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A Novel Profluorescent Dinitroxide for Imaging Polypropylene Degradation

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Free-radical processes underpin the thermo-oxidative degradation of polyolefins. Thus, to extend the lifetime of these polymers, stabilizers are generally added during processing to scavenge the free radicals formed as the polymer degrades. Nitroxide radical precursors, such as hindered amine stabilizers (HAS),[1,2] are common polypropylene additives as the nitroxide moiety is a potent scavenger of polymer alkyl radicals ($R^\bullet$). Oxidation of HAS by radicals formed during polypropylene degradation yields nitroxide radicals ($RR'NO^\bullet$), which rapidly trap the polymer degradation species to produce alkoxyamines, thus retarding oxidative polymer degradation. This increase in polymer stability is demonstrated by a lengthening of the "induction period" of the polymer (the time prior to a sharp rise in the oxidation of the polymer). Instrumental techniques such as chemiluminescence or infrared spectroscopy are somewhat limited in detecting changes in the polymer during the initial stages of degradation. Therefore, other methods for observing polymer degradation have been sought as the useful life of a polymer does not extend far beyond its "induction period".[3]

A sensitive technique for monitoring the alkyl radical precursors to polymer degradation involves spin-trapping by profluorescent nitroxides. These compounds, which possess a fluorophore tethered by a short covalent link to a nitroxide moiety, are effective scavengers of carbon centered radicals and quenchers of excited electronic states. They exhibit low fluorescence due to enhanced intersystem crossing from the first excited singlet state to the triplet state via electron exchange interactions of the nitroxide radical. Upon radical trapping to form a diamagnetic alkoxyamine, normal fluorophore emission is enabled, and thus, these nitroxide–fluorophore adducts can be employed as extremely responsive fluorescent probes for the detection of free-radical species.[4] This property has been previously applied to evaluate radical formation in various polymer contexts;[5−7] however, these probes possess nitroxide-containing piperidine or pyrrolidine units tethered through ester or amide linkages to a fluorophore. For monitoring polymer degradation, linkages that are susceptible to hydrolysis and subsequent scission of the nitroxide moiety from the fluorophore are not ideal.

Nitroxides based on the more rigid isoindoline structure exhibit somewhat superior chemical and thermal stability in polymers.[8,9] Herein, we describe the synthesis and properties of the novel dinitroxide, 9,10-bis(1,1,3,3-tetramethylisoindolin-2-yloxyl-5-yl)anthracene (BTMIOA), **6**, a markedly superior, enhanced stability profluorescent nitroxide probe analogous to 9,10-diphenylanthracene. This new probe possesses a (masked) high quantum yield and so is more sensitively able to detect free-radical formation during polymer degradation. The high quantum yield facilitates monitoring by spectrofluorimetry but also allows degradation to be readily imaged using fluorescence microscopy.

The new probe was synthesized by a Suzuki cross-coupling reaction between 5-iodo-1,1,3,3-tetramethylisoindolin-2-yloxyl (**3**) and anthracene-9,10-diboronic acid (**5**) in a modest yield (29%) (Scheme 1). The more reactive iodo-nitroxide **3** was preferred over its bromo analogue as a coupling partner. Preparation of **3** was achieved by lithiation of 5-bromo-1,1,3,3-tetramethylisoindoline (**1**), followed by treatment with iodine and subsequent oxidation with hydrogen peroxide in the presence of a tungstate catalyst. The alkylated diamagnetic dinitroxide analogue, 9,10-bis(2-methoxy-1,1,3,3-tetramethyl-

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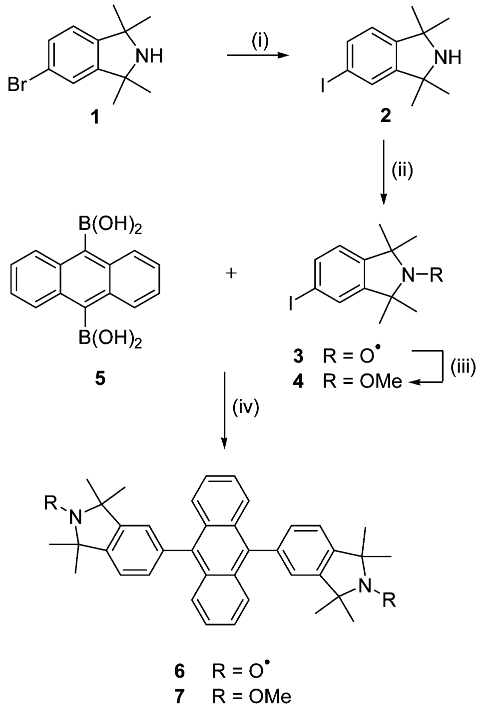
Scheme 1. Synthesis of BTMIOA 6 and BTMIOA-Me 7[a]



[a] Reagents and conditions: (i) (a) ^{n}BuLi, THF, −78 °C, 15 min, (b) I_2, THF, −78 °C to RT, (c) $NaHCO_3$, H_2O_2, MeOH-DCM; (ii) $NaHCO_3$, $Na_2WO_4{\cdot}2H_2O$, H_2O_2, MeOH, 3 days; (iii) $FeSO_4{\cdot}7H_2O$, H_2O_2, DMSO, 15 min; (iv) $Pd(PPh_3)_4$, Na_2CO_3, THF−H_2O, 80 °C, 3 days.

