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Profluorescent nitroxide sensors for monitoring photo-induced degradation in polymer films

Vanessa C. Lussini,^{a,b} John M. Colwell,^{a,b} Kathryn E. Fairfull-Smith^a and Steven E. Bottle*^[a,b]

^aARC Centre of Excellence for Free Radical Chemistry and Biotechnology. School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology (QUT), GPO Box 2434, Brisbane, QLD 4001, Australia

^bDefence Materials Technology Centre, School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology (QUT), GPO Box 2434, Brisbane, QLD 4001, Australia

E-mail: s.bottle@qut.edu.au

Abstract

A range of profluorescent nitroxides (PFNs) were tested as probes to monitor photo-induced radical-mediated damage in polymer materials. The most stable and sensitive probe of the PFNs tested was an alkyne-linked perylenediimide PFN, **6b**, with naphthalimide and 9,10-bis(phenylethynyl)anthranene-based versions giving lower stability and sensitivity. Results from photo-ageing of poly(1-trimethylsilyl)-1-propyne (PTMSP) and the ethylene norbornene copolymer (TOPAS®) films doped with PFN probes demonstrated that sensors employing these support materials deliver significantly enhanced sensitivity compared to traditional techniques used to monitor photo-oxidative degradation of polymers, such as infrared spectroscopy. This enhanced sensitivity for detecting polymer damage improved methods for the determination of the serviceable application lifetime of polymers.

Key words

Profluorescent nitroxide, TOPAS, PTMSP, Fluorescence, Degradation

1. Introduction

The application lifetimes of polymer materials are strongly influenced by the environmental factors to which they are exposed. For many materials, oxidation is a key influence on service lifetimes, with this degradation process being controlled by temperature, oxygen concentration and other local factors such as reactive contaminants that may affect oxidation rates. Laboratory-based studies can be used to assess environmental effects on polymer degradation. However, it is often difficult to translate the data generated in the laboratory to methods for actual service lifetime prediction. This is, in part, due to the broad range of differing environments to which polymer materials may be exposed. By combining laboratory-generated ageing data and a number of field sensors (e.g., temperature, oxygen, chemical), in-service lifetime predictions may be possible. However, to implement effective systems with sufficient sensors would be costly and require significant analytical effort. As an alternative to a suite of sensors, we have developed a simple, sensitive, profluorescent additive that can be used as an oxidative environment sensor. The validity of this approach has been successfully demonstrated [1, 2], however photo-stability and the phase distribution of the probe are factors that control sensor performance. To address some of these issues we have synthesised components with higher photo-stability [3].

The sensor approach described herein is based on the use of profluorescent nitroxides (PFNs) as free-radical probes. PFNs combine a paramagnetic nitroxide covalently linked to a fluorophore where the nitroxide acts to quench the fluorescence of the fluorophore. When the nitroxide radical is removed via radical-radical coupling, the fluorescence is restored (Figure 1) [4, 5]. Radical-radical coupling of nitroxides with transient carbon-centred radicals that are key intermediates in autooxidation reactions allows PFNs to act as integrating sensors for the degradation process through the

formation of stable alkoxyamine adducts that build up over time [6, 7]. PFNs can also show high fluorescence suppression (over 300-fold [8]), which can deliver higher sensitivity for detecting free-radical polymer degradation than many other common degradation monitoring techniques [9].

By combining the sensitivity of PFNs with an oxidisable substrate, oxidative environment sensors may be produced. Such sensors can be used to assess environmental conditions that affect polymer degradation, and therefore give early warning of the failure of the material. Previously described PFN-based sensors for oxidative environment monitoring [1, 2] used an ethylene norbornene copolymer (TOPAS®) as a relatively inert carrier and polyisoprene (PIP) as the oxidisable substrate. It was found that the phase structure of this ternary system limited the sensor response at temperatures below the glass transition of the inert carrier and, therefore, further development of these materials as sensors was required.

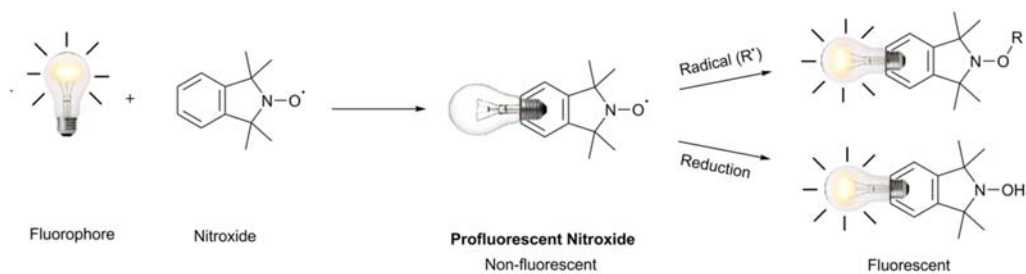


Figure 1: Tethering of a fluorophore to a nitroxide to form a PFN probe

Although the PFN-based sensors described above performed well under thermal ageing conditions, they were found to be less useful for monitoring photo-oxidative degradation due to the limited photo-stability of the 9,10-bis(phenylethynyl)anthracene-based PFN [10]. More robust PFNs, based on naphthalimide and perylenediimide fluorophores

(Figure 3), were therefore developed with these fluorophores providing considerably enhanced photo-oxidative stability [11].

Recently, a perylenediimide-based isoindoline profluorescent nitroxide was used to monitor the degradation of melamine-formaldehyde crosslinked polyesters under accelerated weathering conditions [12]. This PFN probe was used to assess the impact of both temperature and UV radiation on the degradation of two commercial polyesters. The focus of this study, however, was limited to a single PFN. In the work described herein, we have assessed the resistance of a new range of perylenediimide and naphthalimide PFNs in two commercially-available polymers: poly(1-trimethylsilyl)-1-propyne (PTMSP), and the ethylene norbornene copolymer, TOPAS® (8007x10 grade). These polymers can be used to produce easily handled films via solvent casting, which readily allows incorporation of the PFNs under mild conditions. The structures of the polymers studied (Figure 2), allows them to act as model substrates for a range of other polymer materials such as polyethylene (TOPAS® as a model) and unsaturated polymers such as polyisoprene (PTMSP as a model).

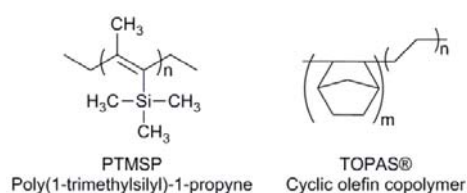


Figure 2: The structures of the polymers used in this study, PTMSP and TOPAS®

Both PTMSP [13-15] and TOPAS® [16] degrade when exposed to heat or UV light in air through radical-mediated mechanisms and therefore, in combination with PFNs, they can be used as sensitive oxidative environment sensors. Here, we describe the use of perylenediimide and naphthalimide PFNs in PTMSP and TOPAS® matrices as photo-

oxidative environment sensors and highlight the most effective PFN based on the photo-oxidative stability of these novel systems in the polymer studied.

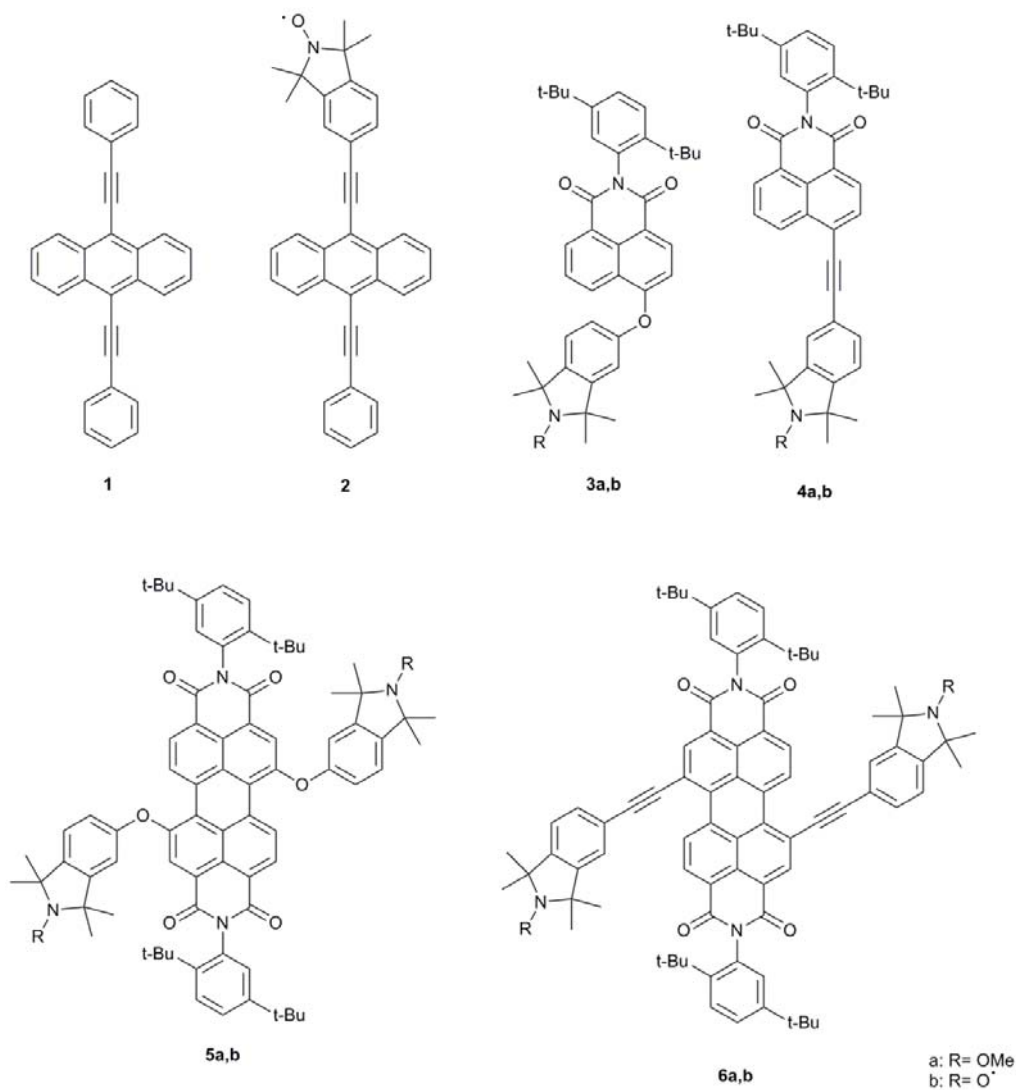


Figure 3: Nitroxides used in this study and their non-radical (fluorescent) methoxyamine derivatives

