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The photolysis in polymer matrices of dyes containing a benzothioxanthene chromophore linked with a hindered amine

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Novel dyes based on a benzothioxantheneimide chromophore covalently linked with a sterically hindered amine (HAS) were prepared and their light stability was tested in polymer matrices. The following dyes: 2-(2,2,6,6-tetramethyl-4-piperidyl)-thioxantheno[2,1,9-dej]isoquinoline-1,3-dione (BTXINH) and *N*-alkoxy derivative 2-(1-(1′-phenylethoxy)-2,2,6,6-tetramethyl-4-piperidyl)-thioxantheno[2,1,9-dej] isoquinoline-1,3-dione (BTXINOR) were prepared. For comparison the parent dye without HAS structural unit benzothioxanthene-3,4-dicarboxylic anhydride and the N-alkyl derivative 2-(1-dodecyl)-thioxantheno[2,1,9-dej] isoquinoline-1,3-dione (BTXID) and the stable nitroxyl radical 2-(1-oxo-2,2,6,6-tetramethyl-4-piperidyl)-thioxantheno[2,1,9-dej]isoquinoline-1,3-dione (BTXINO) were also tested. Their spectral properties, absorption and fluorescence have been examined in polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC) and in isotactic polypropylene (PP). The light stability of these dyes and model compounds were examined in thin polymer films. The photolysis rate was monitored by UV spectroscopy and for all additives under study it was in the range 10^{-4}–10^{-3} h^{-1}. The rate of decomposition was the lowest for the parent amine BTXINH in PMMA, PS and PVC. The rate constants of photolysis are about 10 times higher for all adducts and the lowest rate of decomposition in PP matrix was observed for BTXINOR. A distinct stabilization effect of HAS structural unit on the dye decomposition was not observed. The light stability of the dyes was more influenced by the selection of the polymer. The photolysis proceeds rather fast in PP, and moderately in PS and PVC compared to PMMA.

1. Introduction

The emerging science of photonics, which includes the generation, emission, transmission, modulation, signal processing, switching, amplification, detection and sensing of light, is being explored today as the basis for new technology that exploits the capability of a photon to carry information and energy [1]. To achieve this goal, new specific materials with properties such as large nonlinear susceptibility, fast response, easy preparation and handling should be developed to achieve the parameters necessary for the further development of the photonic material itself and technology based around it.

Even a well established industry like automotive demands a wide variety of new metals, fillers, plastics, pigments and dyes for specific applications. The synthetic polymers represent a growing fraction of materials used for different parts of the car. Special applications are mainly plastics, pigments and dyes is automotive coating. There is a strong drive to develop and apply new polymers, pigments and dye mainly for coatings but also for other items. Thus new dyes with interesting optical properties and photo-stability will be of some interest in different branches of industry especially when doped in the polymer matrix.

All synthetic polymers as well as pigments and dyes suffer from (photo-thermo) degradation. The degradation rate depends on the type of the polymer and the environment especially on sunlight, heat (temperature), humidity. So called UV-degradation is due to combination of photolysis and oxidative reaction. In an inert atmosphere the photolysis is only occurring while photo-oxidation dominates in the presence of air. The ratio between these two mechanisms depends on the environment and on the type of polymers [2].

Polymers currently used on a large scale may be divided into three groups depending on their resistance to photolytic degradation and photo-oxidation: i) highly photo-stable polymers that are commonly used without additives e.g., polytetrafluoroethylene, poly(methyl methacrylate) etc. ii) moderately photo-stable polymers that can be used without additives e.g., poly(ethylene terephthalate), polycarbonate etc. iii) poorly photo-stable polymers which need extensive stabilization for outdoor application e.g., polyolefins,

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poly(vinyl chloride), polystyrene, polyamides, polyurethane, rubbers, cellulose, etc.

The search for ways to inhibit or at least retard this type of degradation has been a major effort of the plastics industry since the middle of the last century [3]. At present a high level of stabilization even with poorly photo-stable polymers might be achieved with available classes of stabilizers, such as 2-hydroxybenzophenones, 2-hydroxyphenylbenzotriazoles, organic nickel compounds and sterically hindered amines (HAS).

The problem, which still persists in photostabilisation of intensively dyed polymers, consists of the stability of the dye itself as well as stability of the polymer in the presence of dye. The solution could be seen in combinations of dyes with structural units of photo-stabilizer type.

In the past we tested the stability of photoactive unit (naphthalene, pyrene) which could serve as model for dye linked with sterically hindered amine (HAS) in isotactic polypropylene [4]. This study revealed that aromatic hydrocarbons used as fluorescence labels are easily destroyed during the early stage of the induction period of photo-oxidation of the matrix. Therefore, they cannot report formation of *N*-oxyl during the induction period. Moreover, the presence of the photoactive unit in the vicinity of HAS decreases the stabilizing efficiency indicating some kind of intramolecular antagonistic effect.

