

Synthesis, photochemical stability and photo-stabilizing efficiency of probes based on benzothioxanthene chromophore and Hindered Amine Stabilizer

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Abstract

New types of combined chromophore–HAS (Hindered Amine Stabilizer) fluorescence probes were prepared and their photo-stability as well as their photo-stabilizing efficiency was tested in polypropylene film. The chromophore was benzothioxanthene and HAS was 2,2,6,6-tetramethylpiperidine. They were prepared by a one-step synthesis from benzothioxanthene-3,4-dicarboxylic anhydride (BTXA) by condensation with 4-amino-2,2,6,6-tetramethylpiperidine to obtain the probe in the form of parent amine (BTXI-NH) and 4-amino-1-oxy-2,2,6,6-tetramethylpiperidine in the case of stable nitroxyl radical form (BTXI-NO). Kinetics of BTXA photo-decomposition followed by UV spectroscopy were similar to kinetics of photo-decomposition for derivatives with covalently linked HAS i.e. BTXI-NH and BTXI-NO. It consists of two parts, slower in the beginning and very fast at the end of the process. Better stability of BTXI-NO in comparison with BTXI-NH can be explained by the presence of stable nitroxyl radical in its structure. The rate of decomposition of the fast part is similar for both additives. As soon as the decomposition starts there is no influence of NO or NH on this process. Times represented the start of the fast decomposition of probes correspond to the induction period of photo-oxidation of PP films. Possible effect of mutual interaction of chromophore and HAS coupled in one molecule (BTXI-NH or BTXI-NO) during photo-oxidation was followed by comparison with the course of photo-oxidation of PP film containing physical mixture of chromophore in the form of BTXA and HAS in the form of parent amine (4-hydroxy-2,2,6,6-tetramethylpiperidine) and stable nitroxyl radical (4-hydroxy-2,2,6,6-tetramethylpiperidin-*N*-oxy).
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1. Introduction

Free radicals play the central role in a variety of chemical processes [1,2]. The lack of methods able to detect and especially identify very low concentrations of free radicals in condensed phases represents a major obstacle for understanding the impact of this highly

reactive species on chemical and biological processes. The direct detection of radicals by electron paramagnetic resonance (EPR) or optical spectroscopy is generally not possible because of high reactivity or low steady-state levels of these species. More often, the radicals are detected indirectly by employing radical traps or scavengers which react rapidly with the transient radicals to form more stable products. Spin trapping is one of the most often used indirect methods of radical detection. Rånby and Rabek [3] have reviewed the application of this method in polymer research. In this method free radicals are trapped by nitrones or nitroso

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compounds to produce nitroxyl radicals – spin adducts. Identification of the spin adducts might help to understand the mechanisms of the action and reactivity of the free radicals responsible for inhibition. Spin adduct instability, the inability to resolve mixtures of structurally similar spin adducts by EPR and the need for high concentrations of spin traps (due to low rate constants for the trapping reactions) are the main limitations of this technique.

As compared to spin traps, 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 characterization. Rate constant for the coupling is generally at least one order of magnitude higher than for the reaction of spin traps [4]. So, a much lower concentration of nitroxide is needed for the same effect. When the nitroxide contains some chromophore in the molecule, radical trapping 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 as alkoxy or aryloxy amines [5–9]. Stable nitroxyl radicals are well known quenchers of excited states [10,11]. Nitroxyl radicals are active species produced during the protection of polymers for the big family of photo- and thermo-stabilizer of Hindered Amine Stabilizers (HAS).