2. Experimental

2.1. Materials

TOPAS® 8007x10 was a gift from Ciba Speciality Chemicals. PTMSP was purchased from ABCR GmbH. Cyclohexane was purified using a literature procedure[17] where it was washed with concentrated sulphuric acid until the wash was colourless. The

organic layer was then washed with water, aq. Na₂CO₃ and again with water until the wash solution was at a neutral pH. The washed cyclohexane was then distilled over calcium hydride. PFNs **2**, **3b**, **4b**, **5b**, and **6b** along with the methoxyamine, non-radical analogues, **3a**, **4a**, **5a** and **6a** were synthesised as described previously [3, 8]. All other materials and reagents were of analytical reagent grade purity, or higher and were purchased from Sigma Aldrich, Australia.

2.2.PTMSP sample preparation

Each of the compounds shown in Figure 3 (1.94×10^{-7} mol) was dissolved in freshly distilled cyclohexane (7.45 mL) in a 25x75 mm soda glass vial. PTMSP (293 mg) was then added to each solution and the vials sealed and stirred for 48 hours in the dark. Each solution was then poured into a Petri dish and the solvent allowed to evaporate slowly over two days in the dark. Once the films were dry to the touch, they were placed under vacuum until they reached a constant weight (24 h).

2.3.TOPAS® sample preparation

Each of the compounds shown in Figure 3 (4.36×10^{-7} mol) was dissolved in freshly distilled cyclohexane (16.94 mL) in a 25x75 mm soda glass vial. TOPAS® pellets (660 mg) were then added to each solution and the vials sealed and stirred for 4 hours in the dark. Each solution was then poured into a Petri dish and the solvent allowed to evaporate slowly over two days in the dark. Once the films were dry to the touch, they were placed under vacuum until they reached a constant weight (24 h).

2.4.Photo-oxidation of films

Film samples were irradiated in an Heraeus Suntest CPS+ device delivering 250 W/m². The temperature in the chamber was set to 40°C. The films were oriented in parallel to

the lamp. Samples were removed periodically and analysed using UV-Vis, Fluorescence and FTIR-ATR spectroscopy.

2.5. Thermo-oxidation of films

Films were placed in an oven at 70°C on metal racks, and separated by a 5 mm gap.

2.6. Characterisation

2.6.1. FTIR-ATR Spectroscopy

Infrared spectra were recorded as neat samples using a Nicolet 5700 Nexus Fourier Transform infrared spectrometer equipped with a DTGS TEC detector and a Smart Endurance single reflection ATR accessory equipped with a composite diamond IRE with a 0.75 mm² sampling surface and a ZnSe focussing element (Nicolet Instrument Corp., Madison, WI). An Optical Path Difference (OPD) velocity of 0.6329 cm s⁻¹ and a gain of 8 were used. Spectra were collected over the range 4000-525 cm⁻¹ using 32 scans at 4 cm⁻¹ resolution. Oxidation indices were calculated by taking the ratio of the maximum peak height in the carbonyl stretching region (1700-1715 cm⁻¹) to the area under the C-H deformation band (1400-1500 cm⁻¹).

2.6.2. UV-Vis Spectroscopy

UV-Vis spectra were recorded on a Varian Cary 50 UV-Vis spectrophotometer. Spectra were collected from 200-700 nm at a scan rate of 600 nm min⁻¹. All spectra were corrected to give an absorbance of zero at 700 nm.

2.6.3. Fluorescence Spectroscopy

Fluorescence spectroscopy was undertaken using a Varian Cary Eclipse fluorescence spectrophotometer. Samples were loaded into a custom-made holding device and excited at an angle of 45° to the surface, with the emission recorded from the back face of the sample in order to minimise scattering effects. The excitation wavelength used

changed according to the compound present in the sample: **1**; 383 nm, **2**; 383 nm, **3a**; 362 nm, **3b**; 360 nm, **4a**; 378 nm, **4b**; 374 nm, **5a**; 540 nm, **5b**; 536 nm, **6a**; 568 nm, **6b**; 564 nm. Spectra were collected from 5 nm past the excitation wavelength up to 700 nm at a scan rate of 600 nm min⁻¹.

3. Results and Discussion

3.1 Film Preparation

PTMSP and TOPAS® films were prepared by solvent casting, which allowed the PFNs to be evenly dispersed into the films at well-defined concentrations, without the need for heating. Previous studies using PFNs and polymer systems have typically relied on solution swelling of PFNs or melt processing, each of which lead to limitations in precisely controlling the concentration of dopant. For melt processing, thermal reactions at high temperature can consume some of the nitroxide before degradation monitoring can be undertaken [10, 18]. The mass of the PFN added to the films (0.025 wt%) was kept low to reduce aggregation of the PFNs within the film. There was no evidence of any bathochromic shifts in the bands or any obvious fluorescence quenching that might arise from aggregation, shown in Figure 4 [12, 19-21].

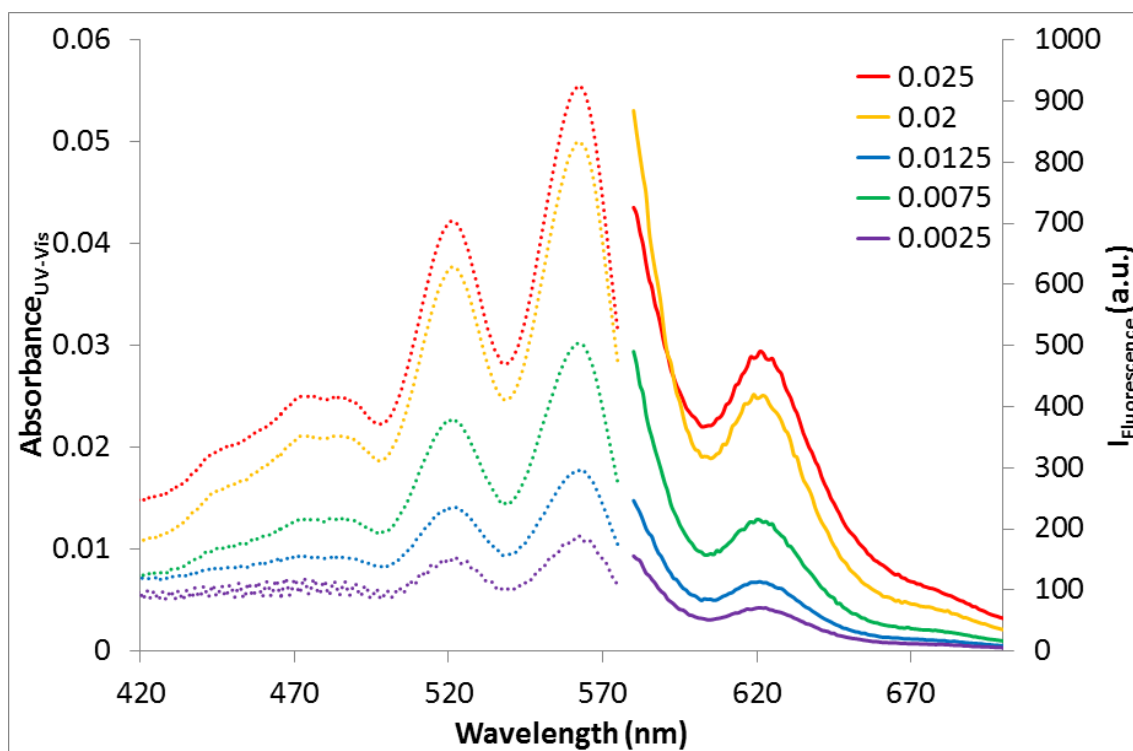


Figure 4: UV-Vis absorbance (dotted lines) and fluorescence emission (solid lines) spectra of perylene fluorophore 6a in TOPAS® at various concentrations ranging from 0.025 to 0.0025 w%, showing no evidence of any bathochromic shifts in the bands or any obvious fluorescence quenching that might arise from aggregation.

3.2 PTSMF films

3.2.1 Photo-oxidative degradation

PTMSP has the highest gas permeability of all known synthetic polymers [15, 22, 23] due to it being a loosely packed polymer with 20-34% free volume [22]. As a result, oxygen permeability is not limited through this glassy material and PTMSP is therefore a good model for situations where diffusion-limited oxidation is not dominant.

PTMSP films were aged in an Heraeus Suntest xenon-arc solar simulator delivering an irradiance of 250 W/m² (21.6 MJ/m²/d), which corresponds to the approximate average daily terrestrial irradiance received during the 2014-2015 summer in Brisbane, Australia (21.4 MJ/m²/d)[24]. Films were periodically monitored by fluorescence, UV-Vis and FTIR-ATR spectroscopy. The films doped with PFNs were compared to films doped with the structurally-related non-radical methoxyamine analogues. Analysis in this way

provides insight into the rate of fluorescence switch-on from the PFN as compared to the degradation rate of the parent fluorophore, as shown by the decrease in fluorescence emission intensity for the non-radical adducts (**1**, **3a-6a**) during ageing of the PTMSP-doped films.