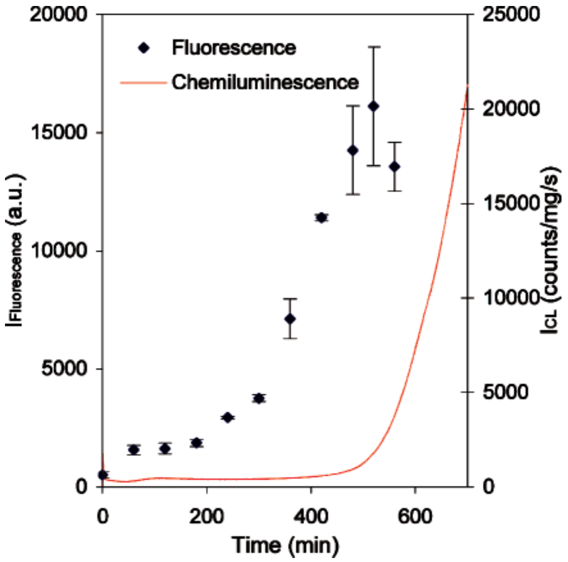


Figure 1. Fluorescence and chemiluminescence emission of BTMIOA **6** doped polypropylene aged under O_2 at 150 °C (260 nm excitation). Note the induction period for chemiluminescence from undoped polypropylene is essentially zero over this time scale.

isoindolin-5-yl)anthracene (**7**), was obtained by Suzuki coupling of 5-iodo-2-methoxy-1,1,3,3-tetramethylisoindoline (**4**) (formed using Fenton chemistry by reaction of 5-iodo-1,1,3,3-tetramethylisoindolin-2-yloxyl (**3**) with methyl radicals generated from dimethyl sulfoxide and hydrogen peroxide) and anthracene-9,10-diboronic acid (**5**) in a more moderate yield (43%). A comparison of the fluorescence of dinitroxide **6** and its methoxyamine derivative **7** reveals the substantial suppression of the fluorescence of the 9,10-diphenylanthracene core in compound **6** arising from the presence of the two nitroxides. This effect is evident from the quantum yields (Φ_F) of 2.9×10^{-3} and 0.89 obtained for compounds **6** and **7**, respectively, following excitation at 375 nm (ϵ 14 500 M^{-1} cm^{-1}).

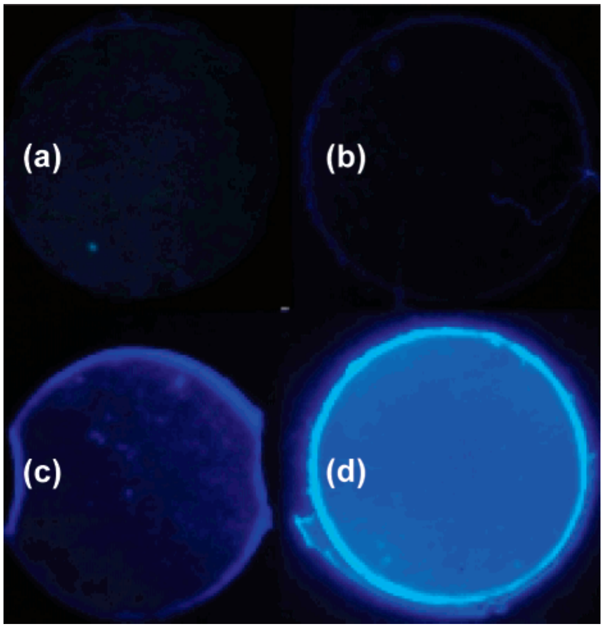


Figure 2. Polypropylene plaque images excited between 254 and 290 nm using short-range UV lamp (a) blank, (b) doped with BTMIOA **6** at 0.17 mM, (c) doped with TMDBIO-Me at 1.1 mM, and (d) doped with BTMIOA-Me **7** at 0.17 mM.

