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The application of a novel profluorescent nitroxide to monitor thermo-oxidative degradation of polypropylene

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Abstract

The novel profluorescent nitroxide, 1,1,3,3-tetramethyldibenzo[e,g]isoindolin-2-yloxyl (TMDBIO) was investigated as a probe for the formation of polymer alkyl radicals during the thermo-oxidative degradation of unstabilised polypropylene. TMDBIO possesses a very low fluorescence quantum yield due to quenching by the nitroxide group, however when the free radical moiety is removed by reaction with alkyl radicals (to give an alkoxyamine), strong fluorescence is observed. Using spectrofluorimetry, the reaction of the nitroxide with polymer alkyl radicals during oxidation has been monitored. Significantly, the trapping of polymer alkyl radicals during the "induction period" at 120^{o}C is observed, when it is not possible to detect changes in the polymer using either chemiluminescence or infrared spectroscopy. This highlights the sensitivity of this method and represents the direct observation of free radical generation in polypropylene in the "induction period". TMDBIO also successfully stabilises polypropylene under thermo-oxidative conditions, which is consistent with its action as a radical trap. At elevated temperatures (150^{o}C), at the end of the "induction period" when the polymer is extensively degraded, the fluorescence decreases, due to secondary oxidation of the TMDBIO.

Keywords: Profluorescent nitroxide, Radical trap, Alkoxyamine, Polypropylene, Thermal oxidation, Stabilisation, Degradation, Induction period, Fluorescence, Chemiluminescence

1. Introduction

Polypropylene is intrinsically susceptible to photo- and thermo-oxidative degradation, with both processes generally accepted as being mediated by free-radical species. The stability of polypropylene during processing and its long-term performance consequently depend heavily upon the use of stabilisers, which are designed to quench free-radicals or their reactive precursors. The oxidation stability is shown by an increase in the "induction period" – the time before there is a rapid increase in the oxidation of the polymer as measured by oxygen uptake, carbonyl index or chemiluminescence.[1] It has been shown that the useful life of a polymer does not extend much beyond this "induction period."[1] Hindered amine light stabilizers (HAS) are effective at inhibiting the photo-oxidative degradation of polypropylene and in certain circumstances, also thermo-oxidative degradation.[2,3] HAS have been well studied and the mechanism of action involves the rapid trapping of alkyl radicals by nitroxide radicals $RR'NO^{\bullet}$ formed by oxidation of the hindered piperidine group by polymer alkyl-peroxy or acyl-peroxy radicals. Commercial HAS stabilizers typically consist of two or more piperidine units joined through UV-stable groups such as esters (e.g. Tinuvin 770, Cyasorb UV-3765). The further development of HAS[2] has included polymeric versions which are less likely to migrate from the polymer (e.g. Tinuvin 622) and non-ester variants such as Chimmasorb 944 which are less susceptible to

hydrolysis. Polymeric HAS featuring tertiary amines (e.g. Chimassorb 119), rather than secondary amines, are also less affected by low pH environments.

The effectiveness of HAS relies on the oxidation of the secondary or tertiary amine by polymer hydroperoxide (ROOH), to form the nitroxide moiety ($RR'NO^{\bullet}$) which is a potent scavenger of polymer alkyl radicals, $R^{\bullet}$. This trapping reaction, which produces alkoxyamines, must be competitive with the reaction of $R^{\bullet}$ with oxygen (which gives the chain-carrying peroxy radical, $RO_2^{\bullet}$) if this stabilization process is to be important in HAS inhibition of thermo-oxidative degradation of polyolefins. In fact, the rate of this reaction is very high and, in solution, rate coefficients up to $9x10^8$ l mol^{-1} s^{-1} have been determined.[4] It has been recognised that HAS function as **retarders** of thermo-oxidative degradation of polypropylene in contrast to the hindered phenols which are **inhibitors** of oxidation. Thus while the HAS extend the oxidation "induction period" there may be a small but measurable oxidation that accompanies this stabilisation. This arises from the cycle of formation and decomposition of the nitroxide that is the key element in the stabilization of the polymer.[5]

The alkoxyamines generated are quite stable, however under some conditions thermolysis may result in the formation of the hydroxylamine RR'NOH, a process which is strongly dependent upon the structures of both the parent nitroxide and the trapped radical, as well as the reaction temperature. The hydroxylamine can subsequently be attacked by alkylperoxy radicals to regenerate the nitroxide. Alternatively, the alkoxyamine may react directly with alkylperoxy

or acylperoxy radicals to reproduce the nitroxide.[6,7] There is thus a cycle of reaction and regeneration of the nitroxide radical that results in the efficient stabilization of the polymer against thermo-oxidative degradation.