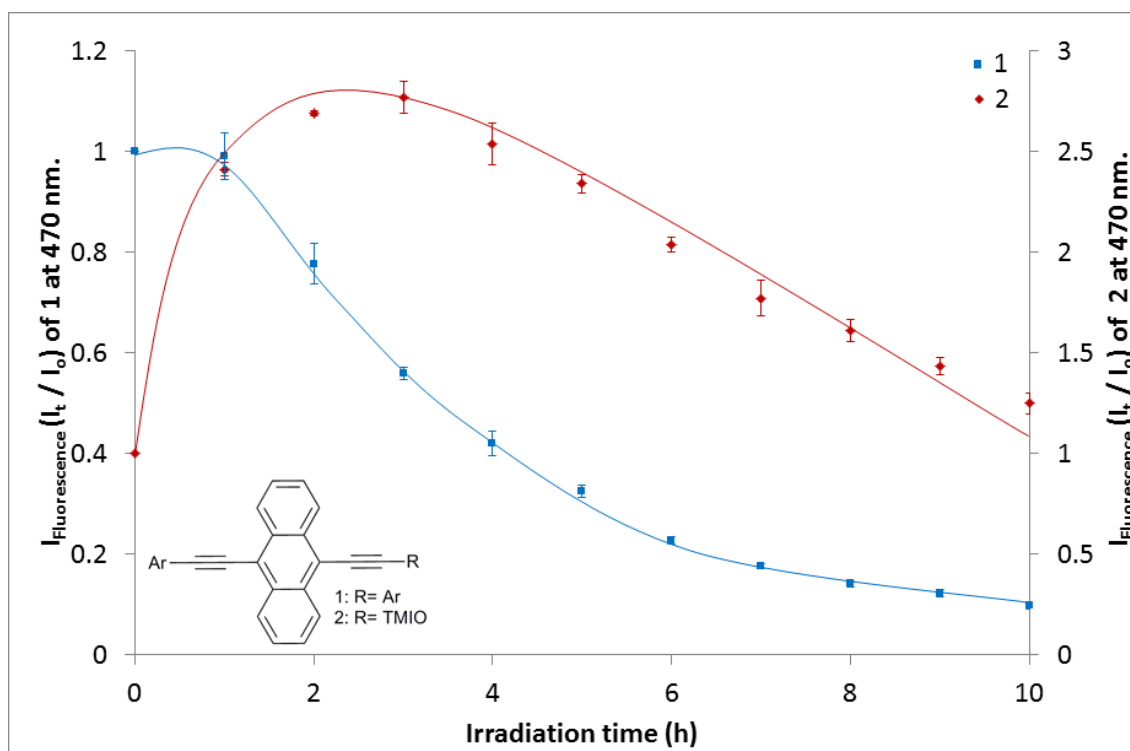


Figure 5: Change in fluorescence emission of PTMSP films doped either with BPEA, **1** (■/left axis) or the nitroxide analogue, **2** (◆/right axis) with respect to UV ageing time (hours).

The non-radical fluorophore 9,10-bis(phenylethynyl)anthracene, BPEA (**1**), shown in Figure 5, started to degrade within two hours of UV exposure and its fluorescence emission had decreased to 50% after 4 hours. BPEA **1** is known for its thermal stability and its PFN analogue **2** has been used successfully for detecting alkyl radicals with a high trapping ability [1]. However, it is also known to have limited photostability due to the reactivity of its anthracene core [25, 26]. Despite the rapid photobleaching of the fluorophore, the BPEA-based nitroxide (**2**) still showed a fluorescence emission increase of ~2.5 fold after ~1 hour of irradiation. It is likely that

degradation of the fluorophore and photobleaching occurs predominantly after the conversion of most of the nitroxide free radicals, which act as stabilising antioxidants. However the degradation of the fluorophore, (as shown in Figure 5 by the loss of fluorescence emission from the BPEA parent compound, **1** after 3 hours) is at least as large as the fluorescence increase generated by the PFN **2**. Therefore, this PFN has limited value as a sensor for photo-oxidative damage.

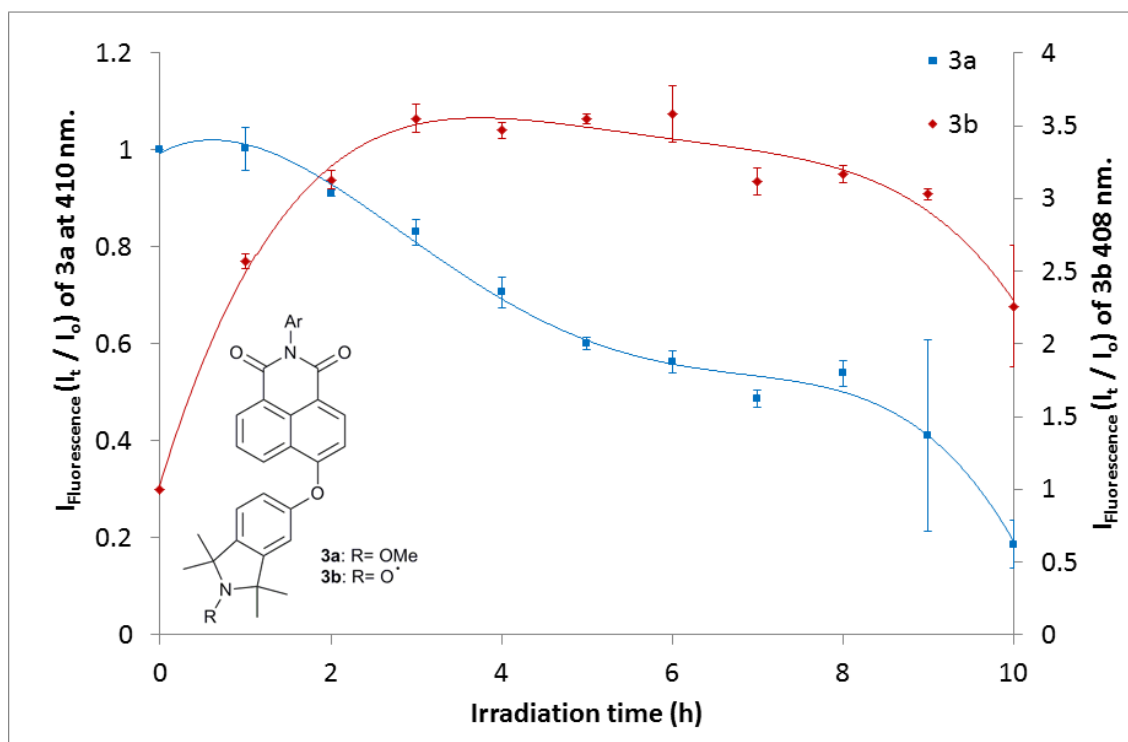


Figure 6: Change in fluorescence emission of PTMSP films doped either with ether-linked naphthalimide fluorophore **3a** (■/left axis) or the nitroxides analogue **3b** (◆/right axis) with respect to UV ageing time (hours).

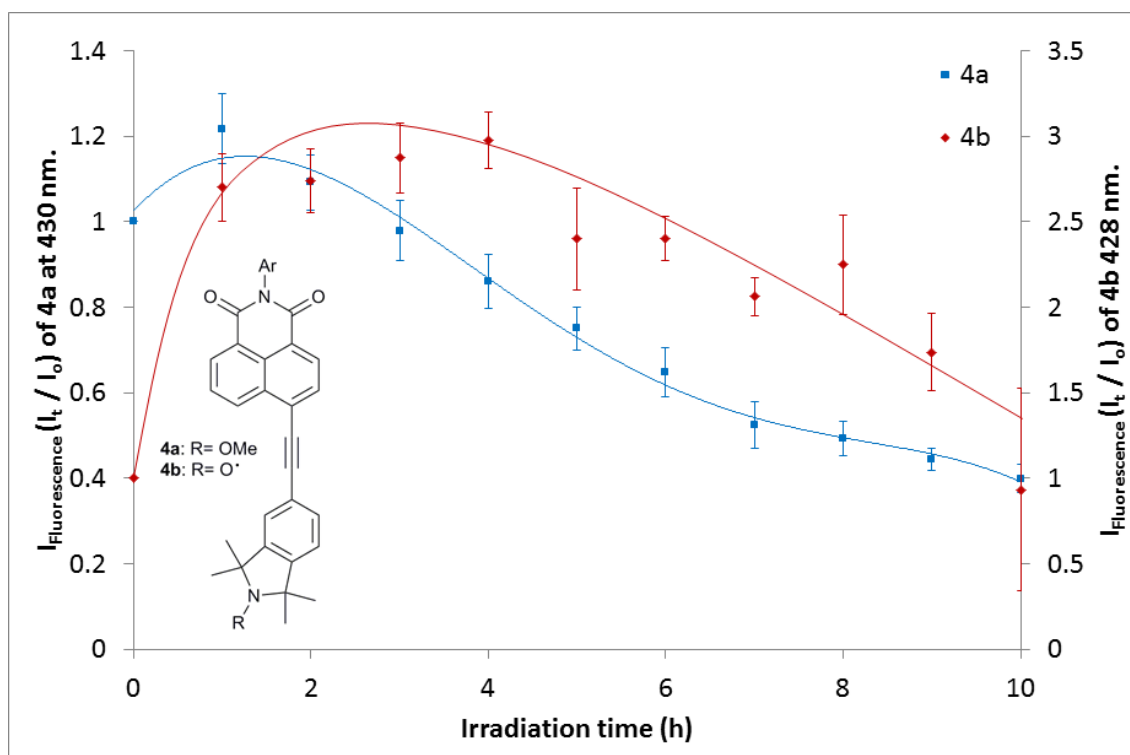


Figure 7: Change in fluorescence emission of PTMSP films doped either with alkyne-linked naphthalimide fluorophore **4a** (■-/left axis) or the nitroxides analogue **4b** (◆-/right axis) with respect to ageing time (hours).

