PP film). MASS spectrum: 336(M$^+$), 321, 264, 222, 198, 152, 124, 82.

2.2. N-*(1-Oxo-2,2,2,6-tetramethylpiperidin-4-yl)-1,8-naphthaleneimide* (***II***)

I (5 g, 15 mmol) was dissolved in 50 ml of CH_2Cl_2 and m-chloroperbenzoic acid (3 equiv.) was added in small parts under stirring at room temperature. After 3 h, CH_2Cl_2 was removed under vacuum rotary evaporation. The rest was extracted 2× with ether and washed with diluted $NaHCO_3$ water solution and 2× with water. After drying (Na_2SO_4) ether was evaporated. Product was crystallised from methanol to give 3.5 g (70%) of slightly orange crystals with m.t. 227–229°C. FTIR ($CHCl_3$): ν(CO sym.) 1700 cm^{-1}, ν(CO asym.) 1660 cm^{-1}, ν(N–O·) 1353 cm^{-1}, ν(C–N) 1342 cm^{-1}, ν(O–C–N) 1240 cm^{-1}, δ(napht.) 780 cm^{-1} (from PP film). MASS spectrum: 351 (M$^+$), 321, 265, 222, 198, 152, 126, 81.

2.3. N-*(1-Acetyl-2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthaleneimide* (***III***)

I (1g, 3 mmol) was dissolved in 20 ml of acetic anhydride and the mixture was refluxed for 24 h. After cooling the mixture was poured on ice with ammonia. The precipitated crude product was washed with water and purified on a column of silica gel using ethyl acetate as eluent. Final product was obtained as white crystals (acetone) in 22% yield. M.t. 200–201°C. ^{1}H NMR ($CDCl_3$) δ: 1.63 (s, 6H 2× CH_3 2 + 6 axial.), 1.69 (s, 6H, 2× CH_3 2 + 6 equat.), 1.75 (m, 2H, CH_2 3 + 5 axial.), 2.33 (s, 3H, CH_3CO), 3.0 (m, 2H, CH_2 3 + 5 equat.), 5.65 (m, 1H, N–CH), 7.66–8.64 (m, 6H, napht.). FTIR ($CHCl_3$): ν(CO sym.) 1699 cm^{-1}, ν(CO asym.) 1659 cm^{-1}, ν(CO acetyl) 1627 cm^{-1}, ν(C–N) 1346 cm^{-1}, ν(O–C–N) 1240 cm^{-1}, δ(napht) 780 cm^{-1} (from PP film).

2.4. N-*(1-Hydroxy-2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthaleneimide* (***IV***)

Hydrogen was bubbled through a solution of **II** (0.8 g, 2.3 mmol) in 100 ml methanol containing 10 mg of powdered PtO_2 until the red of **I** disappeared. The reaction mixture was then bubbled with argon and filtered. Crystallisation afforded 0.56 g (70%) of white crystals with m.t. 224–228°C. ^{1}H NMR ($CDCl_3$) δ: 1.27 (s, 6H, 2× CH_3 2 + 6 axial.), 1.32 (s, 6H, 2× CH_3 2 + 6 equat.), 1.6 (m, 2H, CH_2 3 + 5 axial.), 2.87 (m, 2H, CH_2 3 + 5 equat.), 4.15 (m, 1H, N–OH), 5.6 (m, 1H, N–CH), 7.66–8.68 (m, 6H, napht.). FTIR ($CHCl_3$): ν(CO sym.) 1700 cm^{-1}, ν(CO asym.) 1660 cm^{-1}, ν(C–N) 1343 cm^{-1}, ν(O–C–N) 1240 cm^{-1}, δ(napht.) 780 cm^{-1} (from PP film).

2.5. N-*(1-Acetyloxy-2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthaleneimide* (***V***)

To a solution of **IV** (0.5 g, 1.4 mmol) in 30 ml of pyridine cooled in the ice bath, acetic anhydride (2 ml) was added dropwise. The reaction mixture was maintained for 2 days at room temperature. Water and ethyl acetate was added and the ethyl acetate layer was separated, washed with diluted water solution of $NaHCO_3$ and with water. The solution was dried and ethyl acetate was evaporated. The residue was chromatographed (silica gel, ethyl acetate) and the obtained product was recrystallized from ether to give 0.3 g (44%) of white crystals with m.t. 186–188°C. ^{1}H NMR ($CDCl_3$) δ: 1.16 (s, 6H, 2× CH_3 2 + 6 axial.), 1.37 (s, 6H, 2× CH_3 2 + 6 equat.), 1.6 (m, 2H, CH_2 3 + 5 axial.), 2.14 (s, 3H, CH_3CO), 3.1 (m, 2H, CH_2 3 + 5 equat.), 5.64 (m, 1H, N–CH), 7.64–8.63 (m, 6H, napht.). FTIR ($CHCl_3$):