Similarly the photochemical stability and photostabilising efficiency of HAS in the presence of free and bound 1,8-naphthalimide chromophore was evaluated [5]. It was observed that the 1,8-naphthalimide is photolysed and the photo-stabilizing efficiency of HAS is higher in the mixture and less efficient when HAS is linked with 1,8-naphthalimide chromophore.

Adducts of another chromophore namely anthracene linked in position 9 with HAS was tested in isotactic polypropylene as well [6]. Anthracene, even if linked with HAS, photolysed rapidly in polymer matrices. The decomposition of anthracene produced free radicals containing HAS, which then grafted on polymer matrix and improved overall performance of adducts.

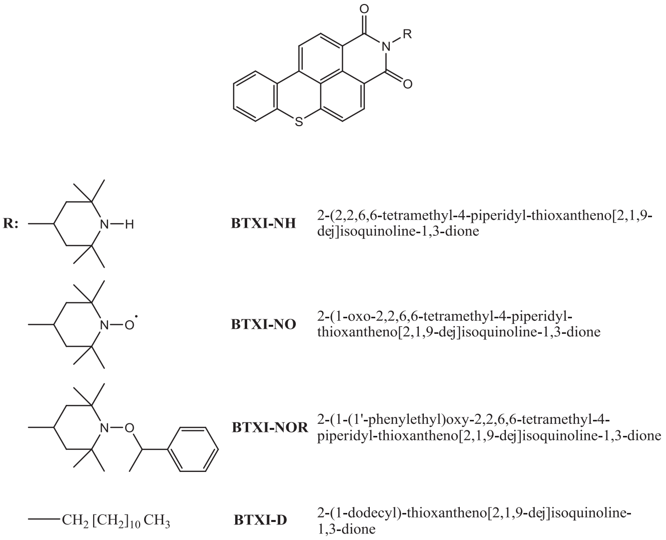
Recently, we have investigated possible effect of mutual interaction of novel chromophore of benzothioxanthene type and HAS coupled in one molecule [7]. These compounds exhibited sufficient photo-stability during induction period of photo-oxidation of isotactic polypropylene. The spectral properties of these new combined dyes were studied in solution and in polymer matrices. These dyes exhibit intense fluorescence in solution and doped in polymer matrix which might be of some interest in construction of probes and sensors [8].

In this paper, we extend studies of adducts of benzothioxanthene and HAS and evaluate their photo-stability in polymer matrices such as poly(methyl methacrylate), polystyrene and polyvinylchloride. For comparison, the photo-stability of dyes in isotactic polypropylene were evaluated as well. The aim of the study is to test the feasibility of linking of dye (chromophore) and HAS in one molecule to achieve higher stability of adduct doped in the polymer matrix and polymer matrix itself as well.

2. Experimental

2.1. Synthesis

The structures of the dyes linked with sterically hindered amines tested on their photo-stability are given in Scheme 1. Benzothioxanthone-3,4-dicarboxylic anhydride (BTXA) was commercial product (HY-anh., Clariant Huningue S.A., France). The details of synthesis of BTXINH, BTXINO, BTXINOR and BTXID are given elsewhere [7,8]. Some characteristics are also given here.



Scheme 1. Chemical structures, abbreviations and full names of investigated compounds.

2-(2,2,6,6-Tetramethyl-4-piperidyl)thioxantheno[2,1,9-dej] isoquinoline-1,3-dione (BTXINH) was prepared by the condensation of anhydride (**BTXA**) with 4-amino-2,2,6,6-tetramethylpiperidine in dry dimethylformamide (DMF) in the presence of small amount of glacial acetic acid. The purity of orange powder as product (m.p. 300–302 °C) was confirmed by NMR and FTIR spectroscopy [9].

^{1}H NMR (CDCl$_3$): δ (ppm) 1.21 (s, 6H, 2× CH$_3$ 2 + 6 axial.), 1.37 (s, 6H, 2× CH$_3$ 2 + 6 equat.), 1.64–1.69 (dd, 2H, CH$_2$ 5 + 3 axial.), 2.44–2.53 (t, 2H, CH$_2$ 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.).

^{13}C NMR (CDCl$_3$): δ (ppm) 26.9 (2C, axCH$_3$), 33.9 (2C, eqCH$_3$), 40.2 (2C, 2× $\underline{\text{CH}_2}$–CH–N), 46.5 (1C, CH–N), 60.7 a 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 (CHCl$_3$): ν(C=O asym.) 1646 cm^{-1}, ν(C=O sym.) 1690 cm^{-1}.