Both naphthalimide-based compounds (ether-linked, **3** (Figure 6) and alkyne-linked, **4** (Figure 7)) showed comparable changes in fluorescence emission during ageing. The non-radical analogues began to show photobleaching after 3 hours and their fluorescence emission had decreased by a factor of two after 7-8 hours of irradiation. This indicated that these structures were more photo-stable than the anthracene-based fluorophores; **1** and **2**. Both naphthalimide nitroxides showed significant fluorescence switch-on under irradiation, with the ether-linked compound **3b** reaching ~3-4-fold levels of increased fluorescence emission and the alkyne-linked compound **4b** peaking at a 3-fold increase in fluorescence emission. However, degradation of the fluorophore (the rate of which is demonstrated by the photobleaching of the methoxy amine) resulted in a 50% decrease in fluorescence emission intensity after 7 hours of

irradiation, indicating that photo-degradation remains a significant factor in determining the probe response.

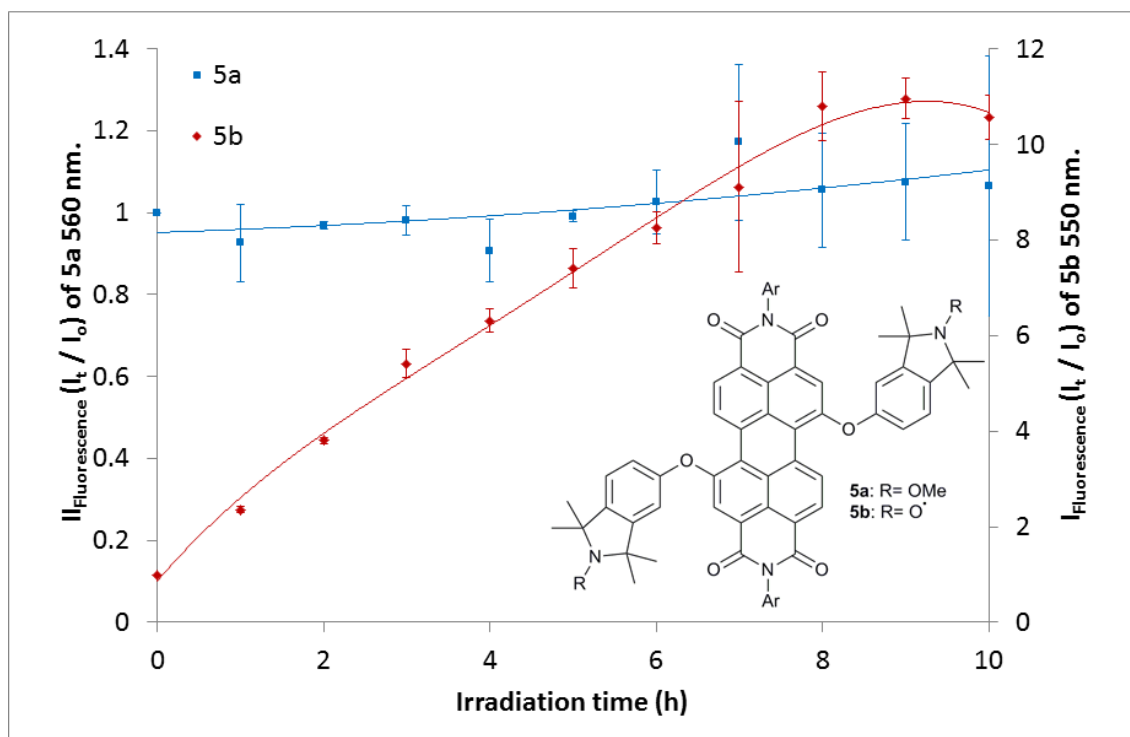


Figure 8: Change in fluorescence emission of the PTMSP films doped with either ether-linked perylenediimide fluorophore 5a (-■-/left axis) or the nitroxides analogue 5b (-♦-/right axis) with respect to ageing time (hours).

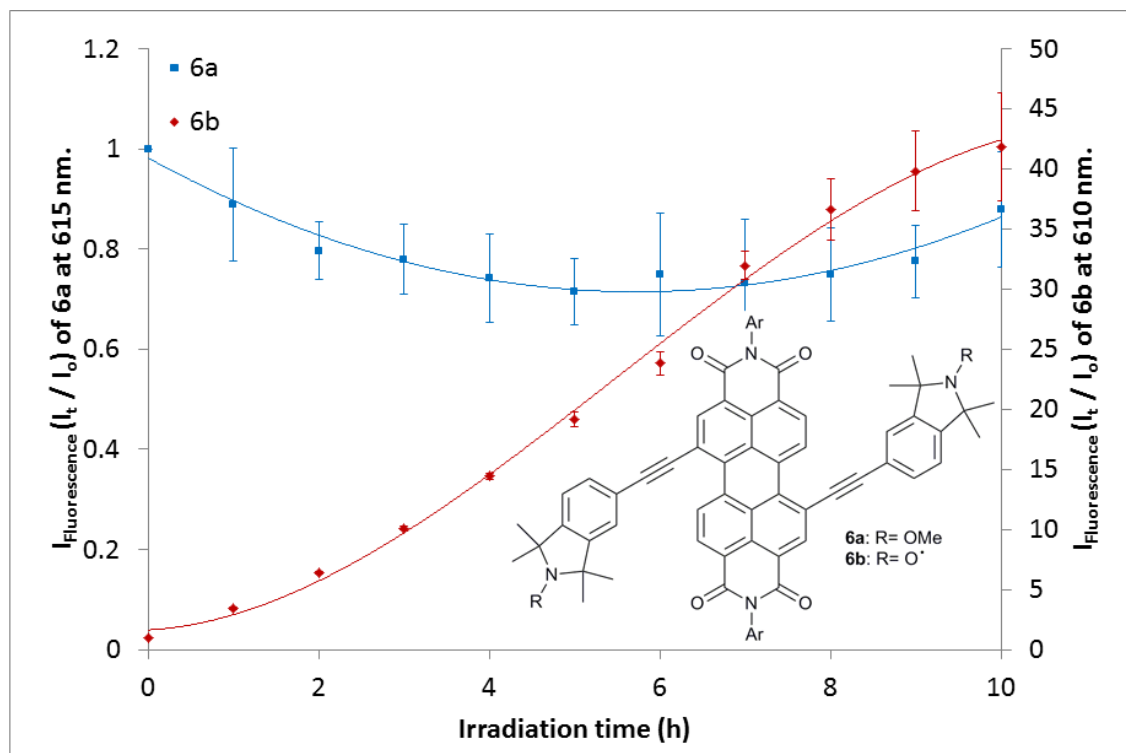


Figure 9: Change in fluorescence emission of the PTMSP films doped with either alkyne-linked perylenediimide fluorophore 6a (-■-/left axis) or the nitroxides analogue 6b (-♦-/right axis) with respect to ageing time (hours).

The perylenediimide-based compounds on the other hand, both the ether-linked, **5** (Figure 8) and the alkyne-linked, **6** (Figure 9) showed superior photo-oxidative stability. Both of the non-radical analogues showed a lower rate of photobleaching than the other chromophores studied and both of the nitroxides continued to display increasing fluorescence emission during the ageing studies.

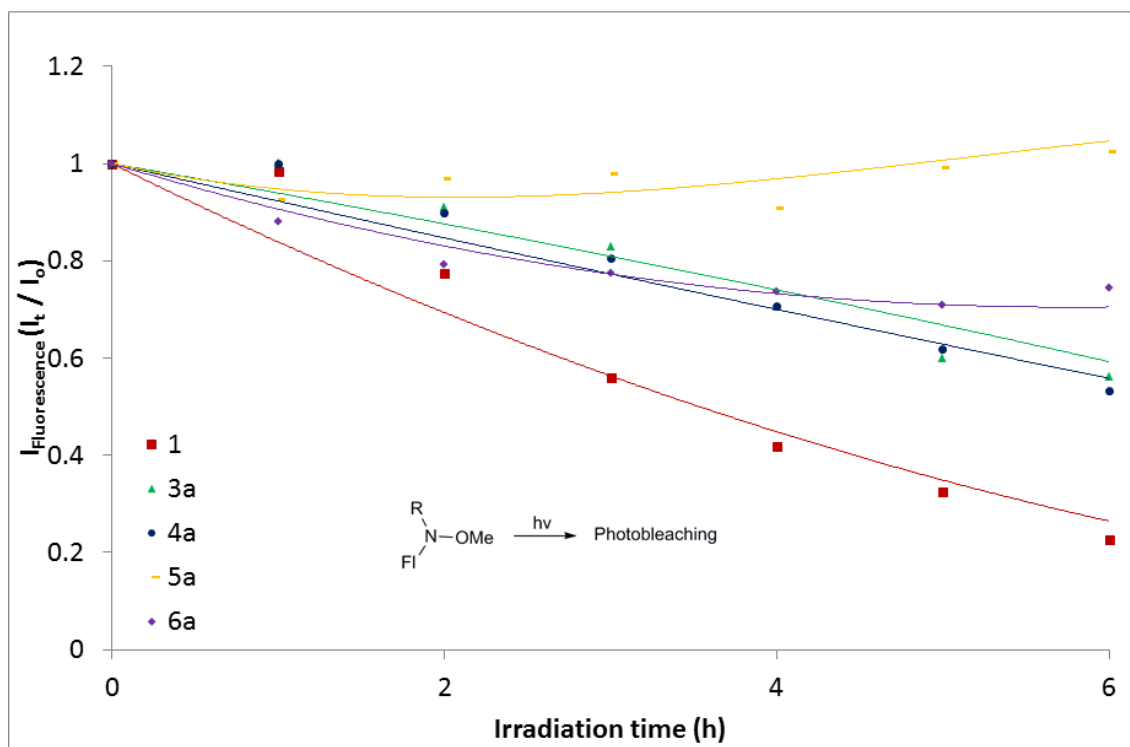


Figure 10: Changes in the fluorescence emission of PTMSP films doped with non-radical analogues, 1 (-■-, $\lambda_{\text{max}} = 470$ nm), 3a (-▲-, $\lambda_{\text{max}} = 410$ nm), 4a (-●-, $\lambda_{\text{max}} = 430$ nm), 5a (-■-, $\lambda_{\text{max}} = 560$ nm) and 6a (-◆-, $\lambda_{\text{max}} = 615$ nm) following photo-irradiation at 250 Wm^{-2} and 40°C for up to 6 h. Note: data collection was stopped at 6 hours as discolouration gave higher intensities than I_0 .