While free radical processes clearly dominate the photo- and thermo-oxidative degradation of polypropylene, previous methods for studying these processes in the condensed phase have been limited. The low steady-state concentrations and/or high reactivity of the free radicals of interest restricts their direct observation by Electron Paramagnetic Resonance (EPR) and other forms of spectroscopy. Schlick *et al*[8] have used EPR imaging to follow the spatial variation in the free radical formation in a HAS [Tinuvin 770: bis(2,2,6,6- tetramethyl-4-piperidinyl) sebacate] doped propylene-ethylene copolymer during oxidation at 120 and 160^{o}C. Oxidation for over 30 days at 120^{o}C was necessary before the HASNO$^{\bullet}$ could be detected. Spin-trapping with nitrone or nitroso compounds produces persistent radicals which can be detected by EPR, but this technique is hindered by the lack of structural information provided by EPR, instability of the adducts and need for high concentrations of the trap due to the relatively low rate constants for the spin-trapping reaction.[9]

Spin-trapping by nitroxides however, offers a number of advantages. Nitroxides trap carbon-, sulphur- and phosphorous-centred radicals at close to diffusion-controlled rates (10^{9} l mol^{-1} s^{-1}), but do not trap oxygen-centred radicals, although they are implicated in quenching these species.[10,11,12,13] When nitroxides trap carbon-centred radicals, the products are the more stable diamagnetic

alkoxyamines, rather than the reactive species arising from nitrone and nitroso scavengers. Although the majority of spin-trapping experiments with nitroxides involve commercially-available piperidine or pyrrolidine species, in a polymer context, nitroxides based on a rigid isoindoline structure exhibit a number of advantages, including superior thermal and chemical stability.[14,15,16]

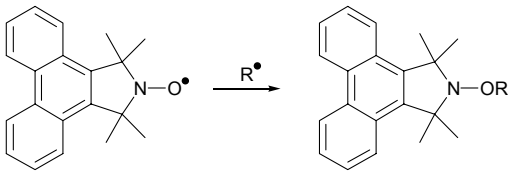
As well as being powerful free radical scavengers, nitroxides are also very effective quenchers of excited electronic states due to enhanced intersystem crossing (ISC) from the first excited singlet state to the ground state through electron exchange interactions of the nitroxide radical.[17,18,19] Thus, in the presence of a nitroxide moiety, even strong fluorophores display markedly suppressed fluorescence emission. When the nitroxide traps an alkyl radical however, the resulting diamagnetic alkoxyamine is fluorescent, so the emission intensity is a measure of the number of reactions that have occurred. In a polymer context, this property has been utilised in the quantification of radical formation during pulsed laser photolysis[20] and the kinetic profiling of cap separation in nitroxide-regulated living polymerisation.[21] Scaiano *et. al.* have also used profluorescent nitroxides to trap radicals generated from thermal- and photo-initiators in thin polymer films[22,23] and to evaluate the antioxidant ability of phenols.[24] In other areas, reactive oxygen species have been quantified using profluorescent nitroxides[25,26,27] and/or their secondary amine analogues.[28,29]

Much of the profluorescent nitroxide probes used previously involve nitroxide-containing pyrroline or piperidine rings attached to the fluorophore *via*

an ester or amide linkage. Other probes are fluorescamine derivatives of pyrrolidine or piperidine nitroxides. It must be noted that all of these compounds are susceptible to hydrolysis and consequential separation of the nitroxide moiety from the fluorophore. Where this process occurs, the fluorophore will no longer be quenched and the resulting fluorescence may give misleading experimental results.

Here, we introduce a new profluorescent nitroxide 1,1,3,3-tetramethyldibenzo[e,g]isoindolin-2-yloxyl (TMDBIO), which contains the phenanthrene fluorophore covalently fused to a 5-membered nitroxide-containing ring. This nitroxide exhibits the favourable chemical and physical characteristics of isoindoline nitroxides, and in contrast to other profluorescent nitroxides in the literature, is not susceptible to hydrolysis. TMDBIO has a very small fluorescence quantum yield as the spin is in close proximity to the aryl system, strongly enhancing the electron exchange interactions which lead to ISC quenching of the excited state. On the other hand, when the free radical moiety of TMDBIO is removed (by reaction with alkyl radicals to give an alkoxyamine, or through redox chemistry), strong fluorescence is observed (Scheme 1).