2-(1-Oxo-2,2,6,6-tetramethyl-4-piperidyl)thioxantheno[2,1,9-dej] isoquinoline-1,3-dione (BTXINO) was prepared by the same procedure as BTXNH using BTXA and 4-amino-1-oxo-2,2,6,6-tetramethylpiperidine as reagents. The purity of red-orange crystals with m.p. 269–279 °C has been proved by EPR spectroscopy. EPR spectrum of BTXNO in toluene revealed the typical triplet with line of equal intensity. The hyperfine splitting is the result of interaction of the unpaired electron with the nucleus ^{14}N. Integral of EPR spectra of BTXNO was compared with the integral of the standard (4-hydroxy-1-oxo-2,2,6,6-tetramethylpiperidine, TEMPOL). The values of the integrals are proportional to the number of radicals. The concentration of radicals in standard is assumed to be 100%. The value of relative concentration 95% proves the acceptable purity of BTXNO.

Elemental analysis for $C_{27}H_{25}N_2O_3S$ (Fw = 457.57). Calcd. C, 70.87; H, 5.51; N, 6.12%. Found: C, 70.58; H, 5.59; N, 5.92%.

FTIR (CHCl$_3$): ν(C=O asym.) 1646 cm^{-1}, ν(C=O sym.) 1690 cm^{-1}.

2-(4-(1-(1′-phenylethyl)oxy)-2,2,6,6-tetramethyl)piperidine)-thioxantheno [2,1,9-dej]isoquinoline-1,3-dione (BTXINOR). The nitroxide (BTXINO) (0.67 g, 1.47 mmol), Mn(OAc)$_3$ × 2H$_2$O (1.96 g, 7.3 mmol) and styrene (0.84 ml, 7.3 mmol) were suspended in mixture of solvents toluene/ethanol/acetic acid (2/2/1 v/v/v). Reaction mixture was vigorously stirred at laboratory temperature and $NaBH_4$ (0.43 g, 11.4 mmol) was added in three portions. TLC chromatography on Al_2O_3 plates eluting with mixture dichloromethane and hexane (1/1 v/v) showed only one new product. Reaction dispersion was filtered, filtrate was washed with dichloromethane and mother liquor was extracted three times with water solution of $NaHCO_3$ and additionally twice with water. The organic layer was dried over Na_2SO_3. After evaporation of solvent, the crude solid orange product was obtained by chromatography on alumina column eluting with mixture CH_2Cl_2/hexane (1/1 v/v) as eluting solvent. Crystallization of product from ethyl acetate, collected as a first fraction, gave 0.14 g (21%) of bright orange crystals with m.p. 212–215 °C.

^{1}H NMR ($CDCl_3$): δ (ppm) 0.75 (s, 3H, axCH_3,), 1.25 (s, 3H, axCH_3,), 1.38–1.39 (m, 6H, eqCH_3,), 1.45–1.67 (m, 2H, axCH_2) 1.53 (d, $J = 6.6$ Hz, 3H, $\underline{CH_3}$–CH–Ph), 2.82 and 2.94 (2× t, 2H, eqCH_2), 4.86 (q, $J = 6.7$ Hz 1H, CH_3–$\underline{CH}$–Ph), 5.54 (m, 1H, CH–N), 7.22–7.37 (m, 9H (5H Ph + 4H arom.)), 8.0–8.10 (m, 2H, arom.), 8.27 (d, 1H, arom.), 8.45 (d, 1H, arom.).

^{13}C NMR ($CDCl_3$): δ (ppm) 20.8 (1C, $\underline{CH_3}$–CH–Ph), 23.3 (2C, axCH_3), 34.1 a 34.4 (2C, eqCH_3), 41.5 (2C, 2× $\underline{CH_2}$–CH–N), 45.7 (1C, CH–N), 60.7 a 60.8 (2C, 2× C–N), 83.2 (1C, CH–Ph), 118.4–140.1 (21C, Ph + arom.), 145.6 (1C, C(Ph)), 164.0 (1C, C=O), 164.4 (1C, C=O).

FTIR ($CHCl_3$): ν(C=O asym.) 1646 cm^{-1}, ν(C=O sym.) 1688 cm^{-1}.

2-(1-Dodecyl)-thioxantheno[2,1,9-dej]isoquinoline-1,3-dione (BTXID) has been prepared by the same procedure as BTXINH using BTXA and dodecylamine as reagents. Reaction was followed by FTIR spectroscopy. After separation of orange powder from reaction mixture, product was obtained by chromatography on silica gel column using mixture chloroform/hexane (1/2 v/v) as eluent. Product was collected as a first fraction. Recrystallisation from ethyl acetate gave red-orange crystals with m.p. 120–123 °C.