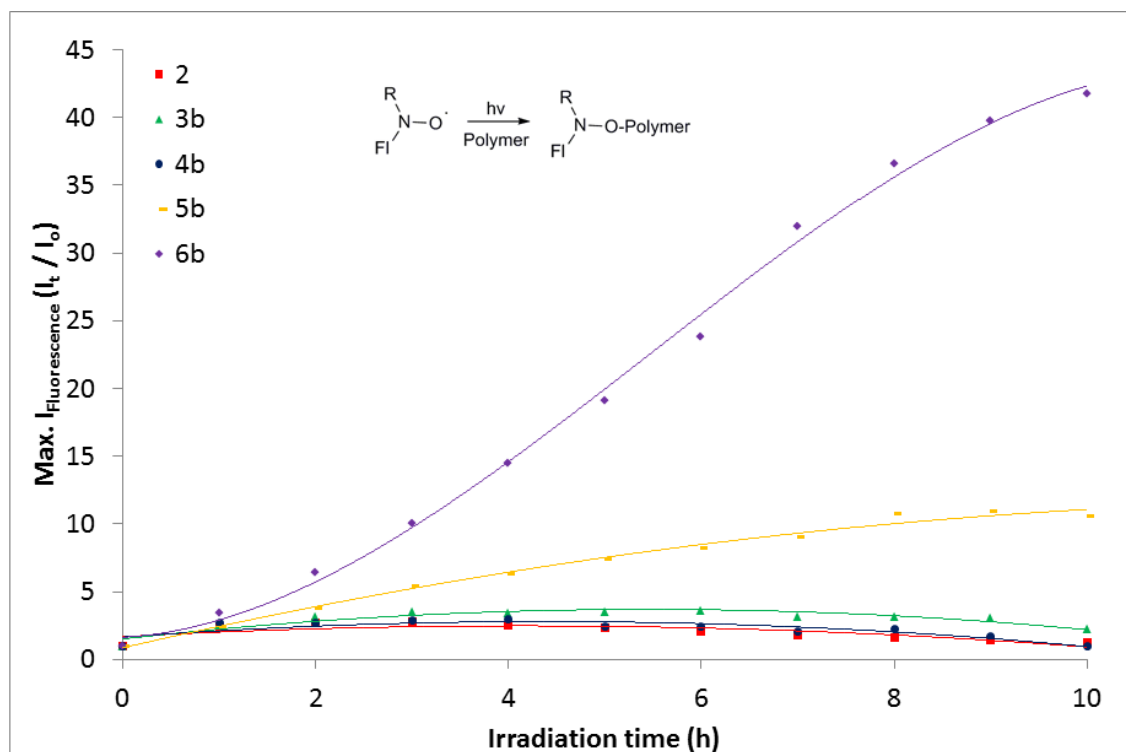


Figure 11: Changes the fluorescence emission of PTMSP films doped with the nitroxides, BPEANO 2 (-■-, $\lambda_{\text{max}} = 470$ nm), 3b (-▲-, $\lambda_{\text{max}} = 408$ nm), 4b (-●-, $\lambda_{\text{max}} = 428$ nm), 5b (-—, $\lambda_{\text{max}} = 550$ nm) and 6b (-◆-, $\lambda_{\text{max}} = 610$ nm) following photo-irradiation at 250 Wm^{-2} and 40°C for up to 10 h.

When comparing the non-radical analogues (**1**, **3a-6a**), Figure 10, there is a clear distinction between the photo-oxidative stability of the fluorophores. Perylenediimides were the most stable compounds, showing no decrease in fluorescence emission over 10 hours of ageing. Their PFN analogues showed continuing increases in fluorescence emission intensity with increasing irradiation time. However, the alkyne-linked PFN **6b** displayed the highest fluorescence emission increase (40-fold) compared to the ether-linked PFN **5b** (10-fold), as shown in Figure 11.

It has previously been demonstrated that both nitroxide radical need to be removed before complete fluorescence switch-on is apparent for PFNs comprising 2 nitroxide moieties [3]. This results in a different rate of fluorescence switch-on between difunctional perylenediimide-based PFNs and the monofunctional naphthalimide-based PFNs. However, this is not always apparent with the competing nature of photobleaching of the fluorophore. Fluorescence data for the aged PTMSP-doped films are summarised in Table 1.

Table 1: Summary of PFN fluorescence changes in PTMSP films doped with PFNs or their non-radical analogues during ageing.

	Time to reach maximum fluorescence emission (h)	Relative fluorescence increase from time zero	Non-radical analogue stability (h) ^[a]	Relative fluorescence achieved (%) ^[b]
2	3	2.7	3.5	49
3b	5	3.5	7	73
4b	4	3.0	7	23
5b	>10	11 (10 h)	>10	32

6b	>10	42 (10 h)	>10	49
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^[a] time at which the non-radical analogue was reduced to 50% fluorescence intensity compared to an unaged sample.

^[b] Fluorescence increase achieved relative to the maximum fluorescence emission from the corresponding non-radical analogue.

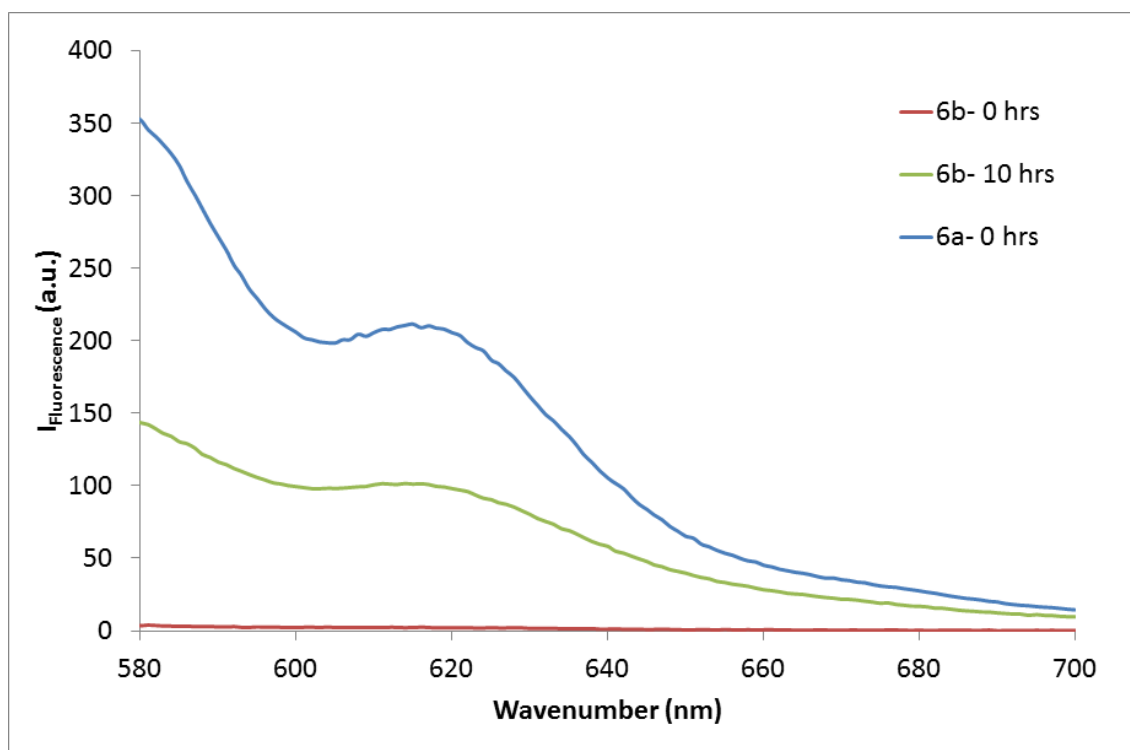


Figure 12: Change of the fluorescence emission for the PFN 6b in PTMSP from 0-10 h ageing compared to its non-radical analogue, 6a at time zero in PTMSP, showing that the PFN 6b has not achieved complete switch-on after 10 h ageing.

The pure PTMSP films degraded rapidly under the photo-oxidation conditions delivered by the Heraeus Suntest CPS+ to the point of becoming too brittle to handle after 10 hours of irradiation. PTMSP is known to degrade through a chain scission mechanism to form low molecular weight products that contain carbonyl and hydroxy groups [15, 27]. Infrared spectroscopy can be used to follow the degradation process. Here, FTIR-ATR was used and it was found that variations in the contact of the degrading films with

the ATR internal reflection element surface showed a large variation across each of the samples (even after normalisation of the data referenced to the total peak area from 1600-650 cm^{-1}). Although FTIR-ATR analysis was unable to provide a reproducible measure of the levels of oxidation of the samples, it did confirm oxidative degradation was occurring. Along with FTIR-ATR data, evidence of oxidation was provided through noticeable yellowing and enhanced film brittleness after 6 hours irradiation. The films became too brittle to handle after 10 hours of irradiation, independent of the additive present in the samples, with all films breaking apart under the pressure from the anvil used in measuring the FTIR-ATR spectra.