ν(CO ester.) 1764 cm^{-1}, ν(CO sym.) 1701 cm^{-1}, ν(CO asym.) 1659 cm^{-1}, ν(C–N) 1342 cm^{-1}, ν(O–C–N) 1240 cm^{-1}, δ(napht.) 780 cm^{-1} (from PP film).

2.6. *N-Octadecyl-1,8-naphthaleneimide (**VI**)*

1-Octadecylamine was used in place of 4-amino-2,2,6,6-tetramethylpiperidine in the above mentioned procedure (**I**). The crude product was chromatographed (silica gel, benzene: *iso*-hexane = 1:1) to give after removal of solvents 5.96 g (83%) white powder with m.t. 48–50°C. ^{1}H NMR (CDCl$_3$) δ: 0.88 (t, 3H, CH$_3$), 1.25 (m, 32H, CH$_2$), 4.19 (t, 2H, N–CH$_2$), 7.64–8.66 (m, 6H, napht.). FTIR (CHCl$_3$): ν(CO sym.) 1699 cm^{-1}, ν(CO asym.) 1658 cm^{-1}, ν(C–N) 1345 cm^{-1}, ν(O–C–N) 1237 cm^{-1}, δ(napht.) 780 cm^{-1} (from PP film).

1,8-Naphthalelnedicarboxylic acid anhydride, 1-octadecylamine, 2,2,6,6-tetramethyl-4-aminopiperidine were commercial products (Aldrich, Steinheim, Germany).

1,8-Dimethylester of naphthalene dicarboxylic acid-**VII** was prepared from silver salt of acid with methyl iodide yielding after crystallization (hexane) white crystals with m.t. 91–93°C.

Absorption spectra were measured on Specord UV VIS and M-40 (Carl Zeiss, Jena, Germany), ^{1}H-NMR on 80 MHz Tesla (Tesla, Brno, CR), mass spectra on HP 597 1A (Hewlett Packard, Palo Alto, USA) and infrared spectra on Specord IR-75 (Carl Zeiss, Jena, Germany) and on Impact 400 (Nicolet, USA).

Films of polystyrene (PS, Chemische Werke Huels, Germany) and poly(vinyl chloride) (PVC, Neralit, Spolana Neratovice, CR) were prepared by casting 0.02 2 mg of probe in 1 ml chloroform or tetrahydrofurane solution (5 g/100 ml) on glass plate (28×35 mm). The solvent was let to evaporate slowly. The thickness of film was 50 μm.

Polypropylene (PP) films were prepared in the following way: The additives (5.95×10^{-3} mol/kg) dissolved in 20 ml of dichloromethane were added to 25 g of non-stabilised isotactic PP powder (Daplen, PCD Polymere, Schwechat, Austria). The slurry was kept at room temperature for 18 h when the solvent was removed. The blends were mixed and homogenised in a Brabender Plastograph at 190°C for 5 min under air and then pressed into ca. 0.1 mm films in an electrically heated laboratory press (Fontune, The Netherlands) at 200°C for 1 min.

Photooxidation was performed on the merry-go-round type set up. Medium pressure 125 W mercury arc with luminophore envelope (RVL, Tesla Holesovice, CR) was used as the source of radiation. The temperature of photooxidation was 30°C. The course of photooxidation was followed by IR spectroscopy in carbonyl region 1700–1740 cm^{-1}. Decomposition of the additive in the course of photooxidation was followed by FTIR and UV spectroscopy.