Scheme 1. Radical trapping by profluorescent TMDBIO gives fluorescent alkoxyamine derivatives (e.g. TMDBIO-Me)



TMDBIO
profluorescent

R = CH_3; **TMDBIO-Me**
FLUORESCENT

We have exploited this property by using quantitative fluorescence spectroscopy to follow the reaction of the nitroxide with alkyl radicals during the earliest stages of the oxidation of polypropylene. Moad *et. al.*[20] have shown that the measured emission intensity is proportional to the concentration of alkoxyamine (representing the number of radicals that have been trapped) and this in turn is proportional to the number of free radicals generated in the system. Significantly, using spectrofluorimetry, we are able to observe the generation of free radicals in polypropylene during the so-called "induction period," when it is not possible to observe changes in the polymer using any other instrumental techniques, including chemiluminescence (CL) and infrared spectroscopy. This highlights the sensitivity of this method at detecting free radical generation in polypropylene. We have also shown that TMDBIO successfully stabilises polypropylene under thermo-oxidative conditions, which is consistent with its action as a radical trap. This provides a sensitive technique for determining the rates of initiation of oxidation; an important pre-requisite in the prediction of polymer lifetime.

2. Experimental

2.1 Materials

Unstabilised polypropylene was supplied by the Toho Catalyst Company Ltd and had M_n 86 750 mol g^{-1}; M_w 318 500 mol g^{-1}; M_w/M_n 3.7. The properties of this material and its oxidation characteristics have been described previously.[30] Melt-pressed polypropylene plaques (40 x 40 x 0.4 mm) were prepared at 180 °C with an applied pressure of 10 ton over 5 min. The polymer granules were loaded between polyacetate sheets on a steel die and were quenched in air after pressing.

The profluorescent nitroxide 1,1,3,3-tetramethyldibenzo[e,g]isoindolin-2-yloxyl (TMDBIO) was synthesised according to a modified version of the literature synthesis of isoindoline nitroxides,[31] in a 5-step process starting from 9,10-dicarboxyphenanthrene anhydride. The methyl adduct of the phenanthrene nitroxide (TMDBIO-Me) was prepared by exposing the nitroxide to methyl radicals generated from DMSO in the presence of H_2O_2 and Fe(II).[32] The full details of these syntheses will be published elsewhere. The UV-Vis spectrum of TMDBIO exhibits a typical phenanthrene-type absorbance with λ_{max} 256 nm (ε 67 000) and an analytically useful shoulder at 300 nm (ε 14 500).

HPLC-grade heptane was used for the preparation of doped plaques and Soxhlet extractions. All other solvents used during these studies were AR grade unless otherwise specified.

2.2 Doping of polypropylene plaques

The expected formation of some alkyl radicals during melt-processing of the polypropylene[33] precluded the introduction of the nitroxide dopant prior to the plaque formation. Radical trapping by the nitroxide during the melt-processing would generate fluorescent alkoxyamines and undesirable background emission. Consequently, the polypropylene plaques were doped by immersion in heptane solutions (5 mM) of TMDBIO or TMDBIO-Me, in the dark, for 6 days. An undoped control plaque was similarly swelled in heptane. Upon removal from the swelling solutions, the plaques were rinsed with a minimum of heptane and placed under high vacuum for 24 h.

The nitroxide content of the doped plaques was determined using UV/Vis spectroscopy. The plaques were held in the instrument beam path and a baseline obtained using the undoped control plaque. Quantification was obtained using the 300 nm vibronic band (ε 14 500) which is in a region with low background from the polymer. This band displayed an absorbance of <1 absorbance unit in the doped plaques. The concentration of nitroxide in the TMDBIO-doped plaque was found to be ~1.1 mM, corresponding to ~0.035 wt % (assuming a polypropylene density of 0.9 g cm^{-3}), which is considerably lower than commercial loadings of HAS in polypropylene (0.1 – 0.2 wt %). The concentration of alkoxyamine in the TMDBIO-Me-doped plaque was calculated to be ~1.3 mM, corresponding to 0.043 wt %.

2.3 Chemiluminescence (CL)

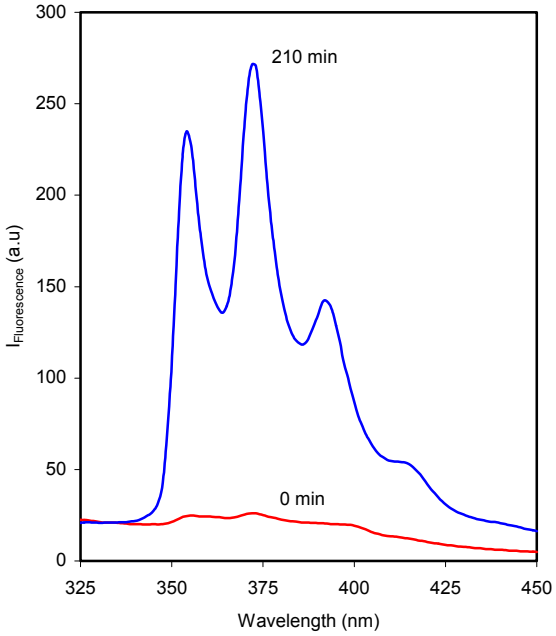
Polypropylene disks for chemiluminescence analysis were removed from the plaque of interest using a hole-punch. Each disk was weighed accurately and placed in an aluminium pan for analysis in the photon counting CL apparatus described in other publications.[34,35] The sample stage of the instrument was heated to the oxidation temperature under a nitrogen atmosphere. Once the temperature had stabilised the sample pan was placed on the stage, the atmosphere switched to oxygen at a flow rate of 70 ml min^{-1} and the shutter opened to commence photon counting. The photon counts were integrated over 10s.