3.2.2 *Thermal Degradation*

PTMSP films that did not contain a stabilising nitroxide radical, but retained the fluorescent unit (**1**, **3a-6a**) were thermally aged in the dark in an oven at 70°C. This was done to ensure that the fluorophores were not affected by the temperatures experienced during testing in the solar simulator. Thermally-aged films showed no visible degradation, such as brittleness or loss in fluorescence emission (Figure 13), which indicates that the fluorophores and the polymer used in this study are thermally stable under the conditions used.

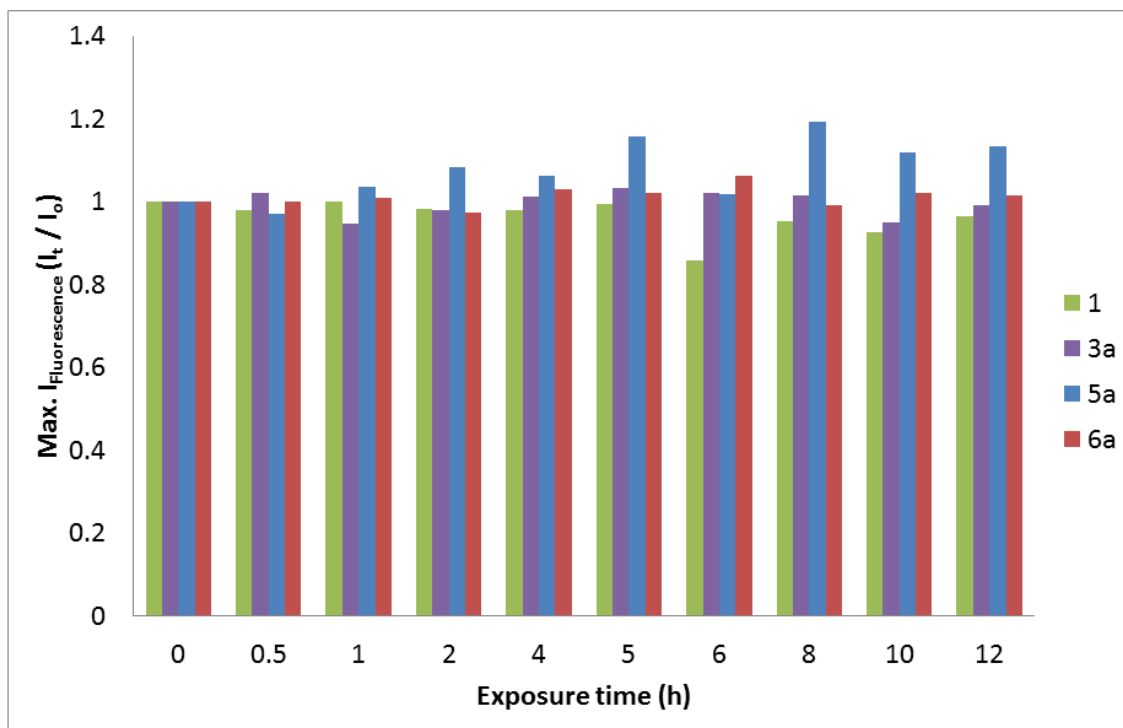


Figure 13: Change in fluorescence emission from PTMSP films doped with PFN non-radical analogues (1, 3a, 5a and 6a) over time at 70°C in the dark.

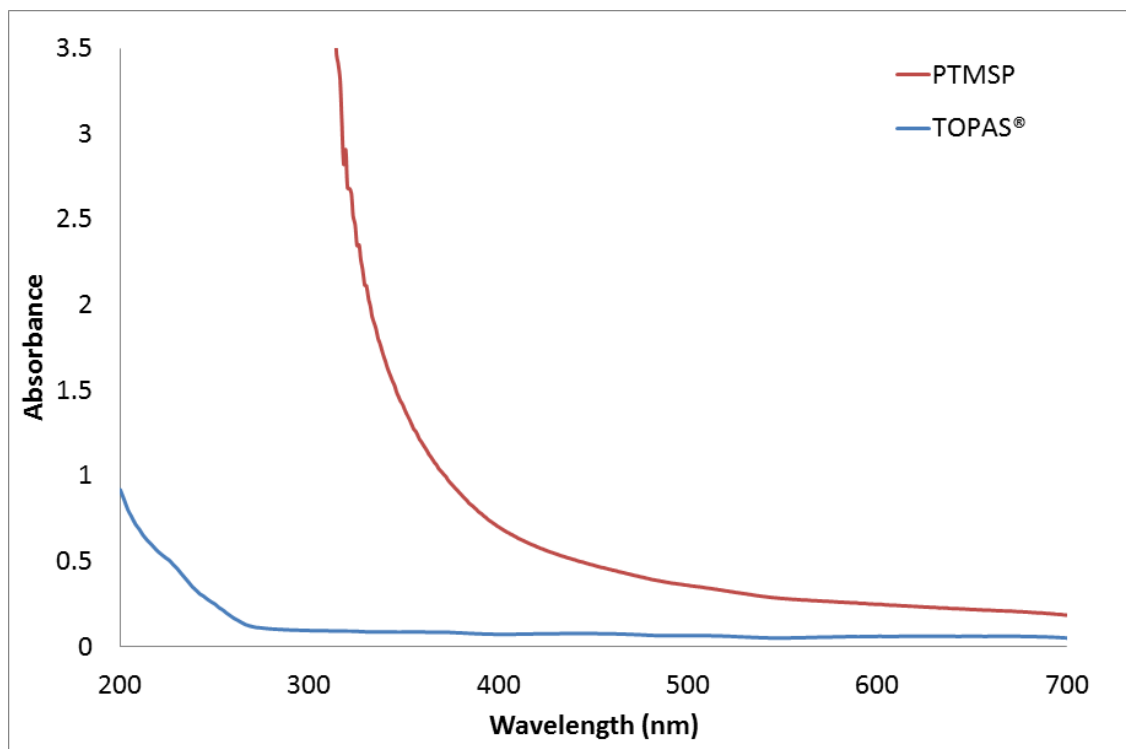


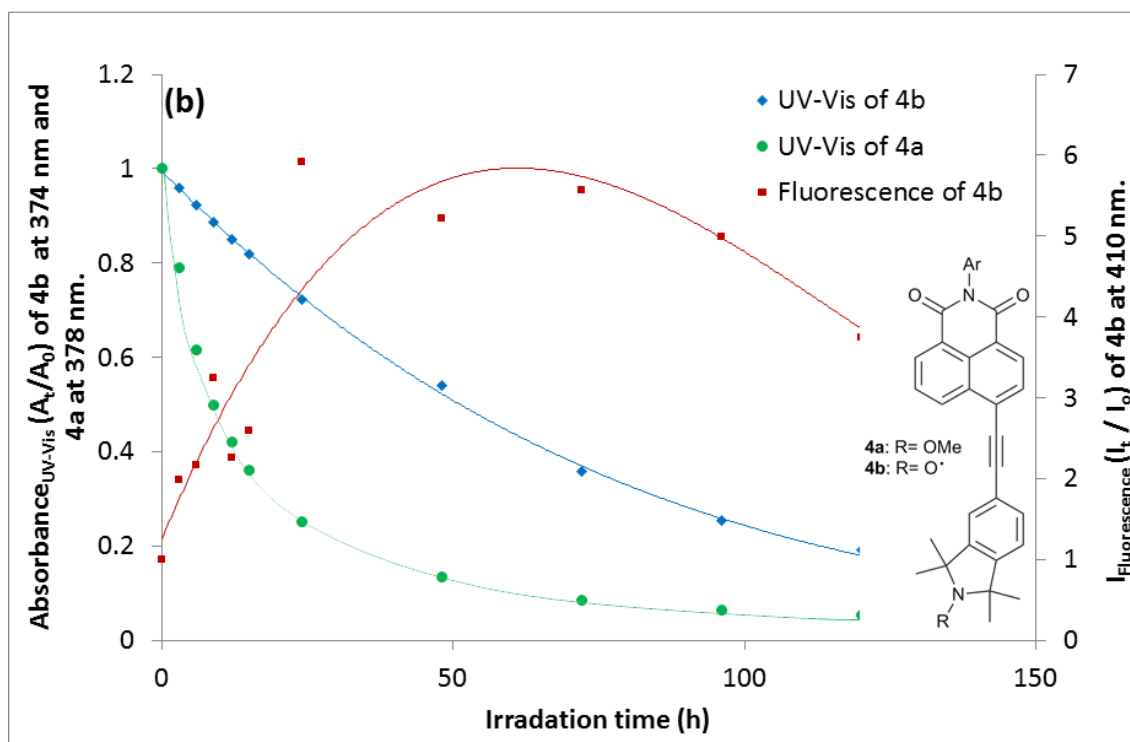
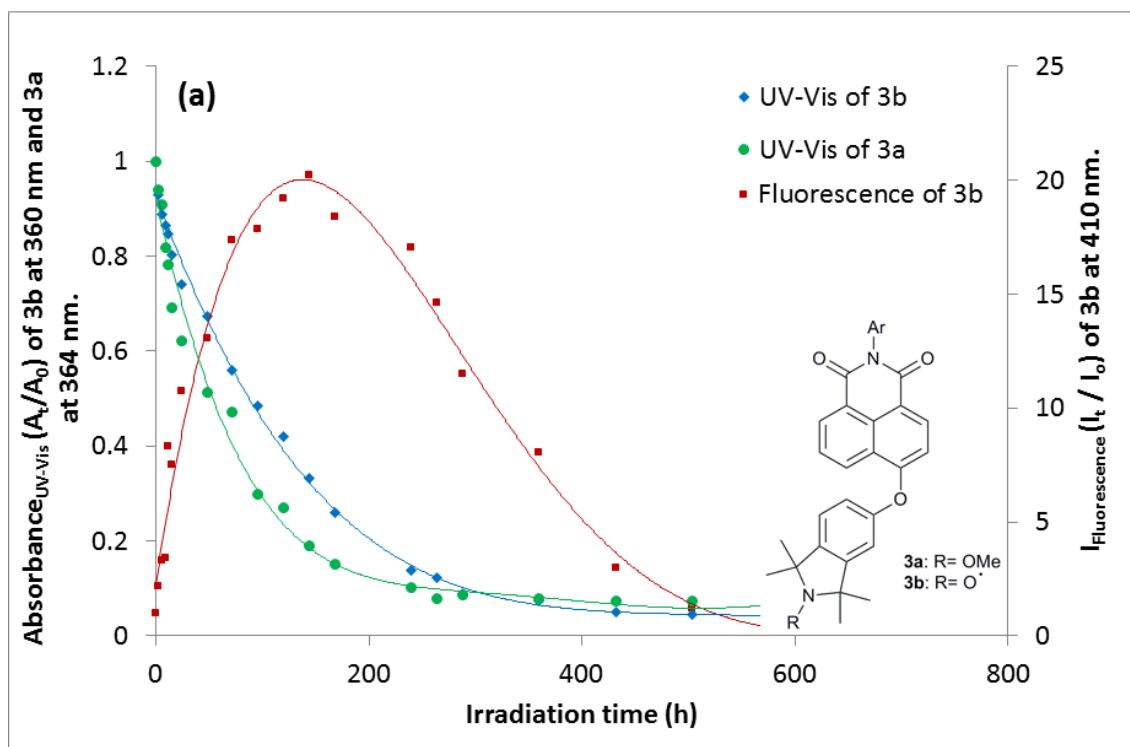
Figure 14: UV-Vis spectra from undoped (blank) PTMSP (-) and TOPAS® (-) films.

