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Initiation of Polypropylene Photooxidation. 1. Polynuclear Aromatic Compounds[1a]

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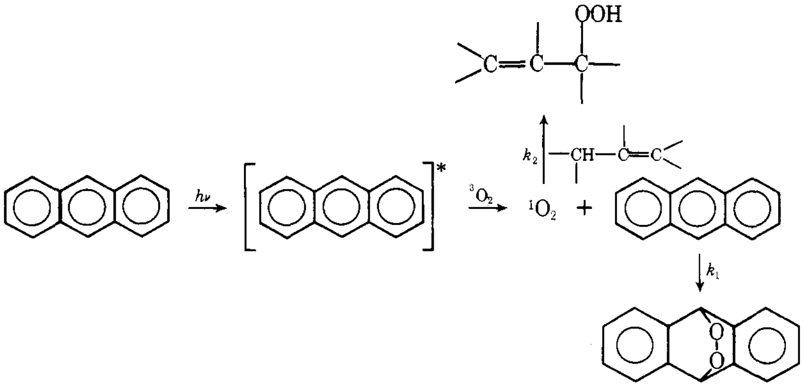
ABSTRACT: The effects of various polynuclear aromatic compounds on the photooxidation of polypropylene have been examined, and the photooxidation products from anthracenes have been investigated. Anthracene, dimethylanthracene endoperoxide, anthraquinone, and naphthalene were all found to sensitize the photooxidation of polypropylene and of model liquid systems. The interconversion of anthracene, anthracene dimer, endoperoxide, and anthraquinone was followed in the liquid phase, using liquid chromatography to separate the products. Quantum yields for the reactions involved were estimated. These results are relevant to the study of the various photoinitiation processes in commercial PPH articles.

Pure polyolefins do not themselves absorb sunlight (≥290 nm) but commercial polyolefins are nevertheless very susceptible to light initiated degradation. This degradation must result from initiation by various chromophoric impurities.[2,3] Of the possible photoinitiators in polyolefins, one of the least understood groups is that of the polynuclear aromatic (PNA) compounds. The accumulation of these compounds in polyolefins is now well established.[3-5] They are apparently absorbed from the urban atmosphere up to equilibrium concentrations of $\sim 1 \times 10^{-3}$ M naphthalene, $\sim 1 \times 10^{-4}$ M phenanthrene, and $\sim 1 \times 10^{-5}$ M anthracene.[5] From fluorescence spectroscopy, the absorbed compounds may be alkyl-substituted derivatives or the unsubstituted parent aromatics.[5] All can be removed by hexane washing but reaccumulate to their equilibrium levels within ~10 days storage in air.[3-5] These compounds absorb strongly or intensely (in the case of anthracenes) in the near uv to give excited states. Quenching of these triplet states by atmospheric oxygen is efficient and gives singlet oxygen ($^1\Delta_g$, $^1O_2$[6-8]).

In the case of anthracene and its derivatives, these compounds can themselves react with $^1O_2$ to give endoperoxides.[9] The thermal decomposition of anthracene endoperoxide is known to initiate free radical polymerizations,[10] although little has been published on its photolysis products. The rate constant (k_1 in reaction Scheme I) for $^1O_2$ attack on anthracene is $\sim 1.5 \times 10^5\ M^{-1}\ s^{-1}$ [9] in the liquid phase but is much higher for 9,10-dimethylanthracene ($\sim 2.1 \times 10^7\ M^{-1}\ s^{-1}$).[9] Naphthalene does not react with $^1O_2$.[9] Although phenanthrene has been estimated to have an extremely low rate constant for $^1O_2$ attack,[9] oxidation products have been reported from dye sensitized oxidation.[11] Endoperoxide formation in polymer films containing a benzanthracene derivative has been found to proceed in the same way as found in the liquid phase.[12]

As an alternative to reacting with the PNA compound, $^1O_2$

Scheme I



may diffuse to a residual unsaturation site in the polyolefin, and then rapidly react to give an allylic hydroperoxide.[2,13] For example the rate constant (k_2) for $^1O_2$ attack on 2-methyl-2-pentene is ~1 × 10^6 M^{-1} s^{-1}.[14] These possibilities are shown in Scheme I.