^{1}H NMR ($CHCl_3$) δ: (ppm) 0.87 (t, 3H, CH_3), 1.18–1.43 (m, 18H, CH_2–$\underline{CH_2}$–CH_2), 1.72 (qui, 2H, N–CH_2–$\underline{CH_2}$), 4.13 (t, 2H, CH_2–N), 7.32–7.39 (m, 4H, arom.), 8.02–8.05 (d, 1H, arom.), 8.06–8.10 (m, 1H, arom.), 8.30–8.33 (d, 1H, arom.), 8.47–8.50 (d, 1H, arom.).

^{13}C NMR ($CHCl_3$) δ: (ppm) 14.1 (1C, CH_3), 22.7 (1C, $\underline{CH_2}$–CH_3), 27.2 (1C, CH_2), 28.0 (1C, CH_2), 29.37 (1C, CH_2), 29.42 (1C, CH_2), 29.6 (1C, CH_2), 29.65 (1C, CH_2), 29.66 (1C, CH_2), 29.68 (1C, CH_2), 31.9 (1C, –$\underline{CH_2}$–CH_2–N), 40.5 (1C, CH_2–N), 118.0 (1C, =C= arom.), 119.0 (1C, =CH– arom.), 120.2 (1C, =CH– arom.), 121.2 (1C, =C= arom.), 125.3 (1C, =C= arom.), 125.9 (1C, =CH– arom.), 126.3 (1C, =CH– arom.), 127.5 (1C, =CH– arom.), 127.8 (1C, =C= arom.), 129.9 (1C, =CH– arom.), 130.1 (1C, =C= arom.), 130.6 (1C, =CH– arom.), 131.5 (1C, =C= arom.), 132.3 (1C, =CH– arom.), 136.4 (1C, =C= arom.), 140.2 (1C, =C= arom.), 163.3 (1C, C=O), 163.7 (1C, C=O).

FTIR ($CHCl_3$): ν(C=O asym.) 1646 cm^{-1}, ν(C=O sym.) 1688 cm^{-1}.

2.2. Materials

Anthracene was zone refined (Lachema n.e., Brno, CR). Chloroform, tetrahydrofuran (Lachema n.e., Brno, CR), dimethylformamide, toluene and ethanol (Centralchem, SR) were analytical reagents. Polymer films doped with adducts were prepared either by casting from solution or by hot pressing. Films of polystyrene (PS) (Chemische Werke Huels, F.R.G.) and poly(methyl methacrylate) (PMMA) (Diakon, ICI, England) were prepared by casting of 1 ml chloroform solution of polymer (5 g/100 ml) containing the respective amount of sample on a glass plate (28 × 35 mm). The solvent was evaporated slowly. Films of poly(vinyl chloride) (PVC) (Neralit, Spolana Neratovice s.e., CR) were prepared by similar way by film casting from tetrahydrofuran solution (5 g/100 ml). The final concentration of the sample in the film was either 0.002 mol kg^{-1} for spectral measurements or 0.02 mol kg^{-1} for photolysis. The thickness of the films was 50 μm. Films of isotactic polypropylene (PP) (powder without additives Tatren HPF, Slovnaft, Bratislava, Slovakia) were prepared by following way: The additives (0.002 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 (Fontijne, The Netherlands) at 200 °C for 1 min. The thickness of films was 80–120 μm.

2.3. Spectral measurements

NMR spectra (^{1}H at 300 MHz, ^{13}C at 75 MHz) were obtained in $CDCl_3$ using a Varian spectrometer with tetramethylsilane (TMS) as the internal standard. Reactions and the collected fraction samples were monitored by TLC (Merck 60 F254 silica gel). Visualization was afforded using a UV hand lamp with 254 nm wavelength light. Melting points were recorded on a Kofler block and are uncorrected. Infrared spectra (KBr) were determined on a Nicolet 8700 (Thermo, USA) system. Elemental analyses were measured by means of Carlo Erba Elemental Analyzer 1108. Absorption spectra were obtained on a UV 1650 PC spectrometer (Shimadzu, Japan). Emission spectra were recorded on a Perkin–Elmer MPF-4 spectrofluorimeter (Perkin–Elmer, Norfolk, Conn. U.S.A.), which was connected through interface and A/D converter to ISA slot of PC using home made program for data collection. Program Origin 6.1 (Microsoft) was used for data plotting. Polymer film fluorescence was measured using the front face arrangement in a solid sample holder. The quantum yield of anthracene fluorescence in different media was determined by comparing the fluorescence of anthracene in cyclohexane (value 0.25 discussed in reference [10]) and various other media. It was found to be 0.20 in PMMA, 0.16 in PS, 0.11 in PVC and 0.25 in PP. The quantum yield in film was corrected to different absorptions at the excitation wavelength [11]. The fluorescence spectra were obtained by exciting at the maximum of the longest wavelength absorption band.