In our previous work we described the synthesis of bi-functional fluorescence probes containing chromophore and HAS in the form of parent amine as well as stable nitroxyl radical. We have demonstrated the extent of quenching occurring in the bi-functional fluorescence probes containing as a chromophore pyrene [12], naphthalene [13], 1,8-naphthaleneimide [14], and anthracene [15]. The ways as well as the length of spacer between pyrene and nitroxyl radical were investigated, too. 1-Oxo-2,2,6,6-tetramethyl-4-hydroxypiperidine was used as a stable nitroxyl radical. Photochemical stability of these probes in the form of parent amine as well as stable nitroxyl radical was tested in polypropylene. Unfortunately their stability was very low and most of these derivatives were destroyed very fast during several hours under irradiation. Therefore, it was not possible to follow the changes in fluorescence at the time of induction period of PP photo-oxidation due to the conversion of parent amine to nitroxyl radical (decreasing of fluorescence) or in the case of using probes in the form of nitroxyl radical after its conversion to substituted alkoxyamine (increasing fluorescence).

In this article we describe the preparation of new types of fluorescent probes containing as a chromophore benzothioxanthene. The selected chromophore absorbs radiation and emits very intense fluorescence. Due to the earlier mentioned problems of low photo-stability of the probes we checked this property for these

additives before using them in the study of their conversion during induction period of polypropylene photo-oxidation followed by spectrofluorimetry. Photo-stabilizing efficiency of these combined fluorescence probes as well as the mixtures of starting benzothioxanthene anhydride and HAS in the form of parent amine and stable nitroxyl radical was tested, too.

2. Experimental

2.1. Materials

Benzothioxanthene-3,4-dicarboxylic anhydride (BTXA) was a commercial product (HYanh., Clariant Huningue S.A., France). Powdered isotactic polypropylene (Tatren HPF) containing no additives was supplied by Slovnaft (Bratislava, Slovakia). Reagent grade solvents were used as received. *N,N*-dimethylformamide (DMF, AFT Ltd. Bratislava, Slovakia) was distilled under reduced pressure and stored over molecular sieves. 4-Amino-2,2,6,6-tetramethylpiperidine-*N*-oxyl was achieved in a three-step synthesis from 4-amino-2,2,6,6-tetramethylpiperidine (Aldrich) via protection of amino group, oxidation with H₂O₂ and deprotection according to procedure described in Ref. [16]. Thin-layer chromatographic (TLC) plates (silica) were purchased from Fisher Scientific, Germany.

2.2. Synthesis

2.2.1. Synthesis of 2-(4-(2,2,6,6-tetramethyl)piperidine)-thioxantheno[2,1,9-dej]isoquinoline-1,3-dione (BTXI-NH)

To the suspension of anhydride (BTXA) (10 g) in 80 ml of dry DMF a solution of 4-amino-2,2,6,6-tetramethylpiperidine in DMF (70 ml) was added dropwise. Reaction mixture was stirred in the presence of small amount of acetic acid under reflux condenser at 85 °C for 16 h and additionally at 120 °C for 2 h. After that TLC chromatography on silica plates with UV-detection (eluting with toluene/methanol (4/1) mixture (v/v)) showed only a small amount of anhydride as a first spot and slowly moving product. Half of the DMF was distilled out from the resulting orange suspension. To the residue 100 ml of methanol was added and crude powder was filtered, washed with methanol and dried in vacuum oven at 80 °C for 6 h. Product was purified by column chromatography on silica with toluene/MeOH/CHCl₃ elution mixture (4/2/1, v/v/v). The purity of orange powdered product with m.p. 300–302 °C was confirmed by NMR and FTIR spectroscopy.

¹H NMR (CDCl₃): δ (ppm) 1.21 (s, 6H, 2 × CH₃ 2 + 6 axial.), 1.37 (s, 6H, 2 × CH₃ 2 + 6 equat.), 1.64–1.69 (dd, 2H, CH₂ 5 + 3 axial.), 2.44–2.53

(t, 2H, CH₂ 5 + 3 equat.), 5.64–5.78 (tt, 1H, >CH–N), 7.26–7.41 (m, 3H, arom.), 7.43–7.52 (d, 1H, arom.), 8.19–8.22 (m, 2H, arom.), 8.38–8.41 (d, 1H, arom.), 8.58–8.61 (d, 1H, arom.).