PNA compounds may then have two important effects in the initiation of polypropylene (PPH) photooxidation. The PNA compounds or their oxidation products may absorb light to give free radicals directly or they may act as sources of $^1O_2$ within the polymer. Hydroperoxide formation by $^1O_2$ attack on the residual PPH unsaturation (~0.05 M) has been shown to reduce the photostability of the polymer.[3]

We have previously shown that high concentrations (~1 × 10^{-3} M) of anthracene in PPH can accelerate its photooxidation,[3] although no attempt was made to investigate the nature of the reactive intermediates. In this paper, a more detailed study of the effects on PPH photooxidation of PNA compounds in general and anthracene derivatives in particular is presented, together with work in model liquid phase systems.

Experimental Section

Stabilizer-free commercial PPH films (Enjay, 25 μm) were freed from absorbed PNA impurities by hexane extraction. PNA compounds or derivatives were then deliberately introduced into these film samples by storing the film over crystals of these compounds in closed containers for 3–10 days or by allowing reabsorption from the atmosphere over a 10–14 day period. Aromatic concentrations in the films were determined by uv or fluorescence spectroscopy calibrated with film or solution standards.

Film photooxidations were initiated with the radiation from a xenon arc Weather-Ometer (Atlas 6000 W, Pyrex inner and outer filters) and were monitored by ir spectroscopy. PPH film samples were irradiated inside sealed, air-filled, low-density polyethylene (LDPE) pouches (1 mil wall) containing crystals of the aromatic compound with which the film was presaturated. Each pouch contained about 100 times the O_2 level consumed at brittle failure (~0.1 M OOH).

Solutions of anthracene, 9,10-dimethylanthracene, or their respective endoperoxides, anthraquinone or anthracene dimer, were irradiated with the xenon arc Weather-Ometer in 0.1 cm quartz cells. Solvents were air saturated spectro grade Freon 113 (1,1,2-trichlorotrifluoroethane) or isooctane (2,2,4-trimethylpentane). Squalene (2,6,10,15,19,23-hexamethyltetracosane-2,6,10,14,18,22-hexaene) was purified by vacuum distillation and was passed through a bed of alumina immediately before use. Starting material and product concentrations were monitored by uv spectroscopy; peroxide analysis was carried out by iodometry.[3] Reaction products were separated by high pressure liquid chromatography, HPLC (Waters ALC 201 fitted with a Pharmacia uv detector set at 254 nm and a Varian septumless injection system). Separations were performed with a 5μm Si–60 Lichrosorb (SiO_2) column (25 cm × 2.1 mm i.d.) using 5 vol % 2-propanol in isooctane as eluent. Separated components were characterized by comparison with the retention times of pure materials, together with analysis of collected fractions by uv absorption, peroxide analysis, and where possible by mass spectrometry or ir spectroscopy using the KBr "eye" technique.[15]

Approximate quantum yields for the xenon arc irradiations were calculated from the kinetic data, the spectral distribution of the source,[16] and the extinction coefficient of the aromatics.

Results and Discussion

PPH Films Containing Polynuclear Aromatics. The high volatility of the PNA compounds leads to their rapid loss from PPH films during the xenon arc irradiations (sample temperature ~42 °C). To minimize this loss, films presaturated with PNA's and reference films were irradiated inside sealed LDPE bags containing ~0.1 g of the compound in question. The aromatics were not in direct contact with the PPH films. Use of the bags caused only an ~10% drop in incident irradiation on the PPH films at wavelengths above 290 nm, and negligible deterioration of the LDPE bags occurred within the lifetimes of the PPH samples.