3. Results and discussion

Compounds **I–VI** containing carbonyl groups in position 1 and 8 bound with imino group are photochemically active in relatively inert matrices where photo-oxidation does not occur during their photolysis. At irradiation with $\lambda > 310$ nm, the derivatives such as **I–V** disappear even they contain structural unit typical for light stabilisers. The longest wavelength band disappears at radiation with $\lambda > 310$ nm irreversibly (Fig. 1). At the short wavelength edge there is some indication of isosbestic point what can mean that simple transformation of A to B occurs. The photochemical reaction (photobleaching) is slow in PS as compared with PMMA [6] and PVC matrices (Fig. 2). In all matrices, the kinetics follows approximately the first order. The dependence of $\log A/A_0$, where A and A_0 are absorbancies at reaction time t and at $t = 0$, is linear at the beginning but in later stages is curved. The initial rate of disappearance of the compound with oxo bridge 1,8-naphthalenedicarboxylic acid anhydride is about three times higher in all matrices. The rate of derivatives as parent amine **I**, oxidised derivatives **II** and **IV** and surprisingly 1-acetyloxy derivative **V** was lower in all

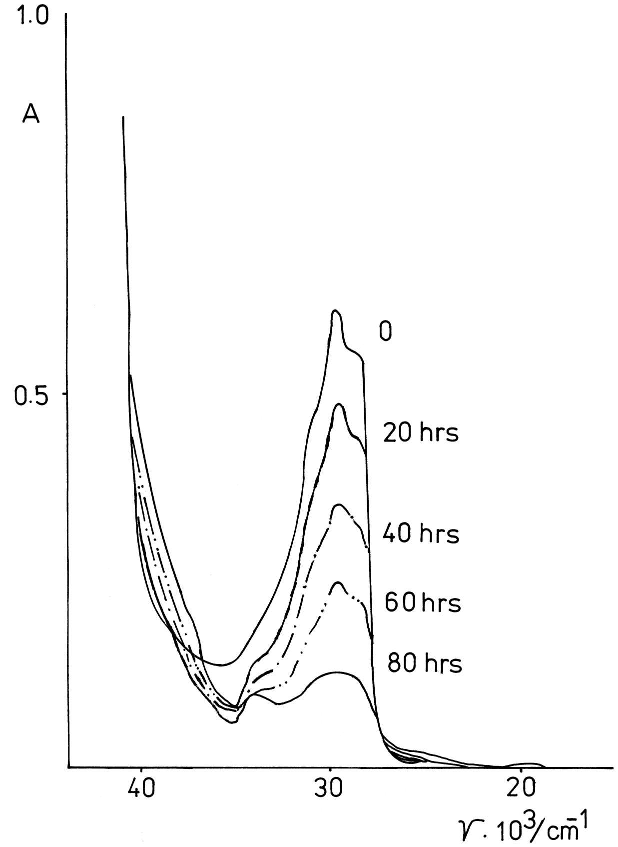

Fig. 1. Photolysis of *N*-(2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthaleneimide in PVC matrix at irradiation $\lambda > 310$ nm. Initial concentration 0.01 mol/kg.

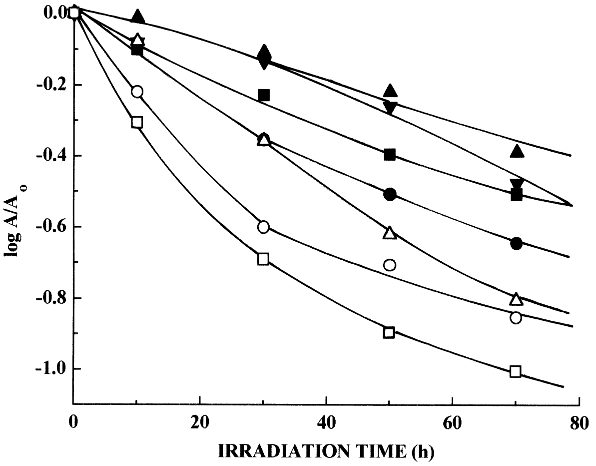

Fig. 2. Kinetics of photolysis ($\lambda > 310$ nm) of PVC films containing: □, 1,8-naphthalenedicarboxylic acid anhydride; ○, *N*-octadecyl-1,8-naphthaleneimide; ■, *N*-(2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthaleneimide; ▼, *N*-(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthaleneimide; ▲, *N*-(1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthaleneimide; ●, *N*-(1-acetyloxy-2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthaleneimide; △, *N*-(1-acetyl-2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthaleneimide. Additives concentration was 0.1 mol/kg.