¹³C NMR (CDCl₃): δ (ppm) 26.9 (2C, axial. CH₃), 33.9 (2C, equat. CH₃), 40.2 (2C, 2 × CH₂–CH–N), 46.5 (1C, CH–N), 60.7 and 60.8 (2C, 2 × C–N), 118.1 (1C, =C= arom.), 119.4 (1C, =CH– arom.), 120.6 (1C, =CH– arom.), 121.3 (1C, =C= arom.), 125.4 (1C, =C= arom.), 126.3 (1C, =CH– arom.), 126.6 (1C, =CH– arom.), 127.8 (1C, =CH– arom.), 127.9 (1C, =C= arom.), 130.2 (1C, =CH– arom.), 130.4 (1C, =C= arom.), 130.9 (1C, =CH– arom.), 131.7 (1C, =C= arom.), 132.7 (1C, =CH– arom.), 136.9 (1C, =C= arom.), 141.0 (1C, =C= arom.), 164.4 (1C, C=O), 164.8 (1C, C=O).

FTIR (CHCl₃): ν (C=O asym.) 1644 cm⁻¹, ν (C=O sym.) 1688 cm⁻¹.

2.2.2. Synthesis of 2-(4-(1-oxo-2,2,6,6-tetramethyl)-piperidine)-thioxantheno[2,1,9-de]isoquinoline-1,3-dione (BTXI-NO)

BTXI-NO was prepared by the same procedure as BTXI-NH using 4-amino-1-oxo-2,2,6,6-tetramethylpiperidine. Reaction was followed by FTIR spectroscopy. After separation as orange powder from the reaction mixture, the product was purified by column chromatography on alumina using chloroform/hexane (2/1 v/v) mixture as eluent. The residue of anhydride did not move on the column and the product was collected as the first fraction. Crystallization from toluene afforded red-orange crystals with m.p. 269–279 °C. Purity was checked by EPR spectroscopy (about 95%) comparing with 4-hydroxy-1-oxo-2,2,6,6-tetramethylpiperidine as standard.

Elemental analysis for C₂₇H₂₅N₂O₃S (M_w = 457.57). Calcd. C, 70.87; H, 5.51; N, 6.12%. Found: C, 70.58; H, 5.59; N, 5.92%.

FTIR (CHCl₃): ν (C=O asym.) 1644 cm⁻¹, ν (C=O sym.) 1688 cm⁻¹.

2.3. Preparation of polymer films

Films of PP were prepared in the following way: the additives (6 × 10⁻³ mol kg⁻¹) dissolved in 20 ml of chloroform were added to 25 g of non-stabilized polymer powder. The slurry was kept at room temperature for 18 h until the solvent was evaporated. The blends were mixed and homogenized in a Brabender Plastograph at 190 °C for 5 min under air and then pressed in an electrically heated laboratory press (Fontune, The Netherlands) at 200 °C for 1 min. Films of the same thickness (0.1 mm – checked by micrometer) were cut from the big sheet. Thicknesses were controlled by FTIR spectra – integral value (2.05 ± 0.05) of the peak at

898 cm⁻¹ [17]. Position as well as intensity of this peak does not change during photo-oxidation.