The fluorescence lifetime measurements of adducts doped in polymer matrices were performed in front face arrangement on a LIF 200 (Lasertechnik Ltd., Berlin, F.R.G.), which operates as a stroboscope. The excitation source is a nitrogen laser emitting at 337 nm and the emission is selected by cut-off filter. The output signal of Box Car Integrator was digitized and transferred to the PC using homemade program. The fluorescence decay curves were evaluated by simple phase plane method [12] using program designed by J. Snyder discussed in reference [13]. The standard deviation derived from equation: $G^{1/2} = \Sigma((I_{\mathrm{exp}} - I_{\mathrm{calc}})^2/n)^{1/2}$, where I_{exp} and I_{calc} are intensities of experimental and calculated emission respectively, is used to determine whether the decay is mono-exponential. It is assumed that the decay curve satisfied the mono-exponential condition when the standard deviation is lower than 5%. Alternatively, the fitting of fluorescence decay curves to a model of bi-exponential decay was performed using adapted FluoFit MatLab package [14].

The steady state and time resolved measurements were performed in aerated solutions. All measurements on polymer films were done in the presence of air.

EPR spectra were measured with X band E-4 Varian spectrometer (USA) interfaced with PC with program Symphonia Bruker.

3. Results and discussion

3.1. Spectral properties

Adducts of benzothioxanthene coupled with sterically hindered amine were prepared by standard procedures of organic chemistry.

In fact they consist of photoactive unit exhibiting strong absorption and intense fluorescence and sterically hindered amine which acts as efficient light and thermal stabilizer for common synthetic polymers. One can expect that adduct of this type should exhibit higher photo-stability when doped in common polymer matrices. Therefore at first the spectral properties namely absorption and fluorescence spectra of the substrate under investigation have been taken in polymer matrices of PS, PMMA, PVC and PP.

The environmental (medium) effect on spectral properties of dissolved chromophores is well understood for low viscosity media [15,16]. Less attention was devoted to medium effect on spectral molecules of doped molecules in the polymer matrices [13,15] although polymer environment (support) is very important in many industrial applications in electronic industry as well as in emerging photonics and established industries as automotive or textile. There are two extreme assumptions for considering the effect of polymer matrix [17]:

1. The polymer matrix is inert even at room temperature so that it has no or negligible effect on spectral properties.
2. The polymer matrix influences the spectral properties in a similar way as a low viscosity solvent.

The polymer matrix as a medium differs from low molecular solvent in several respects. Even though the chemical structure of monomeric units is the same as that of low molecular solvent, the polymer matrix might exhibit different micro- and macro-viscosity, and micro- and macro-polarity. This difference is due to interconnectivity of monomer units. It means that the assembly of low molar mass molecules of solvent around solute (doped molecule) has different mobility compared to polymer as surrounding molecule. The main question is whether there is a substantial change in arrangement of surrounded (macro)-molecules during the lifetime the excited state at temperatures either below or above glass transition. The general answer does not exist until now and depends on the given pair doped chromophore–polymer matrix.

Absorption and fluorescence spectra of the parent compounds and adducts in PMMA are shown in Fig. 1 and adducts and model compounds in PS in Fig. 2. As these spectra and summarized data in Table 1 indicate, the longest wavelength absorption band around 450 nm in PP matrix and around 460 nm in all other polymer matrices used and exhibiting more or less distinct shoulder at 470–475 nm for all compounds under study in all matrices. The fluorescence of all compounds is in the range of 490–530 nm in PP matrix and in the range of 500 up to 550 nm in PMMA, PS and PVC. The fluorescence spectrum exhibits either two bands or one band with a sign of a small shoulder. These two bands in absorption and fluorescence spectra are best resolved in non-polar PP and PS as compared to more polar PMMA or PVC.

The Stokes shifts, which indicate changes in structure of the excited state as compared to the ground state, are in the range of 1200–2000 cm^{-1}. These data indicate some change (probably extension) of the benzothioxanthene chromophore in the excited state which is more distinct in polar matrices than in non-polar one. In fact, these data are not so large as compared with some linear structures where this quantity is up to 10 000 cm^{-1} [18].

The quantum yields of fluorescence of BTXA, BTXINH, BTXINOR and model BTXID based on anthracene and corrected to the