3.3 TOPAS® Films

3.3.1 TOPAS® Photo-oxidative degradation

TOPAS® is within the family of cyclic olefin copolymers [16]. It has high transparency, high chemical resistance, low density, high thermal stability, low shrinkage, low moisture absorption, and low birefringence [28, 29]. TOPAS®, like PTMSP, undergoes radical induced degradation when exposed to photo-oxidative environments [16], however at a more controlled rate.

PTMSP absorbs UV (Figure 14) which limits the amount of information that can be collected regarding the fluorophore and its stability. In contrast, TOPAS® has the advantage of being an optically transparent material (see Figure 14), which allows UV-Vis spectra from doped samples to be monitored in parallel with fluorescence emission during photo-oxidation of the films. UV-Vis spectroscopy can be used to give insight into the stability of the fluorophore of the PFN and has been included in the analysis below.



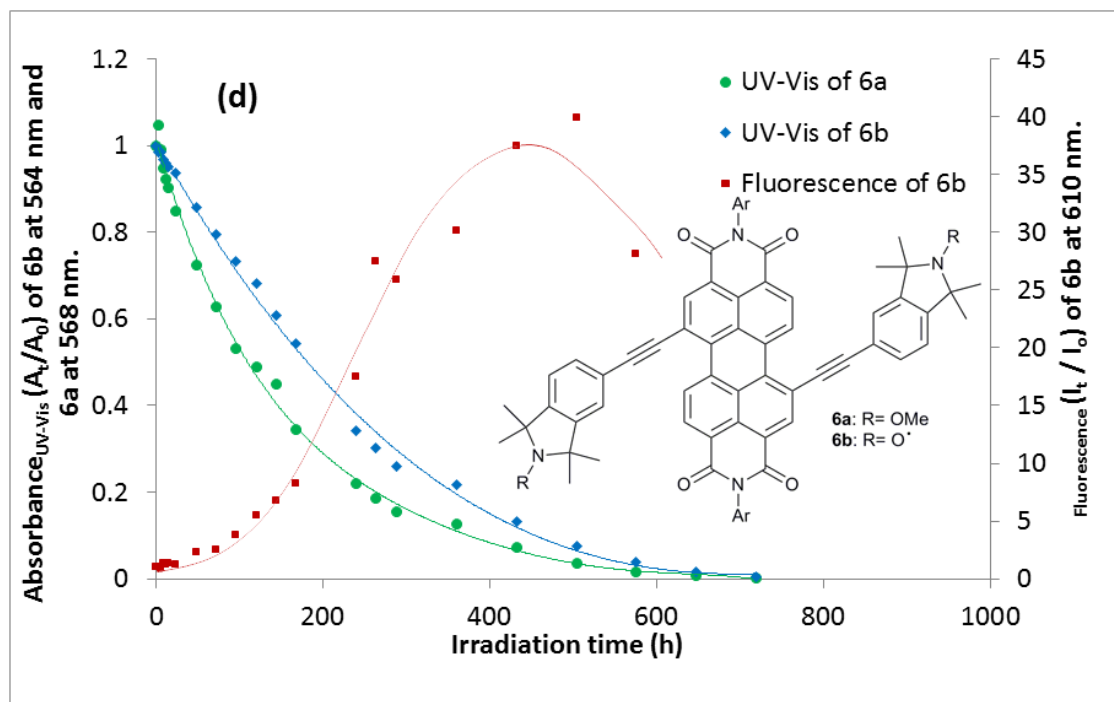
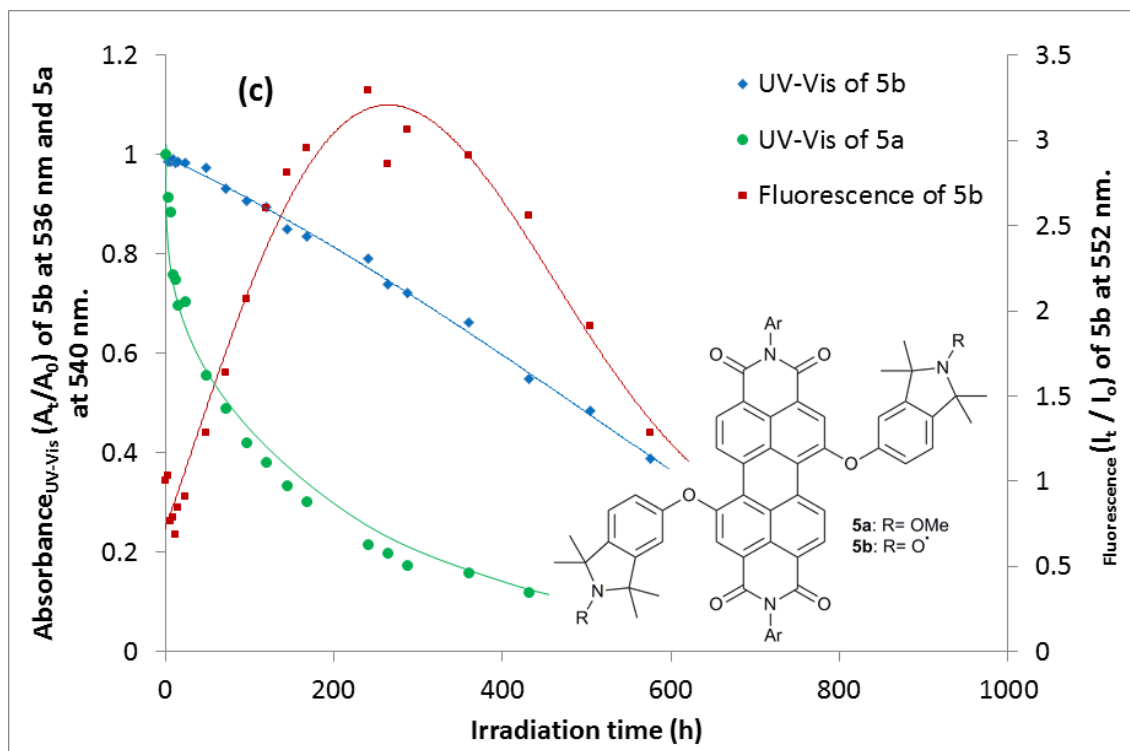


Figure 15: Change in the fluorescence emission from TOPAS® films doped with PFNs (■, Right axes), relative change in UV-Vis absorbance of PFNs (◆, Left axes) and relative change in UV-Vis absorbance of the non-radical analogues (●, Left axes) during photo-ageing. (a) 3a/3b (b) 4a/4b (c) 5a/5b (d) 6a/6b

The PFNs survived longer in TOPAS® than they did in PTMSP due to the higher overall stability of the film after photo-oxidative conditions. The alkyne-linked naphthalimide probe **4b** appeared to be the least stable of the tested PFNs, with its UV-Vis absorbance decreasing by a factor of 2 after 50 hours of ageing. The ether-linked naphthalimide, **3b** was more stable with the fluorophore withstanding 96 hours of irradiation before a loss of 50% of the fluorophore UV-Vis absorbance. The **3b** PFN also gave a 20-fold fluorescence emission response up to 96 hours of irradiation. Both of the perylenediimide PFNs on the other hand demonstrated significant stability, requiring 504 and 168 hours for the ether-linked, **5b** and alkyne-linked, **6b** compounds respectively (Figure 15), at which time the fluorophores had lost half of their absorbance compared to time zero. The free-radical containing PFNs tested displayed enhanced stability compared to their non-radical analogues, showing that the presence of the nitroxide induced a degree of protection, most likely through the recognised antioxidant capabilities of this functional group.

Even though the ether-linked perylenediimide PFN **5b** had a higher stability than the alkyne-linked PFN **6b**, the alkyne-linked PFN showed a higher level of fluorescence emission switch-on (40-fold), Figure 16. PFN **6b** also showed significant fluorescence change during ageing in the PTMSP films, allowing easier detection of radical formation within the films. All of the absorbance and fluorescence data for the aged TOPAS®-doped films are summarised in Table 2.