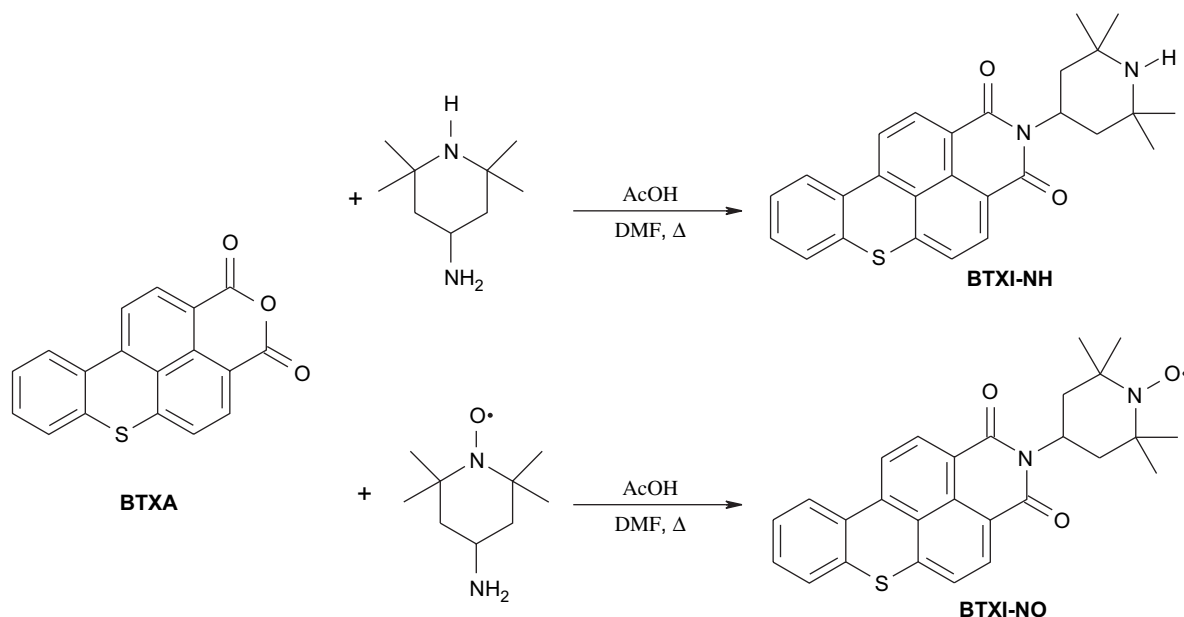
2.4. Techniques

Absorption spectra were taken on a UV–VIS 1650PC Shimadzu, FTIR spectra on Impact 400 (Nicolet, USA), ¹H NMR and ¹³C NMR spectra on Varian 300 MHz instrument, EPR spectrum on Varian E4 spectrometer and emission spectra on spectrofluorimeter Perkin–Elmer MPF-4 (Perkin–Elmer, Norfolk, Conn. U.S.A.), which was connected through an interface and A/D converter to the ISA slot of a PC using home made program for data collection.

Photo-decomposition and photo-oxidation of PP films were performed on the merry-go-round type set up. Medium pressure 250 W mercury arc with lumino-phore envelope (RVL, Tesla Holesovice, CR) was used as the source of radiation with λ > 310 nm. The temperature was 30 °C. The course of photo-oxidation was followed by FTIR spectroscopy in carbonyl region 1700–1740 cm⁻¹. Decomposition of the additive in the course of photo-oxidation was followed by FTIR and UV spectroscopy.

3. Results and discussion

Imidic derivatives BTXI-NH and BTXI-NO were prepared in a one-step synthesis from benzothioxanthene-3,4-dicarboxylic anhydride (BTXA) according to Scheme 1. Condensation reaction of anhydride with 4-amino-2,2,6,6-tetramethylpiperidine in the case of parent amine BTXI-NH and 4-amino-1-oxo-2,2,6,6-tetramethylpiperidine in the case of BTXI-NO, was initiated by the acetic acid and carried out in DMF solvent. Preparation of BTXI-NH by similar way in *N,N*-dimethylacetamide under catalytic action of *para*-toluenesulfonic acid was described in Ref. [18] but without any spectroscopic characterization or melting point of product. As has been already reported for 1,8-naphthalic anhydride [14,19] this process provides closed six-member imidic ring in one step. This reaction proceeds in similar way with some aminoalcohols as has been recently described [20]. The conversion of the reaction was followed by FTIR spectroscopy in the carbonyl region. FTIR spectra of starting anhydride BTXA and final imide BTXI-NH are shown in Fig. 1. Two symmetrical and asymmetrical vibrations of C=O at 1716 and 1767 cm⁻¹ related to anhydride change to new absorption bands of C=O at 1644 and 1688 cm⁻¹ related to symmetrical and asymmetrical vibrations of imide BTXI-NH. Despite some problems with separation of products by column chromatography due to low solubility of final materials, the structure and purity of products were confirmed by ¹H and ¹³C NMR as well as EPR



Scheme 1. Reaction scheme and structures of combined fluorescent additives.