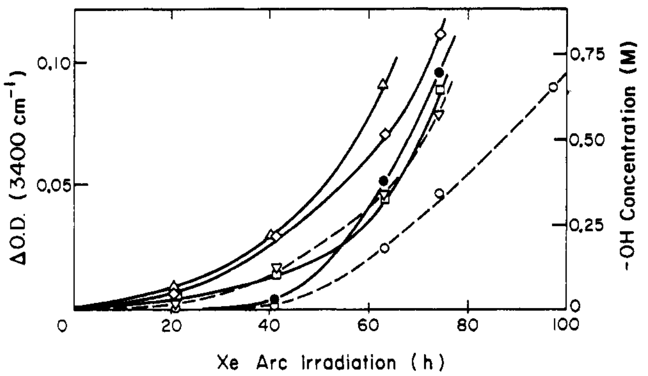


Figure 1. Photooxidation of treated polypropylene film (22 μm) xenon arc irradiation in air: (○) hexane extracted immediately before irradiation; (●) air equilibrated, >10 days; (△) absorbed anthracene (5 × 10^{-3} M); (□) absorbed naphthalene (2 × 10^{-2} M); (▽) absorbed anthraquinone (3 × 10^{-4} M); (◇) absorbed 9,10-dimethylanthracene endoperoxide (5 × 10^{-4} M).

The effects of various PNA compounds and their derivatives on the photooxidation of PPH films are compared with air equilibrated (>10 days) and freshly extracted film in Figure 1. Data for the build-up in the 3400-cm^{-1} ir absorption only (largely due to OOH groups[17]) are shown, together with OH concentrations calculated from an ir extinction of 70 M^{-1} cm^{-1}.[17] Very similar kinetic curves were recorded for the build-up in carbonyl products (~1715 cm^{-1}).

From Figure 1, the hexane extracted film (undetectable concentrations of PNA's) is significantly more stable than the air equilibrated film. The film sensitivity to photooxidation in the early stages of irradiation (≲50 h) decreases in the sequence: anthracene (5 × 10^{-3} M) > 9,10-dimethylanthracene endoperoxide (5 × 10^{-4} M) > anthraquinone (3 × 10^{-4} M) ≃ naphthalene (2 × 10^{-2} M) > air equilibrated > hexane extracted. Despite the relatively high initial concentrations of these aromatic additives, all were undetectable by uv or fluorescence spectroscopy after ~30 h of xenon irradiation. Separate dark experiments showed that naphthalene was rapidly lost from the film sample at 45 °C (30% loss in ~2 h) even though it was mounted in the LDPE pouch containing naphthalene crystals. A 50% loss of anthracene was observed in ~2 h Xe arc irradiation by means of uv and fluorescence spectroscopy. Control film samples in the Weather-Ometer but shielded from irradiation lost only 10–15% in ~2 h owing presumably to thermally induced migration and evaporation.

The most important results from Figure 1 are that the endoperoxide (or its products) is an effective sensitizer, whereas the anthraquinone, although sensitizing, is much less efficient. The interconversion of these aromatic materials on uv exposure is discussed in subsequent sections.

Model Alkane Photooxidations. The importance of trace amounts of PNA's as photooxidation initiators was also demonstrated in model systems. Concentrations of naphthalene, phenanthrene, and anthracene similar to those detected in polyolefins were added to separate isooctane solutions of squalene (>C=C< concentration ~0.05 M, similar to that detected in PPH[3]). The build-up in oxidation products (hydroperoxides from the isooctane and squalene, plus endoperoxides) with irradiation time is shown in Figure 2. Anthracene is the most effective sensitizer, and was itself destroyed completely within ~2 h. In contrast uv spectroscopy showed that naphthalene loss was negligible (<5%) in 20 h irradiation, whereas a ~50% drop in phenanthrene occurred in this period. In the absence of squalene or polynuclear aromatics, isooctane was not oxidized by xenon arc irradiation, and in the absence of squalene, hydroperoxide was undetectable (<1 × 10^{-4} M) after ~10 h of uv exposure of each PNA solution in isooctane.