Polypropylene plaques containing dinitroxide **6** or methoxyamine **7** were obtained by swelling the polymer in 5 mM toluene solutions of **6** or **7**. The amount of compound present in each plaque was quantified using UV−vis spectroscopy (assuming that the concentration in solution is comparable to that in a solid plaque for a set absorbance). The maximum concentration of BTMIOA **6** or BTMIOA-Me **7** in a doped plaque was found to be ~0.17 mM, corresponding to ~0.009 wt % (assuming a polypropylene density of 0.9 g cm^{-3}). The plaques were thermally degraded at 150 °C in a 100% O_2 environment. Samples were removed from the oven periodically and their fluorescence spectra recorded (excitation = 260 nm). Figure 1 shows the fluorescence emission of the BTMIOA **6** doped plaque subjected to oxidation under oxygen for 10 h. The fluorescence of the degrading plaque was found to slowly increase over the first 300 min and then rise more rapidly between 400 and 500 min, indicating the trapping of alkyl radicals and formation of fluorescent alkoxyamines. Interestingly, the fluorescence profile appears to indicate two stages involving sequential trapping of the two nitroxides.

We have previously reported the use of 1,1,3,3-tetramethyldibenzo[*e*,*g*]isoindolin-2-yloxyl (TMDBIO) as a probe for monitoring the thermo-oxidative degradation of polypropylene.[10,11] The new profluorescent probe **6** reported here markedly stabilizes the polymer by trapping radicals which would normally lead to macromolecular oxidation, as demonstrated by the extended induction period before observed chemiluminescence (Figure 1), and is a significant advance over TMDBIO. This new probe allows the monitoring of the thermal degradation of polypropylene for longer periods than TMDBIO, which reaches a maximum fluorescence and then decreases due to secondary oxidation of the TMDBIO adducts. Notably, the oxidative stability of the model alkyl adduct, BTMIOA-Me **7**, is much improved over TMDBIO-Me, with a plaque containing **7** maintaining fluorescence after oxidation for 120 min at 150 °C under oxygen. Under the same conditions TMBDIO-Me samples returned rapidly to background fluorescence levels.