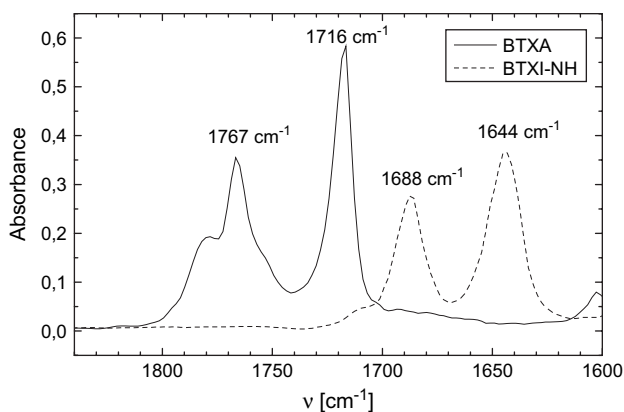
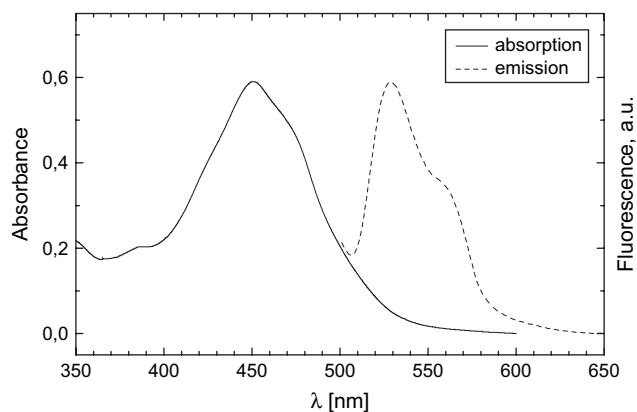
spectroscopy. Standard procedure for the preparation of stable nitroxyl radical, as we described earlier [14,15] is the oxidation of parent amine with 3-chloroperbenzoic acid. In the case of benzothioxanthene derivative, where the sulfur atom is sensitive to oxidation, this method is not suitable. Due to this fact the stable nitroxyl radical was used as starting material.

The EPR spectrum of BTXI-NO measured in toluene revealed the typical triplet with line of equal intensity. The hyperfine splitting is the result of the interaction of the unpaired electron with the nucleus ^{14}N . Integral of EPR spectra of BTXI-NO was compared with the integral of the standard (4-hydroxy-1-oxo-2,2,6,6-tetramethylpiperidine). The values of integrals are proportional to the number of radicals. We assume that the relative concentration of radicals in standard is 100%. The value of 95% relative concentration proves the

high purity of BTXI-NO (preparation of probe solutions was done with certain error – probe weighting, dilution).

Processing of additives into PP in the Brabender Plastograph chamber above the melting temperature of PP is the best way to reach homogeneity of the additive dispersion. Molar concentration of additives in polymer was $6 \times 10^{-3} \text{ mol kg}^{-1}$ (about 0.1 wt% of HAS) and was the same for all derivatives. This is the very common concentration used for testing stabilizing efficiency of HAS.