All TOPAS®-doped films were further tested to ensure films did not experience thermal degradation in the photo-oxidative environment. The TOPAS®-doped films were subjected to a dark oven at 70°C for an extended period of time. Like PTMSP, the

TOPAS® films demonstrated thermal stability with no evidence of spectrographic change or changes in physical properties.

Table 2: Summary of PFN sensor performance and stability in TOPAS® films following photo-oxidative degradation.

	Time to reach maximum fluorescence emission (h)	Fluorescence increase from time zero (×)	PFN stability ^[a]	Non-radical analogue stability (h) ^[a]	Relative fluorescence achieved (%) ^[b]
3b	144	20	96	70	33
4b	72	6	50	20	7.2
5b	264	3.2	504	90	11
6b	504	40	168	100	3.7

[a] time at which the fluorophore had lost half of its maximum absorbance compared to time zero.

[b] Fluorescence increase achieved relative to the maximum fluorescence emission from the corresponding non-radical analogue.

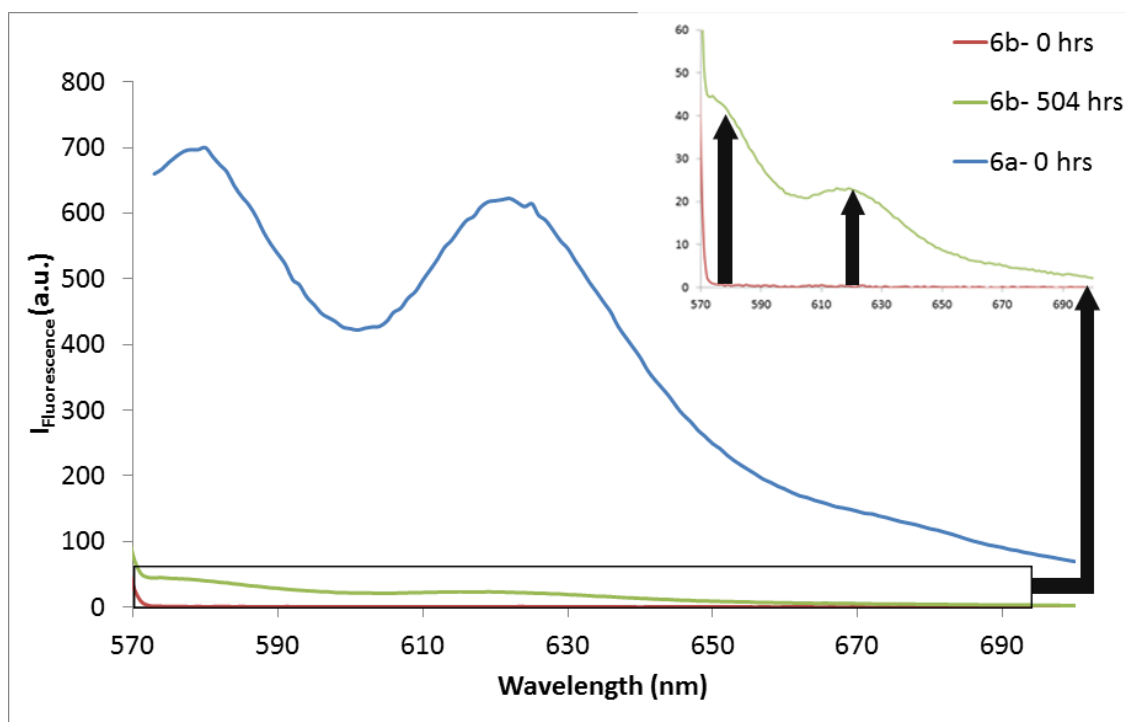


Figure 16: Change of the fluorescence emission for the PFN 6b in TOPAS® from 0-504 h ageing compared to its non-radical analogue, 6a at time zero in TOPAS®, showing that the PFN 6b has only achieved a small fraction of complete switch-on after 504 h ageing.

As in PTMSP, TOPAS® also degrades through a mechanism that involves the formation of reactive free radicals. The alkyl groups are oxidized to alkene and other conjugated systems, which results in the normally transparent films becoming yellow [29, 30]. This yellowing is observed in the UV-Vis, Figure 17. However, this yellowing can be difficult to detect in PFN-doped samples due to the absorbance of the PFN chromophores. Therefore, only the undoped TOPAS® film could be directly monitored for yellowing during ageing.

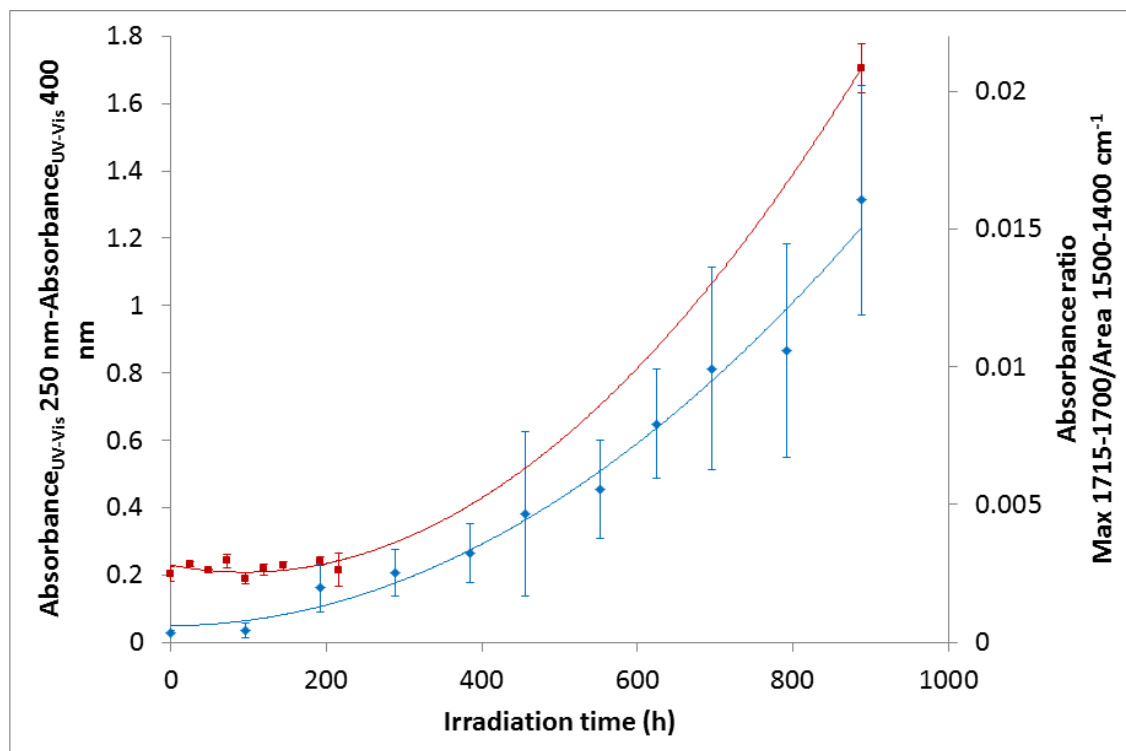


Figure 17: UV-Vis absorbance at 250 nm (subtracted from UV-Vis absorbance at 400 nm) for the blank (undoped) TOPAS® film with respect to time in the suntest (left axis, ■) and the oxidation index calculated from ATR-IR data from the blank (undoped) TOPAS® film with respect to time in the suntest (right axis, ◆)

Analysis of IR spectra from the undoped, irradiated TOPAS® film showed the formation of carbonyl bands due to oxidation at a similar rate to the yellowing at 250 nm detected in the UV-Vis. The correlation between the oxidation of alkyl groups and the formation of carbonyl products during the degradation of film allowed IR to be used as a monitor for photo-oxidative degradation in the presence of the PFN chromophore. However, as the irradiation time increased, the uncertainty in the oxidation index measurements became larger which is a recognised limitation of IR monitoring.

There is no convincing evidence of yellowing and/or carbonyl formation in the aged TOPAS® film until ~240 h, Figure 17 which is consistent with an oxidation induction period. Studies have demonstrated that the useful lifetime of a polyolefin does not extend much past this period [1, 9]. These results indicate that PFNs detect radical

formation from time zero through increases in fluorescence intensity. This demonstrates the usefulness of PFNs as sensitive probes to detect degradation caused from radical formation within the oxidation induction period, where previous techniques have limited success.

4 Conclusions

The aim of this study was to test the photo-oxidative stability of a unique group of additives that probe the nature of degradation of two types of polymer materials, PTMSP and TOPAS®. The nitroxide probe's ability to switch on and report damage occurring in PTMSP was demonstrated. However, degradation in the Heraeus Suntest instrument was too severe, which caused rapid embrittlement of the polymer. TOPAS® was more stable than PTMSP under the testing conditions and its transparency allowed analysis by UV-Vis spectroscopy in parallel with fluorescence spectroscopy, which gave insight into the stability of the fluorophores tested. It was determined that perylenediimide-incorporated PFNs are more photo-stable than naphthalimide PFNs in both the PTMSP and TOPAS® films. It was also determined that the nitroxide-containing compounds have higher stability in the photo-oxidative environment over their non-radical analogues. The alkyne-linked perylenediimide PFN, **6b** has an impressive switch on ability when exposed to photo-induced radicals, and it is the most effective PFN probe of the group tested. UV-Vis and IR gave little information about the early stages of the film's degree of degradation, confirming the value of the PFN technique as a tool to give insight into the oxidation induction period and to predict the overall serviceable lifetime of the polymer. With improved photo-stability, PFNs can now provide a sensitive and simple technique to monitor changes during the induction period of the photo-oxidative degradation of polymers.

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