2.4 Spectrofluorimetry and UV-Vis Spectroscopy

Spectrofluorimetry was performed on a Varian Cary Eclipse fluorescence spectrophotometer equipped with a standard multicell Peltier thermostatted sample holder. Plaques were loaded into a modified cuvette and excited at an angle of 45° to the surface, with emission recorded from the back face of the sample, in order to minimise scattering effects. For the phenanthrene nitroxide TMDBIO (and derivatives) excitation was performed at 294 nm. Figure 1 shows the fluorescence emission of the TMDBIO-doped plaque before and after degradation under O_2 at 150 °C for 210 min. The spectrum after oxidation is identical to that from a solid solution of phenanthrene and shows the characteristic vibronic progression of ca. 1500 cm^{-1} characteristic of condensed polycyclic aromatics[36]

UV-Vis spectroscopy was performed on a Varian Cary 50 spectrophotometer.

Figure 1. Fluorescence emission of TMDBIO-doped polypropylene plaque before and after oxidation under O_2 at 150 °C for 210 min (294 nm excitation).



2.5 FTIR-ATR spectroscopy

Infrared spectra were collected on a Nicolet Nexus 870 Fourier transform infrared (FTIR) spectrometer equipped with a Smart Endurance single bounce horizontal diamond ATR and a TE-cooled deuterated triglycine sulfate (DTGS) detector (Nicolet Instrument Corp. Madison WI). Spectra were recorded using 64 scans, 0.6329 cm s^{-1} mirror velocity and 4 cm^{-1} resolution over the range 4000 – 525 cm^{-1}. Spectra were collected in absorbance mode and ATR correction applied. Final processing was performed using GRAMS software (Thermo Galactic,

Woburn, MA). ATR data was normalised and represented as an "oxidation index" calculated as the ratio of the integral of the carbonyl absorption (1550 - 1850 cm^{-1}) to that of the 1375 cm^{-1} δCH_3 absorption. While the 1375 cm^{-1} absorption has been assigned as a combination of δCH_3 sym., ωCH_2, δCH and υCC_b vibrations,[37] this peak was used in preference to the 1434 cm^{-1} δCH_3 asym. absorption due to the adversely angled baseline in the 1434 cm^{-1} region in highly oxidised samples (due to unresolved C-O stretching vibrations).

3. Results and discussion

3.1 Simultaneous Fluorescence/FTIR-ATR of doped and undoped polypropylene at 120 °C

HAS are reported to be efficient thermal stabilisers of polypropylene at temperatures <130 °C.[2] Here we investigated the retardation of polymer degradation by TMDBIO, monitoring the fluorescence and surface oxidation of both undoped and TMDBIO-doped plaques during oxidation in air at 120 °C for 15h. The samples were removed from the oven at the end of each hour, cooled, and subjected to spectrofluorimetry and ATR spectroscopy.

Figure 2 shows the change in oxidation index of the undoped and TMDBIO-doped plaques. The nitroxide is clearly stabilising the polypropylene against thermo-oxidation at this temperature with essentially no change in the

oxidation index over the observation period. The oxidation index of the undoped plaque in contrast, exhibits a rapid increase and reaches a value of 1.7, corresponding to total embrittlement, after 15 h.

Figure 2. Oxidation indices, as determined by FTIR-ATR, of polypropylene and TMDBIO-doped polypropylene aged in air at 120 °C.

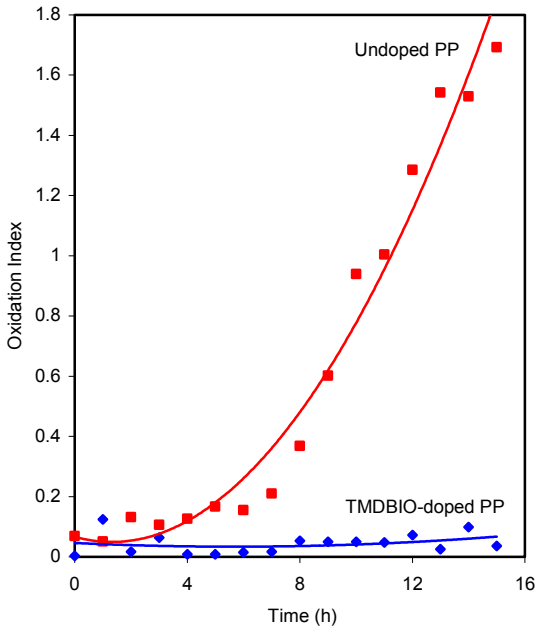


Figure 3. Spectrofluorimetry of polypropylene and TMDBIO-doped polypropylene aged in air at 120 °C (monitored at 373 nm; excitation at 294 nm).