Absorption and emission spectra of BTXI-NH in polypropylene film are shown in Fig. 2. Intense fluorescence in visible region with the maximum at 530 nm makes this probe suitable to follow its conversion to BTXI-NO with much lower fluorescence during photo-oxidation of PP film. Another requirement for useful

Fig. 1. Carbonyl region of FTIR (CHCl_3) spectra of anhydride BTXA and imide BTXI-NH.Fig. 2. Absorption and emission spectra ($\lambda_{\text{exc}} = 470 \text{ nm}$) of parent amine probe BTXI-NH in PP at concentration $6 \times 10^{-3} \text{ mol kg}^{-1}$.

application of this study is reasonably good photostability, especially during the induction period of photo-oxidation. The kinetics of decomposition of anhydride BTXA as well as combined chromophore–HAS probes BTXI-NH and BTXI-NO during irradiation were monitored by UV spectroscopy. Fig. 3 shows the changes in UV spectra of PP film containing probe BTXI-NH where the HAS is in the form of parent amine. Probes BTXI-NO where the HAS part is in the form of stable nitroxyl radical revealed the same absorption spectra in the case of non-irradiated film concerning the positions of absorption bands and intensity. UV spectrum of starting anhydride BTXA in PP matrix was a little different. BTXA exhibits broader absorption band at 460 nm with a sign of shoulder at 475 nm. The intensity of this band was lower when compared with both imides BTXI-NH and BTXI-NO most probably because of possible aggregation in non-polar PP matrix due to the high polarity of BTXA. From the FTIR spectra (carbonyl region and absorption at 760 cm^{-1}) it follows that content of BTXA in PP film was the same as content of BTXI-NH and BTXI-NO. As it has been already mentioned, additional necessary condition is photochemical stability of these probes in the form of parent amine BTXI-NH as well as stable nitroxyl radical BTXI-NO at least during the induction period of polypropylene photo-oxidation. Under these conditions it could be possible to follow the conversion of BTXI-NH with high emission to BTXI-NO, which due to the quenching emitted much lower fluorescence. On the other hand when starting form will be BTXI-NO (low emission) we would be able to follow by fluorescence measurement conversion of BTXI-NO to BTXI-NOR (high emission) as the result of trapping of radicals R^{\bullet} generated from PP. Photochemical stability was monitored by absorption spectroscopy. The absorption band at 460 nm was used for the calculation of decomposition

kinetics. In this region there is no absorption coming from the oxidized PP matrix.

As can be seen in Fig. 3 for BTXI-NH the partially resolved vibrational structure of the additive in non-irradiated PP film is missing after a short time of irradiation and the maximum of the peak is continually shifted to the longer wavelengths. The integral value of the area under the peak was taken for calculation with the baseline from 360 nm to 560 nm. The apparent big change after 30 h of irradiation shown in Fig. 3 for BTXI-NH is due to the baseline change and the real concentration decrease of the additive is very low. This baseline change was just in the case of this additive. Kinetic data of decomposition for all the three additives during photo-oxidation are given in Fig. 4. BTXA and bi-functional fluorescence probes BTXI-NH and BTXI-NO are relatively stable under UV irradiation ($\lambda > 310\text{ nm}$) during the first ca 250 h. It means that BTXI-NH and BTXI-NO are suitable fluorescence probes from the photo-stability point of view. It should be possible to follow the process of radical production from PP and their mutual reaction with these probes by fluorescence measurements at the time of induction period, where other techniques, like FTIR are not sensitive enough. After 250 h of irradiation the rate of photo-decomposition of absorbing species increased rapidly for BTXI-NH and BTXI-NO. For BTXA it was not possible to follow decomposition because after this time the PP film was heavily oxidized (see Fig. 5) and destroyed (too brittle for manipulation). Decomposition in this first stage was different for all the three additives, though the differences were not large. The fastest decomposition takes place in the case of BTXA, followed by BTXI-NH. BTXI-NO was the most stable. Better stability of BTXI-NO in comparison with BTXI-NH can be explained by the presence of stable nitroxyl radical in its