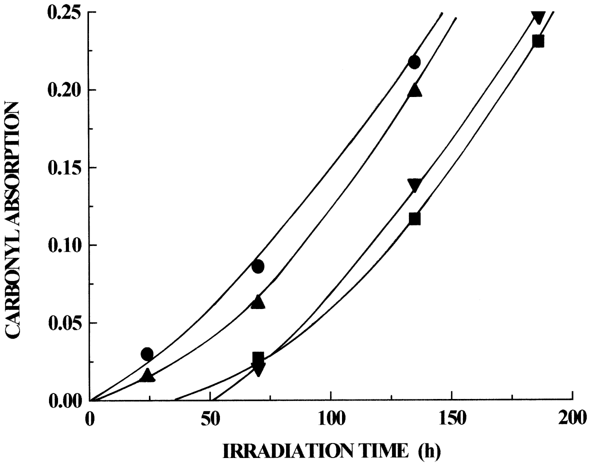

Fig. 3. Rates of photooxidation ($\lambda > 310$ nm) of PP films (ca. 0.1 mm) containing: ▼, no additive; ●, 1,8-naphthalenedicarboxylic acid anhydride; ▲, dimethylester of 1,8-naphthalenedicarboxylic acid; ■, *N*-octadecyl-1,8-naphthaleneimide. Additive concentration 5.95×10^{-3} mol/kg.

matrices than the others. The lowest rate of disappearance was 0.0022 h^{-1} for **IV** in PS and the highest 0.015 h^{-1} for **VII** in PMMA. It is evident that this type of chromophore with oxo or imino bridge is photochemically active due to hydrogen abstraction leading to disappearance of long wavelength absorption. This process is slow in PS matrix and rather rapid in PMMA or PVC matrices.

The course of photooxidation of iPP films containing starting material for synthesis of imides 1,8-naphthalenedicarboxylic acid anhydride, dimethylester of 1,8-naphthalenedicarboxylic acid as well as imide without active HAS *N*-octadecylnaphthaleneimide is shown on Fig. 3. The rates of photooxidation for *N*-substituted derivatives of *N*-(2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthaleneimide are shown on Fig. 4. Molar concentration was the same for all additives 5.95×10^{-3} mol/kg. This value is adequate to 0.2 wt% of cyclic imide with parent amine *N*-(2,2,6,6-tetramethylpiperidin -4-yl)-1,8-naphthylimide. It is a typical concentration used for testing of stabilizing efficiency of HAS. Processing of additives into PP in the Plastograph Brabender chamber is the best way to reach homogeneity of the additive dispersion despite some possibility of the additive thermal decomposition or partial evaporation due to the higher temperature—190°C. Fig. 3 shows that 1,8-naphthalenedicarboxylic acid anhydride as well as dimethylester of 1,8-naphthalenedicarboxylic acid sensitized the PP photooxidation. The production of the unstable chinone structures known as the very efficient sensitizers of PP photooxidation is the most probable reason for this effect. Photochemical decomposition of some additives in PP films was followed by FTIR and UV spectroscopy. All additives show strong and typical absorption bands at 1600–1800 cm^{-1} region of IR spectra (see Section 2). However, this region is not suitable to follow the kinetics of the additive decomposition because of simultaneous increasing of absorption of different carbonyl oxidation product from PP. For all additives the absorption band of the naphthalene ring at 773–780 cm^{-1} was used to follow the decomposition of aromatic ring. The decomposition of cyclic imide structure was followed by the changes of 1235–1243 cm^{-1} absorption adequate to ν(O–C–N) vibration and for dimethylester of 1,8-naphthalenedicarboxylic acid at 1284 cm^{-1} ν(C–O, ester). 1,8-Naphthalenedicarboxylic acid anhydride does not absorb at this region. The decomposition of naphthalene ring was followed by UV spectroscopy at 334 nm too. In the case of cyclic imides as well as dimethylester the course of intensity decreasing of 773–780 cm^{-1} band belonging to naphtyl absorption was the same as for 1235–1243 cm^{-1} ν(O–C–N) of cyclic imides and 1284 cm^{-1} ν(C–O) for methylester. This means that the photooxidation splits the naphthalene ring as well as cyclic imides and ester structures with the same rate. The course of naphthyl absorption vanishing was the same if measured by UV or IR spectroscopy.

The dependence of UV absorbance decreasing at 334 nm on the irradiation time for some additives is shown on Fig. 5. The most rapid decrease, i.e. the fastest decomposition has been reached for 1,8-naphthalenedicarboxylic acid anhydride (especially at the last phase of process) and for dimethylester of 1,8-naphthalenedicarboxylic acid. Reflection of this fact is sensitized photooxidation of PP films containing these additives in