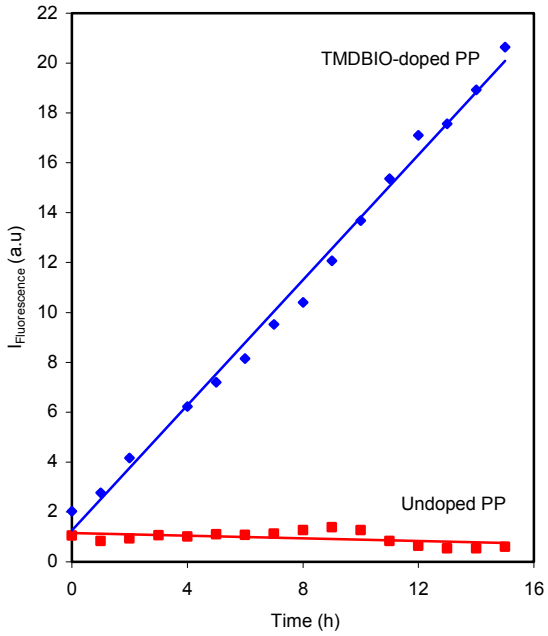


Figure 3 shows the change in fluorescence emission of the undoped and TMDBIO-doped plaques, measured at 23 °C. While the undoped plaque exhibits baseline fluorescence throughout the course of the experiment, the nitroxide-doped plaque shows an *immediate* increase in emission, consistent with the trapping of (unidentified) alkyl or macro-alkyl radicals ($R^{\bullet}$) to form fluorescent alkoxyamines (TMDBIO-R; Scheme 1). The increase in fluorescence is linear with time (at this oxidation temperature) and commences with the onset of oxidation, indicating the immediate formation of alkyl radicals in the polymer.

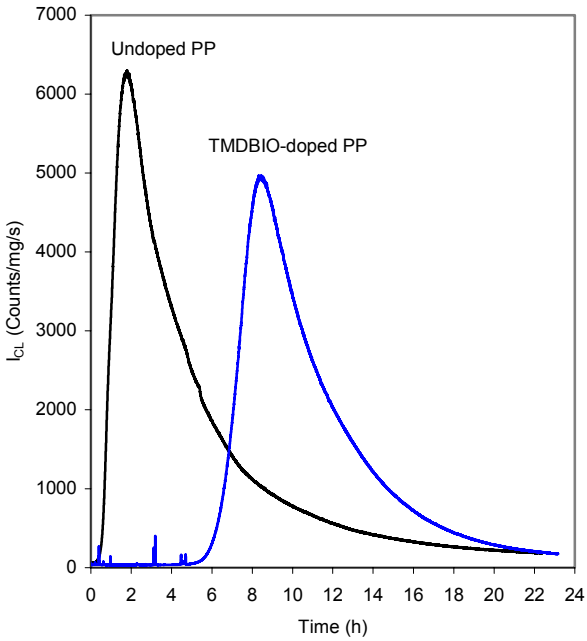
Notably, this fluorescence technique does not suffer from any "lag-time" in the detection of free radical generation. This appears to be the most sensitive technique for detection of homolytic bond cleavage and other radical formation processes from the onset of thermolysis. The linearity of the fluorescence response with time has implications for the mechanism of thermo-oxidative

initiation and implies direct homolysis of trace hydroperoxides. We are currently undertaking further studies in the absence of air to eliminate chain branching reactions through peroxy radical formation and so enable the determination of the initiation efficiency at the onset of thermo-oxidation.