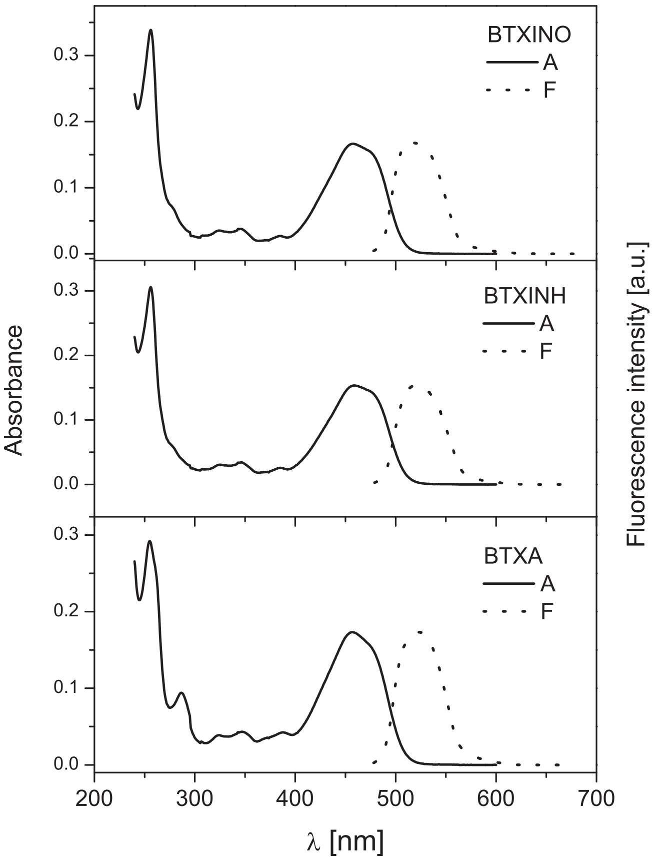


Fig. 1. Absorption and fluorescence spectra of BTXA and BTXINH and BTXINO dyes in PMMA film (thickness = 50 μm) at 0.002 mol kg^{-1} of dye.

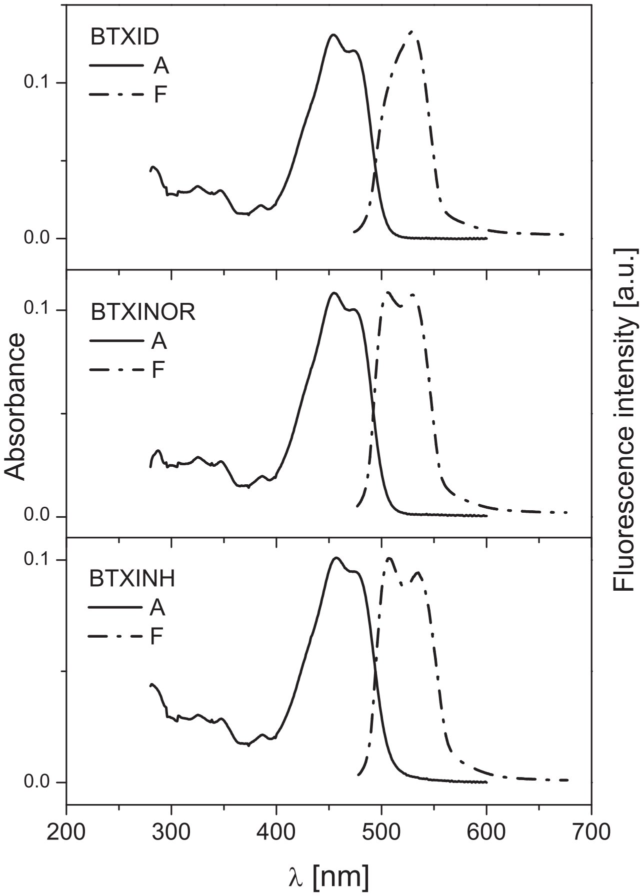


Fig. 2. Absorption and fluorescence spectra of BTXINH, BTXINO and model BTXID dyes in PS film (thickness = 50 μm) at 0.002 mol kg^{-1} of dye.

Table 1
Spectral properties of BTXA, BTXID and adducts BTXI and HAS in polymer matrices.

Dye/Matrix[a]	λ_{abs}[b] nm	log ε[c]	λ_{em}[d] nm	$\Delta\nu$[e] cm^{-1}	Φ[f]	τ[g] ns	Φ_{NR}/Φ_{NO}[h]
BTXA							
PS	452, 471sh	4.24	510sh, 534	1620	0.70	8.0	
PMMA	452, 474sh	4.05	510	1490	1.00	8.7	
PVC	465, 480sh	4.22	522	1640	0.70	8.6	
BTXINH							
PS	457, 473sh	4.00	508sh, 535	1460	0.13	7.7	4.3
PMMA	459, 474sh	4.18	512	1900	0.25	8.9	3.1
PVC	464, 478sh	4.21	523, 540sh	1800	0.52	8.4	8.6
PP	452, 469sh	3.95	494, 525	1370	0.39	6.3	1.4
BTXINO							
PS	457, 476sh	4.11	506, 531	1250	0.03	0.20 (82%) 4.71 (18%)	
PMMA	459, 475sh	4.22	519	1785	0.08	0.87 (3%) 6.60 (97%)	
PVC	452, 475sh	4.16	513sh, 531	1560	0.06	0.27 (77%) 4.14 (23%)	
PP	450, 468sh	3.99	494, 525	1333	0.28		
BTXINOR							
PS	455, 473sh	4.04	507, 530	1420	0.23	8.7	7.6
PMMA	455, 474sh	4.44	526	2080	0.13	8.3	1.6
PVC	461, 474sh	4.21	516sh, 531	1673	0.56	9.2	9.3
PP	450, 469sh	4.06	494, 525	1333	0.37	7.2	1.3
BTXID							
PS	455, 473	4.04	507, 530	1420	0.24	8.9	
PMMA	455, 474sh	4.44	526	2080	0.13	9.1	
PVC	461, 475sh	4.21	516sh, 531	1673	0.56	9.3	
PP	450, 469sh	4.12	492, 525	1333	0.40	7.6	