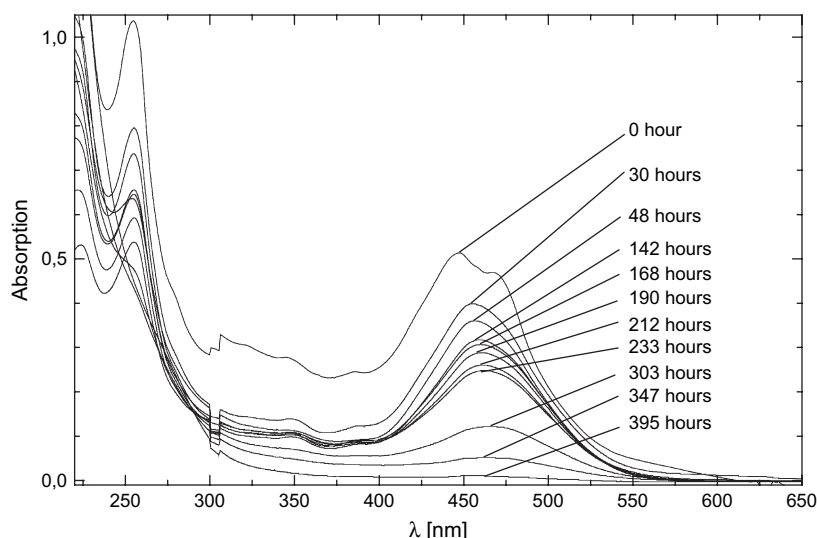


Fig. 3. Changes in absorption spectra of PP films containing BTXI-NH during irradiation ($\lambda > 310$). Additive concentration was $6 \times 10^{-3}\text{ mol kg}^{-1}$.

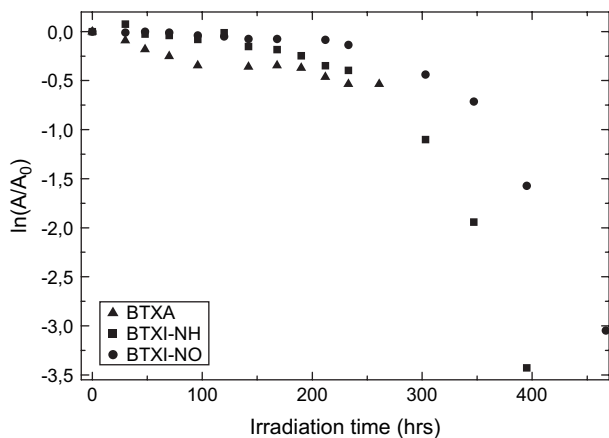


Fig. 4. Kinetics of benzothioxanthene derivatives' decomposition in PP films during irradiation ($\lambda > 310$ nm). Additive concentration was 6×10^{-3} mol kg^{-1} .

structure. This radical is able to quench partially excited singlet as well as triplet states of the benzothioxanthene chromophore to slow down decomposition [21]. This radical is produced from the parent amine BTXI-NH during photo-oxidation but its steady-state concentration is too low to see the effect of quenching, or this effect is more extensive in the case where all additive at the beginning of irradiation is in the form of radical as it is in the case of BTXI-NO. Quenching is the most probable reason for the extension of the time when fast decomposition of BTXI-NO started in comparison with the time for BTXI-NH. The rate of decomposition of this fast part is similar for both additives. As soon as the decomposition starts there is no influence of NO or NH on this process.

The course of photo-oxidation of PP films containing the same molar concentration of BTXA, BTXI-NH and BTXI-NO (6×10^{-3} mol kg^{-1}) is shown in Fig. 5. To see the effect of mutual interaction of chromophore