3.2 Degradation of TMDBIO-doped PP at 150 °C

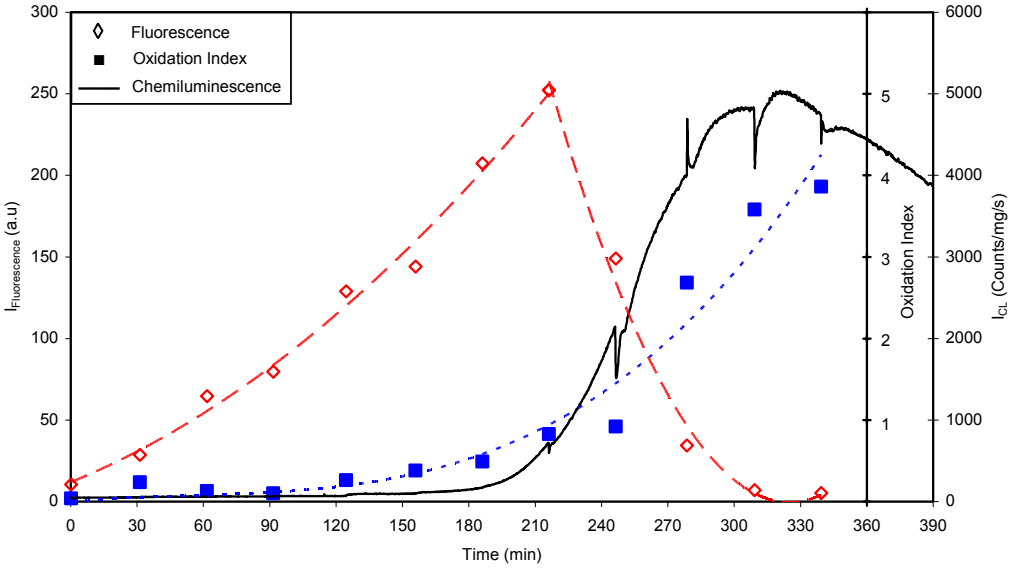
It has been noted from studies of the thermo-oxidative stabilization of polypropylene by HAS that the upper limit to their successful use was around 135^{o}C. In this study, when the polypropylene plaques were oxidised at a higher temperature (150 °C) in oxygen, more complex behaviour was noted than had been observed at 120 °C (Figure 3). Figure 4 shows the chemiluminescence (CL) profiles of disks sampled from the undoped and TMDBIO-doped polypropylene plaques. The "induction period" of the TMDBIO-doped sample is significantly prolonged with respect to the undoped sample. Likewise, the CL maximum is extended from 1.8 h in the undoped polymer, to 8.4 h in the nitroxide-doped sample. This again indicates that the nitroxide is retarding the thermo-oxidative degradation of the polypropylene plaque and this process is occurring before CL measurements detect appreciable hydroperoxide formation.

Figure 4. Chemiluminescence of polypropylene and TMDBIO-doped polypropylene aged under O_2 at 150 °C.



To more fully understand the processes occurring here, the degradation of the plaques was monitored using fluorescence, CL and FTIR-ATR in parallel. Figure 5 shows the growth and decay of fluorescence from a TMDBIO-doped polypropylene plaque subjected to oxidation at 150 °C under oxygen. The course of oxidation is represented by both CL and the oxidation index, which corresponds to the formation of carbonyl species at the plaque surface. The discontinuities in the CL trace correspond to points where the oxidising sample was removed from the CL chamber for the measurement of fluorescence and oxidation index and then replaced.

Figure 5. Degradation of TMDBIO-doped polypropylene aged under O_2 at 150 °C monitored in parallel by chemiluminescence, FTIR-ATR and spectrofluorimetry.



The fluorescence emission of the TMDBIO-doped polypropylene was found to immediately increase during the "induction period" of the oxidation process (low CL count and oxidation index), indicating the trapping of alkyl radicals and formation of fluorescent alkoxyamines (Figure 5). This result is similar to that observed at 120 °C, although at this temperature it is possible to examine the total stabilisation of the polymer by the nitroxide. While the increase in fluorescence was found to be linear over the observation period at 120 °C, here the fluorescence increase follows a more rapid and non-linear increase with time, until it reached a maximum (215 min) and then rapidly decreased. This rapid decrease in fluorescence coincided with the dramatic increase in oxidation of the polypropylene (according to CL and oxidation index). It should be noted that the linear fluorescence increase at 120 °C only corresponded to radical trapping at the very early stages of oxidation and the behaviour at 150 °C may reflect the more

complex chemistry when peroxy radical formation due to oxygen scavenging of alkyl radicals become competitive with trapping by the nitroxide.

On a macroscopic scale, the sample exhibited distinct morphological changes coincident with the major features in Figure 5. The first signs of crazing in the disk were noted at 215 min, corresponding to the end of the CL "induction period" and the fluorescence maximum. The crazing subsequently increased, as did the opacity of the sample, with the first yellowing observed at 280 min. At 310 min, corresponding to the CL maximum and reduction of fluorescence emission to background levels, the disk was very crazed, opaque and appreciably yellow. The sample finally broke under the pressure of the ATR anvil, 340 min after the commencement of the experiment, preventing further fluorescence and FTIR-ATR measurements.