[a] Dye structures according to Scheme 1. Polymer matrix, PS-polystyrene, PMMA-poly(methyl methacrylate), PVC-poly(vinyl chloride), PP-isotactic polypropylene.
[b] Maximum of the longest wavelength absorption band with shoulder (sh).
[c] Log of extinction coefficient (expressed in L mol^{-1} cm^{-1}) at the maximum of the wavelength.
[d] Maximum of the emission band with shoulder (sh).
[e] Stokes shift.
[f] Quantum yield of emission based on anthracene in the given medium.
[g] Lifetime.
[h] Extent of intramolecular quenching expressed as ratio of Φ_{NR} of parent amine or alkyloxy derivative to Φ of *N*-oxyl.

Table 2
Rate of decomposition of BTXA and adducts BTXI with HAS in polymer matrices.

Dye[a]	Matrix[b]	$k \times 10^{-4}$[c] h^{-1}	r[d]
BTXA	PMMA	2.41	0.969
	PS	10.00	0.969
	PVC	9.39	0.996
BTXINH	PMMA	2.30	0.994
	PS	2.41	0.958
	PVC	2.22	0.986
	PP	60.5	0.978
BTXINO	PMMA	2.25	0.977
	PS	3.19	0.995
	PVC	3.80	0.964
	PP	52.5	0.988
BTXINOR	PMMA	1.60	0.974
	PS	6.80	0.852
	PVC	2.99	0.930
	PP	40.9	0.996
BTXID	PMMA	3.52	0.949
	PS	5.90	0.988
	PVC	5.95	0.995

[a] Dye structures according to Scheme 1.
[b] Polymer matrix PMMA-poly(methyl methacrylate), PS-polystyrene, PVC-poly(vinyl chloride), PP-isotactic polypropylene.
[c] Slope of dependence of log A/A_0 where A and A_0 are integrals under the absorption band at time t and zero, respectively.
[d] Correlation coefficient of the dependence of log I/I_0 on time.

respective medium lay in the range 0.03 up to 1.00 (Table 1). The highest value of quantum yield of fluorescence is observed for anhydride (BTXA) in PMMA. In PS and PVC matrices the value of Φ is slightly lower. The change of anhydride (BTXA) to substituted imides (BTXINR) brings decreasing of fluorescence intensity about 2–5 times. The lowest Φ of fluorescence for BTXNO is due to intramolecular quenching by NO (*N*-oxyl) structural motive, which is less efficient in non-polar medium as PP. The more or less rigid structure of BTX does not allow too big changes in the structure.

The lifetime of the parent (BTXA) and model compound (BTXID) as well as adducts BTXINH and BTXINOR lies in the range of 6–9 ns (Table 1). Decay curves can be mathematically fitted by mono-exponential function with standard deviation less than 5%. The decay BTXINO is more complex (usually it is fitted to bi-exponential) due to presence of paramagnetic free radical centre. The lifetime is shorter in all cases and the deviation of the fitting to mono-exponential course is larger than 5%.

3.2. Photolysis

The light stability of these dyes and model compounds were examined in thin polymer films (50 μm) in a merry go round set up

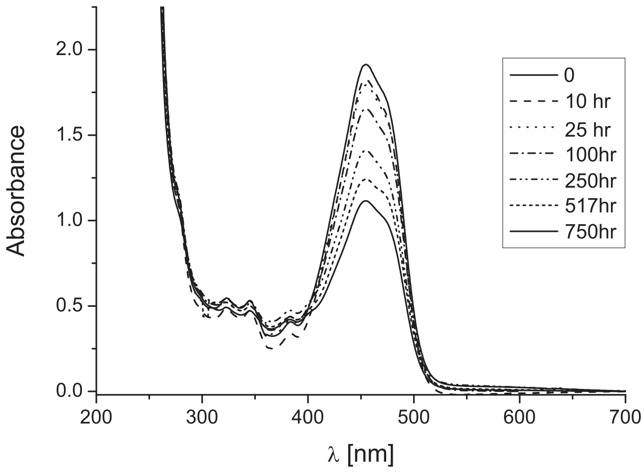


Fig. 3. Photolysis of BTXA in PMMA film (thickness = 50 μm) with concentration 0.02 mol kg^{-1} of dye monitored by UV spectroscopy.