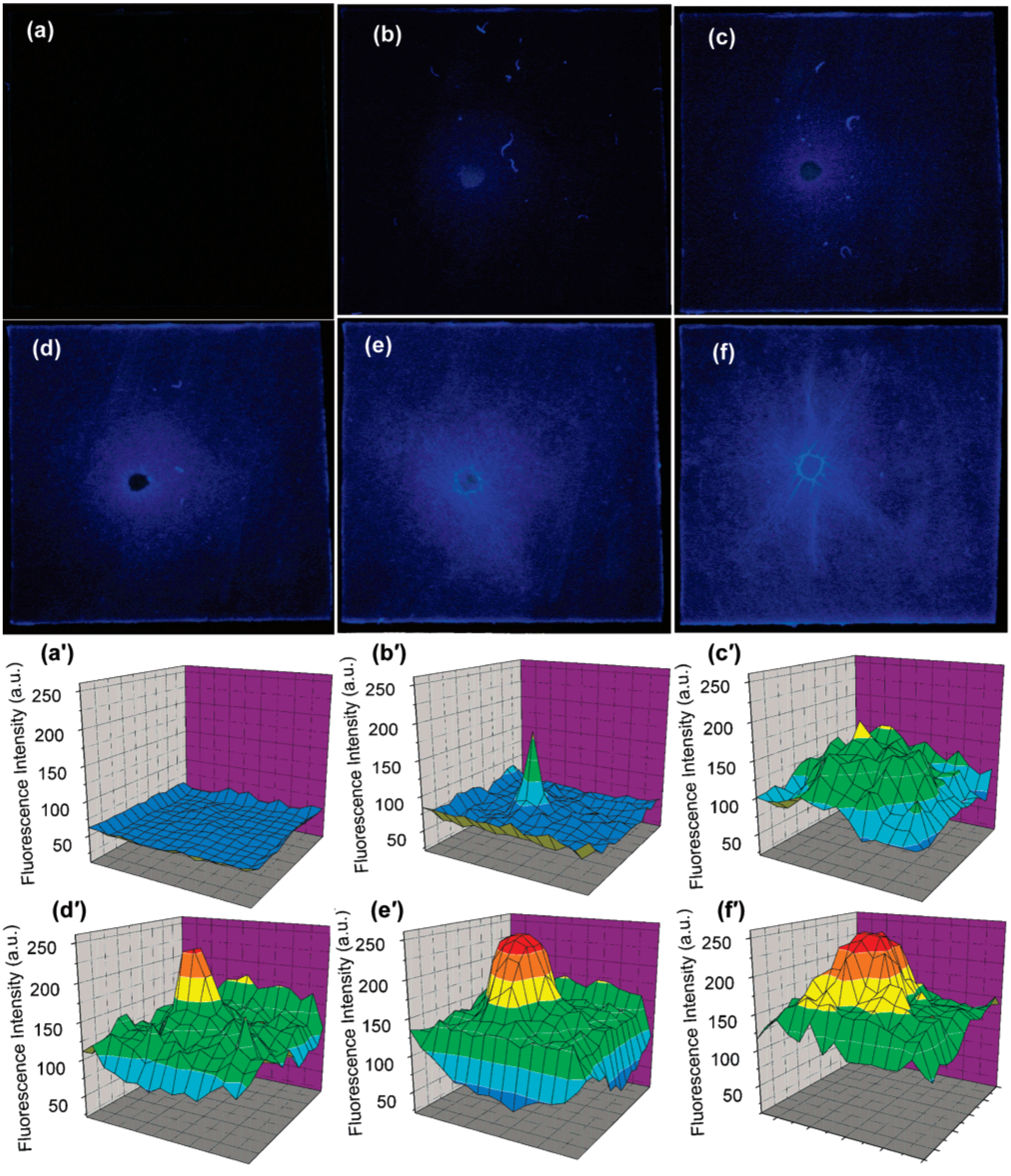


Figure 3. Fluorescent images of a BTMIOA **6** doped, 2.5 cm × 2.5 cm polypropylene plaque spiked with benzoyl peroxide initiator and heated at 100 °C in O_2 for (a) 0, (b) 1, (c) 8, (d) 12, (e) 18, and (f) 24 h. (a′)−(f′) are three-dimensional representations of fluorescence for images (a)−(f).

BTMIOA-Me **7** also has a much higher quantum yield than TMDBIO-Me (0.89 compared to 0.18), which indicates this probe is much more suitable for the imaging and mapping of free radical reactions in polymer degradation. Figure 2 shows images of doped polypropylene plaques excited between 254 and 290 nm using a short-range UV lamp. Like the undoped plaque (Figure 2a), the plaque doped with BTMIOA **6** (Figure 2b) displays low fluorescence due to quenching by the nitroxides. In comparison, the BTMIOA-Me **7** doped plaque (Figure 2d) is extremely fluorescent. Figure 2d gives an indication of the maximum fluorescence possible for dinitroxide **6** following radical trapping to form fluorescent diamagnetic alkoxyamine adducts. Furthermore, the sensitivity of BTMIOA **6** is demonstrated by comparing the images of the BTMIOA-Me **7** doped plaque (Figure 2d) with that of a TMDBIO-Me doped plaque (Figure 2c). Not only is the BTMIOA-Me **7** doped plaque considerably brighter, it also contains a significantly lower concentration of the adduct (0.17 mM compared to 1.1 mM for TMDBIO-Me).

Celina and co-workers[12] have shown infectious spreading of oxidation when polypropylene was spiked with benzoyl peroxide and degraded at 100 °C in an O_2 environment. Using the new dinitroxide probe **6** allows a visual representation of this oxidation process, as can be observed in Figure 3. A polypropylene plaque doped with **6** (∼0.17 mM) was spiked with benzoyl peroxide and degraded at 100 °C in an O_2 environment to accelerate radical formation. After heating for 1 h (Figure 3b,b′), an area of high fluorescence was observed in the center of the plaque due to trapping by **6** of phenyl radicals and the initiated macroradicals. With prolonged heating (Figures 3c−f and 3c′−f′), the fluorescence radiated outward toward the edges of the plaque, revealing the damage from propagating radicals. Thus, BTMIOA **6** is an ideal dual-functioning probe which allows polypropylene degradation to be mapped by imaging with fluorescence microscopy and also imparts stabilization to the polymer due to its effective radical scavenging ability.

In conclusion, a novel dinitroxide probe **6**, based on a 9,10-diphenylanthracene core and incorporating nitroxides, has been developed and shown to image polypropylene degradation. This novel probe was synthesized by a Suzuki cross-coupling reaction and switches on fluorescence as the nitroxides present spin-trap polymer alkyl radicals formed during the thermo-oxidative degradation of polypropylene. Compound **6** allows radical formation, which in the normal course of events would lead to polymer oxidation, to be monitored by spectrofluorimetry and imaged using fluorescence microscopy. Furthermore, probe **6** displays enhanced stability toward further oxidation after trapping and subsequent loss of fluorescence. The ability to image radical damage in polypropylene using this probe indicates the potential for this sensitive technique to be used as a powerful analytical tool to study polypropylene, and other polymer, degradation. These results will be reported in due course.

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Supporting Information Available: Procedures for the doping of polypropylene plaques and synthesis and characterization of compounds **2, 3**, **4**, **6**, and **7**. This information is available free of charge via the Internet at http://pubs.acs.org.

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