The stabilisation of polypropylene by TMDBIO indicates that the trapping of polymer alkyl radicals by the nitroxide during the "induction period" must be competitive with the reaction of alkyl radicals and oxygen (which forms chain-carrying peroxy radicals). The reaction of polymer alkyl radicals with oxygen in solution has a high rate coefficient of 1 to 9 x 10^8 l mol^{-1} s^{-1}.[4] As the nitroxide is consumed, the rate of oxygen capture by the alkyl radicals (and subsequent peroxy radical formation) must eventually become significant. By the end of the "induction period" the nitroxide is consumed and the normal uninhibited degradation mechanisms of polypropylene dominate. Oxidative degradation of the polymer at this point leads to chemiluminescence and an increase in oxidation

index as the primary oxidation products, hydroperoxides, are converted to carbonyl moieties.

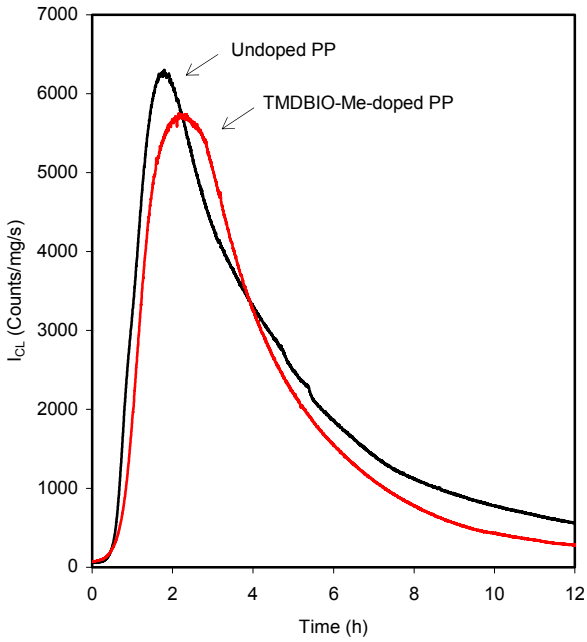
The rapid decrease in fluorescence observed at 215 min in Figure 5 may be interpreted in several ways. It is possible that the profluorescent nitroxide TMDBIO is being regenerated from the fluorescent alkoxyamine products of alkyl radical trapping. Such a process has been implicated in the mode of action of HAS and is reported to be due to the reaction of alkylperoxy and/or acylperoxy radicals with the alkoxyamines.[6,7] Here this does not appear to be a significant process, as the decrease in fluorescence coincides with the onset of polymer oxidation according to CL and oxidation index, which implies that stabilisation by the nitroxide is no longer occurring. It is more likely that the alkoxyamine species are undergoing some other form of degradation without regenerating the nitroxide moiety, possibly involving destruction of the phenanthrene fluorophore through formation of quinone-like analogues. This was investigated further by following the same procedure but with a polypropylene plaque doped with TMDBIO-Me, a fluorescent alkoxyamine analogue of TMDBIO, which serves as a model for the alkyl radical adducts of the nitroxide.

3.3 Degradation of TMDBIO-Me-doped PP at 150 °C

When plaques of TMDBIO-Me-doped polypropylene were oxidised at 150 °C under oxygen the CL profiles of the doped plaques were not significantly different to that of the undoped polymer (Figure 6). The “induction period”

appears to be unaffected by the dopant and the position of the CL maximum is only slightly extended with respect to the undoped sample. The minimal effect of TMDBIO-Me on the CL profile suggests that the regeneration of TMDBIO or HAS analogues of this compound is negligible at the temperatures used here. It must be noted that HAS are generally regarded as effective thermo-oxidative stabilisers at temperatures *below* 135 °C.[3]

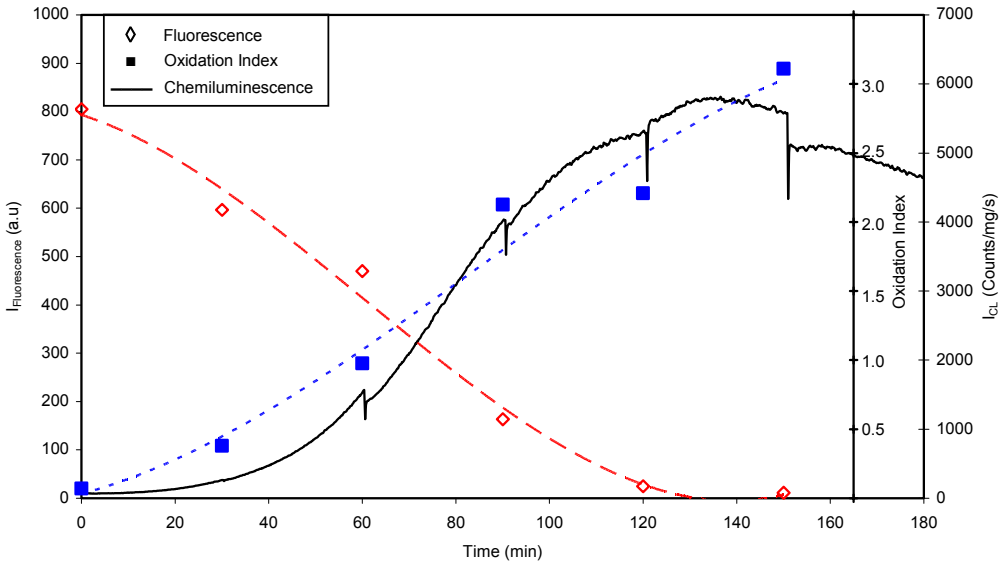
Figure 6. Chemiluminescence of polypropylene and TMDBIO-Me-doped polypropylene aged under O_2 at 150 °C.