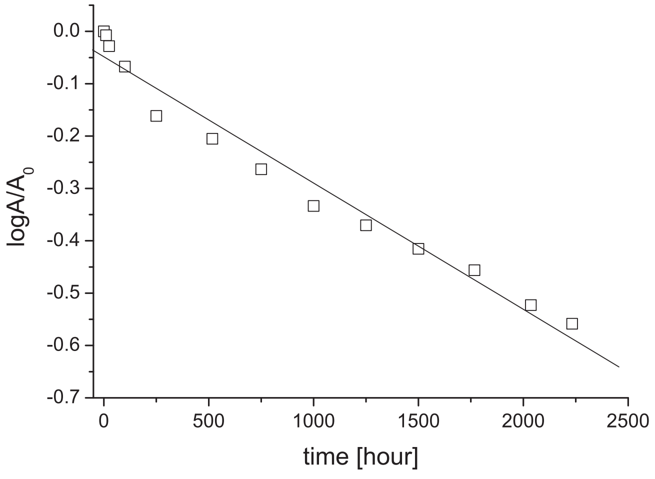


Fig. 4. Kinetics of photolysis of BTXA (c_0 = 0.02 mol kg^{-1}) in PMMA film (thickness = 50 μm).

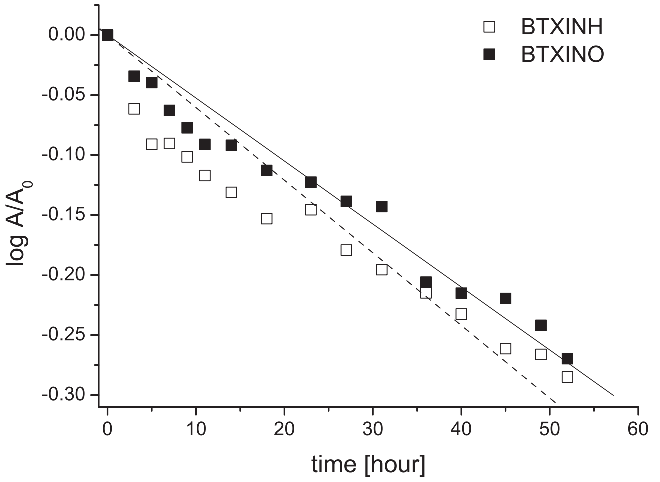


Fig. 5. Kinetics of photolysis of BTXINH and BTXINO ($c_0 = 0.002$ mol kg^{-1}) in PP films (thickness ~100 μm).

equipped with 250 W mercury arc with luminophore envelope. As shown in Fig. 3, the course of photolysis is easily monitored by UV absorption at the longest wavelength band around 450 nm. This type of monitoring is simple and easy and it is more suitable than fluorescence which is more sensitive to the conditions. The course of photolysis was evaluated according to the first order kinetics. The rate of photolysis was determined as the slope of the dependence of log A/A_0 on time. These dependences of log A/A_0 on t were reasonably linear as indicated by correlation coefficient (Table 2). The rate of photolysis rate was in the range 10^{-4}–6×10^{-3} h^{-1}. The rate of photolysis of parent dye BTXA was rather low in PMMA (Fig. 4) and higher in PS and PVC. The rate of decomposition of adducts in PMMA, PS and PVC was much lower than in PP matrix and was the lowest for parent amine BTXINH. In contrast, the rate constant in PP matrix was lowest for BTXINOR. The photolysis rate of all other dyes under study was higher. The distinct stabilization effect of HAS structural unit on the dye decomposition was not observed when compared the rate of photolysis of adducts with parent dye. It seems that the light stability of the dyes was more influenced by the polymer matrix and the effect of stabilization with HAS unit is overlapped by instability of the matrix. The slowest photolysis was observed in PMMA. Especially in PP, the rate of the photolysis of adducts was rather high and the photo-oxidation products of PP matrix strongly affect adduct photolysis even when HAS structures are covalently linked to chromophore (Fig. 5). The rate constants of photolysis of all adduct are about one order higher than in other polymer matrices.

4. Conclusions

Novel adducts of the dye of benzothioxanthene type (chromophore) linked with HAS units were prepared and their spectral properties were examined. The spectral properties of adducts are determined by the benzothioxanthene chromophore and their photo-stability is decisively influenced by the polymer environment. The photolysis data indicate that the linking of the chromophore with HAS does not improve the overall stability of the system to substantial degree. The overall photo-stability of the system is determined by the type of polymer and the non-polar PP seems to the most photolysis prone medium.

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