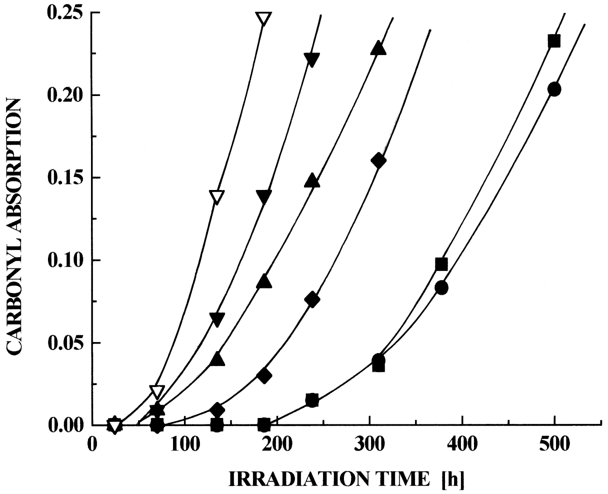

Fig. 4. Rates of photooxidation ($\lambda > 310$ nm) of PP films (ca. 0.1 mm) containing derivatives of *N*-(2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthaleneimide. ▽, no additive; ◆, *N*-(2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthaleneimide; ●, *N*-(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthaleneimide; ■, *N*-(1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthaleneimide; ▲, *N*-(1-acetyl-2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthaleneimide; ▼, *N*-(1-acetyloxy-2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthaleneimide. Additives concentration was 5.95×10^{-3} mol/kg.

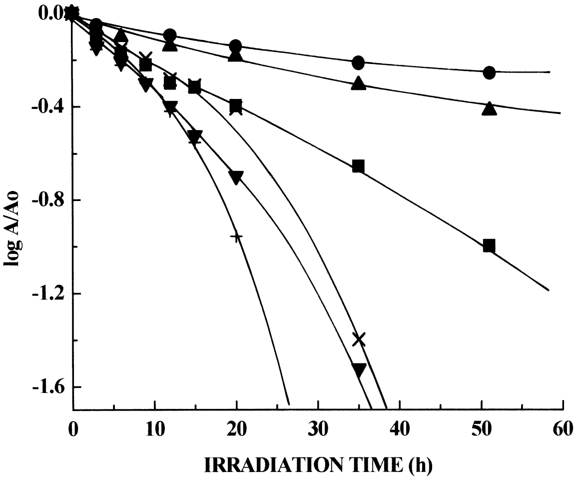

Fig. 5. Rates of the photochemical ($\lambda > 310$ nm) decomposition of additives in PP films (0.1 mm). ■, *N*-(2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthaleneimide; ●, *N*-(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthaleneimide; ▲, *N*-(1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthaleneimide; ×, *N*-octadecyl-1,8-naphthalenimide; ▼, dimethylester of 1,8-naphthalenedicarboxylic acid; +, 1,8-naphthalenedicarboxylic acid anhydride. Initial additive concentration 5.95×10^{-3} mol/kg.

comparison with pure PP film (Fig. 3). *N*-Octadecyl-1,8-naphthaleneimide seems to have no effect on PP photooxidation (the same course as for pure PP film). It can be related with a slower rate of its decomposition (Fig. 5) in combination with low resistance of PP itself to photooxidation. It means that decomposition products which sensitized photooxidation are produced when PP itself starts to oxidise. Photo-oxidation of pure PP after initiation due to some impurities in PP is very fast auto-catalytic process. The effect of decomposition products from *N*-octadecyl-1,8-naphtaleneimide on the course of this fast autocatalytic process is negligible. It seems to be more acceptable than speculation about much lower sensitizing ability of *N*-octadecyl-1,8-naphtaleneimide decomposition products. These ones should be very similar as in the case of 1,8-naphthalenedicarboxylic acid anhydride, where photooxidation is sensitized.

This would be possible to verify at photooxidation of polyethylene (PE). PE is more resistant to photooxidation than PP. Induction period (ca 150 h) is several times longer than for PP and in this period complete decomposition of 1,8-naphthalenedicarboxylic acid anhydride as well as *N*-octadecyl-1,8-naphtaleneimide would happen. Sensitized effect of *N*-octadecyl-1,8-naphtaleneimide and its decomposition products has been proved in PP, too. Four PP films were irradiated. Two of them contained the mixture of *N*-octadecyl-1,8-naphtaleneimide and 4-hydroxy-2,2,6,6-tetramethyl piperidine and 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl, respectively. Another two films did not contain *N*-octadecyl-1,8-naphtaleneimide. Fig. 6 shows that the presence of *N*-octadecyl-1,8-naphtaleneimide reduces the stabilizing efficiency of parent amine (4-hydroxy-2,2,6,6-tetramethylpiperidine) and adequate stable nitroxyl radical (4-hydroxy-2,2,6,6-tetramethylpiperidine -*N*-oxyl) exactly by the same value. This suggests that decomposition of *N*-octadecyl-1,8-naphtaleneimide is very similar in the presence of both additives and that *N*-octadecyl-1,8-naphtaleneimide itself and its decomposition products sensitize the photooxidation of PP.