Again, parallel monitoring of the thermo-oxidative degradation of the plaques using fluorescence, CL and FTIR-ATR gave insight into the polymer breakdown process. Figure 7 shows the decay of fluorescence in a TMDBIO-Me-doped polypropylene plaque subjected to oxidation at 150 °C under oxygen. In

accordance with the properties of TMDBIO-Me, the sample originally displayed strong fluorescence emission. The emission intensity however, rapidly decreased and reached background levels after only 120 min. Concurrently, the CL intensity and oxidation index increased with the CL profile reaching a maximum at 130 min.

Figure 7. Degradation of TMDBIO-Me-doped polypropylene aged under O_2 at 150 °C monitored in parallel by chemiluminescence, FTIR-ATR and spectrofluorimetry.



This data indicates that alkoxyamine adducts degenerate under these oxidative conditions in the absence of the protective nitroxide stabilisers. This may reflect the inherent sensitivity of the phenanthrene fluorophore to peroxidation rather than a feature of the alkoxyamine in itself.

To discount direct thermo-oxidative degradation of TMDBIO-Me, a decane solution of the compound was heated at 150 °C in air. The fluorescence emission of the solution was effectively unchanged for 6 hrs, in distinct contrast to the behaviour of TMDBIO-Me in the polymer matrix, where the fluorescence emission is reduced to effectively zero after only 2 hours at the same temperature. This suggests that the degrading species in the oxidising polymer environment play an important role in the degradation of the alkyl radical adducts of the nitroxide.

In order to assess residual levels of TMDBIO in the polymer after degradation, the polypropylene disk used to generate the data in Figure 5 (after 24 h at 150 °C under oxygen) was subjected to continuous Soxhlet extraction with heptane for 24 h. Spectrofluorimetry and UV-Vis spectroscopy of the extract did not detect any TMDBIO or its alkyl radical adducts, indicating the complete consumption of the stabilising nitroxide and oxidation of its radical adducts by this point in the polymer degradation.

3.4 Conclusions

These results demonstrate the potency of profluorescent nitroxide probes for the investigation of polymer degradation, particularly in the induction period where most analytical techniques are unable to detect any change in the polymer. At temperatures below 120 °C, TMDBIO is a robust probe of polymer degradation kinetics. Even at 150 °C, when unstabilised polypropylene usually

rapidly degrades, the probe is a powerful retarder of thermo-oxidative degradation, such that TMDBIO-doped polypropylene exhibits a significantly prolonged lifetime. Profluorescent nitroxides provide information about the nature of the polypropylene degradation process that surpasses even the highly sensitive CL technique. They provide insight into the nature of the polypropylene degradation process from the onset of decomposition, immediately detecting carbon-centred radicals formed in the thermally stressed polymer. Potentially the detection of the fluorescence provides a predictive tool for indicating polymer lifetime and may allow the determination of usability for modern materials and devices.

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Figure captions

Figure 1. Fluorescence emission of TMDBIO-doped polypropylene plaque before and after oxidation under O_2 at 150 °C for 210 min (294 nm excitation).

Figure 2. Oxidation indices, as determined by FTIR-ATR, of polypropylene and TMDBIO-doped polypropylene aged in air at 120 °C.

Figure 3. Spectrofluorimetry of polypropylene and TMDBIO-doped polypropylene aged in air at 120 °C (monitored at 373 nm; excitation at 294 nm).

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Figure 6. Chemiluminescence of polypropylene and TMDBIO-Me-doped polypropylene aged under O_2 at 150 °C.

Figure 7. Degradation of TMDBIO-Me-doped polypropylene aged under O_2 at 150 °C monitored in parallel by chemiluminescence, FTIR-ATR and spectrofluorimetry.

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