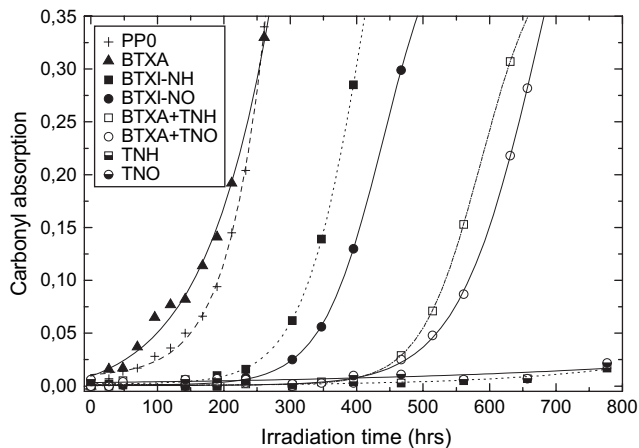


Fig. 5. Courses of photo-oxidation of PP films doped with benzothioxanthene additives at concentration 6×10^{-3} mol kg^{-1} .

and HAS coupled in one molecule (BTXI-NH or BTXI-NO) during photo-oxidation, we compare this with the course of photo-oxidation of PP film containing a physical mixture of chromophore and HAS. Chromophore was in the form of BTXA and HAS in the form of parent amine (4-hydroxy-2,2,6,6-tetramethylpiperidine; TNH) and the stable nitroxyl radical (4-hydroxy-2,2,6,6-tetramethylpiperidin-*N*-oxyl; TNO). Due to the presence of carbonyl vibration bands of additives these bands were subtracted from the bands of carbonyl products of photo-oxidation. BTXA acts as photosensitizer. Its action is more pronounced at the beginning of irradiation. It is difficult to decide if this increase of PP oxidation is due to the decomposition products or due to some physical process connected with excitation and quenching of excited states of present chromophore. Combined chromophore–HAS additives BTXI-NH and BTXI-NO possess some stabilizing efficiency and BTXI-NO is clearly better. It is the reflection of later photo-decomposition of BTXI-NO in comparison with BTXI-NH as was already mentioned. For both these additives the fast parts of PP photo-oxidation start exactly at the same time when fast parts of photo-decomposition take place. Only a small change concerning the amount of additives in original form occurs during the induction period of photo-oxidation of PP films. Fast part of decomposition starts at ca 250 h for BTXI-NH and at ca 300 h for BTXI-NO. It means that the fast photo-decomposition of chromophore moiety resulted in the very effective sensitising species and the rest of molecule containing HAS structure is not able to protect the polymer or that the HAS structure is destroyed too. The time to reach carbonyl absorption $A_{CO} = 0.2$ was 370 h for BTXI-NH and 425 h for BTXI-NO. HAS non-bonded with chromophore (in the form of TNH and TNO) in physical mixtures with chromophore (in the form of BTXA) is more efficient in protecting PP than the HAS in combined molecules with chromophore. Again nitroxyl radical form TNO is more effective stabilizer than the parent amine TNH. The time to reach carbonyl absorption $A_{CO} = 0.2$ was 625 h for the BTXA + TNO mixture and 580 h for BTXA + TNH mixture. The highest efficiencies were reached with TNO and TNH alone. Time to reach $A_{CO} = 0.2$ was 1500 h for TNH and 1600 h for TNO. Comparison of these data with those for physical mixture reflected very high sensitising ability of BTXA chromophore on PP photo-oxidation. Sensitised process was not so pronounced in the case of pure PP due to fast photo-oxidation of pure PP itself. Similar results were obtained for other chromophores such as 1,8-naphthaleneimide [14] and pyrene [12]. Stabilizing efficiencies of these combined molecules with HAS were lower than the efficiencies of physical mixture of chromophore and HAS (TNO and TNH) and these chromophores revealed high sensitising activity, too.

4. Conclusion

Novel probes based on fluorescent benzothioxanthene chromophore and HAS were prepared and the structures were characterized by conventional methods. They exhibit reasonably good photo-stability during the induction period of PP photo-oxidation. Therefore they show some potential for monitoring the transformation of parent amine to stable nitroxyl radical or stable nitroxyl radical to substituted alkoxyamine by fluorescence measurement. This will be subject of the next studies.

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