Among the cyclic imides containing in their molecules structural unit of *N*-substituted HAS the lowest efficiency shows out *N*-(1-acetyloxy-2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthaleneimide (**V**, Scheme 1) (Fig. 4). Slightly more effective was *N*-(1-acetyl-2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthaleneimide **III**. Substitution on sterically hindered nitrogen influences stabilising efficiency of additive by changing the ease of stable nitroxyl radical formation which is the active species in stabilising process. *N*-Acetyloxy derivative of 4-benzoyloxy-2,2,6,6-tetramethylpiperidine was suggested to be inactive intermediate ending stabilizing cycle [8]. Other authors [9] [10] have shown that this derivative as well as *N*-acetyl are not inactive. They posses some small stabilizing activity and are not the products ending stabilizing cyclus.

Stabilizing efficiency of parent amines and adequate stable nitroxyl radicals for different 4-substituted 2,2,6,6-tetramethylpiperidine are generally about the same. It is valid for the substituents which are not photochemically active. In our case the substituent in position 4 is photo active and this results in a large difference

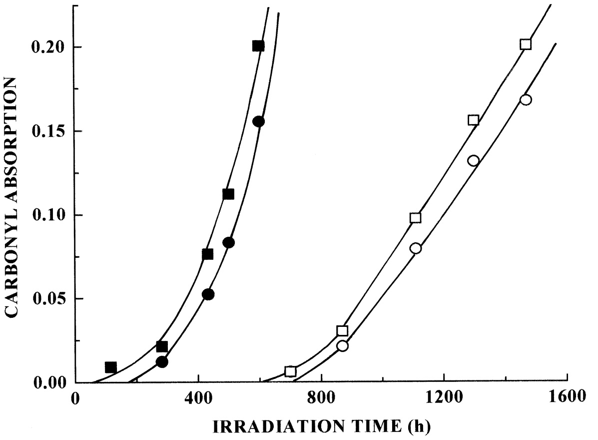

Fig. 6. The course of photooxidation (λ > 310 nm) of PP films (0.1 mm) containing: ■, *N*-octadecyl-1,8-naphthaleneimide and 4-hydroxy-2,2,6,6-tetramethylpiperidine; ●, *N*-octadecyl-1,8-naphthaleneimide and 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl; □, 4-hydroxy-2,2,6,6-tetramethylpiperidine; ○, 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl. Initial additive concentration 5.95×10^{-3} mol/kg.

between efficiency of parent amine **I** and nitroxyl radical **II**. As follows from Fig. 5 photochemical decomposition of parent amine is much faster in comparison with stable nitroxyl radical and *N*-(2,2,6,6-tetramethyl-*N*-hydroxy-piperidin-4-yl)-1,8-naphthaleneimide **IV** (thermal processing of **IV** >N–OH in Plastograph Brabender at 190°C in the presence of oxygen results in conversion of the most >N–OH to >N–O· (ESR spectroscopy)). Nitroxyl radical is able to quench excited state of naphthalene ring and to protect the molecule. Parent amine **I** is able to do this only after some irradiation time when part of it is converted to >N–O·. This partial protection in the case of parent amine is the reason of different course of photochemical decomposition between this additive and derivative containing inactive substituent *N*-octadecyl-1,8-naphtaleneimide **VI** (Fig. 5). In the later stage of reaction parent amine **I** is able to inhibit this process while *N*-octadecyl-1,8-naphtaleneimide decomposes with unchanged rate.

In conclusion, these studies show quite clearly that *N*-substituted derivatives of *N*-(2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthalenimide, 1,8-naphthalenedicarboxylic acid anhydride, dimethylester of 1,8-naphthalenedicarboxylic acid and *N*-octadecyl-1,8-naphthaleneimide are photochemically labile. At photolysis they are decomposed in all polymeric matrices under investigation. At photooxidation they seem to initiate the process effectively and chromophore part of molecule in the case of *N*-(2,2,6,6-tetramethylpiperidin-4-yl)-1,8-naphthalenimide derivatives strongly decrease the stabilizing efficiency of HAS.

Acknowledgements

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