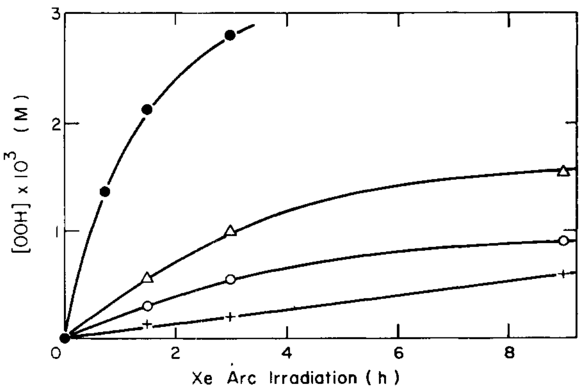


Figure 2. Sensitized oxidations of squalere solutions. Squalene 0.05 M in air saturated spectro isooctane; xenon arc irradiation in 0.1 cm path quartz cells. Sensitizer: (●) anthracene (1 × 10^{-5} M); (△) phenanthrene (1 × 10^{-4} M); (○) naphthalene (1 × 10^{-3} M); (+) none.

Anthracene Photolysis in the Liquid Phase. The photolysis products from air-saturated anthracene solutions are strongly solvent and concentration dependent.[18,19] The effect of solvent is shown in Figure 3. In isooctane, xenon arc photolysis initially gives a high yield of the 9,10-dimer, dianthracene, whereas in Freon 113, roughly equimolar yields of endoperoxide, anthraquinone, and anthracene dimer are formed. In both solvents anthracene loss is complete in <2 h even when a filter transmitting only >340 nm is employed, and the rates of anthracene loss lead to a quantum yield of ~1.9 × 10^{-2}mol Einstein^{-1}. All of the products are photosensitive when exposed to the full xenon arc although anthraquinone is destroyed relatively slowly. This can be seen in the Freon 113 data where the initial long wave exposure was followed by irradiation with the full arc. Both dimer and endoperoxide were destroyed in ~15 h under these conditions to give a ~90% yield of anthraquinone (based on the initial anthracene concentration). A separate irradiation of a sample of pure dimer (from an anthracene/isooctane irradiation) in Freon 113 at long wavelength (>340 nm) for 15 h gave ~30% endoperoxide, ~30% anthraquinone, and complete dimer destruction.

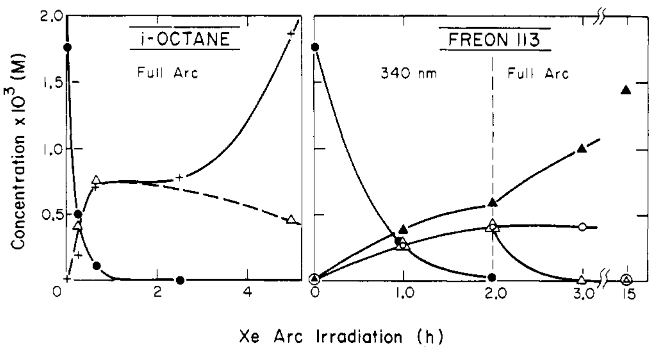


Figure 3. Photolysis of anthracene. Air saturated solutions in 0.1 cm cells, xenon arc irradiation with filters shown: (+) total (OOH + endoperoxide), by iodometry; (●) anthracene (from OD at 374 nm); (○) endoperoxide (from HPLC and iodometry); (△) dimer (from HPLC); (▲) anthraquinone (from HPLC).

The observed products can be rationalized by the tentative Scheme II, although additional transient intermediates may be involved. In isooctane (RH), route A to dimer appears to dominate whereas in Freon 113 both routes A and B appear to be equally important. Bowen[18] has suggested that dimerization proceeds only from the singlet state, because anthracene fluorescence is strongly quenched by solvents giving little dimer. Stevens and Algar[6] have shown that quenching by $^3O_2$ to give $^1O_2$ involves mainly the triplet excited state of the donor. The quantum yield for anthracene loss given in Table I was calculated from the initial rates shown in Figure 3.

9,10-Dimethylanthracene Photolysis in the Liquid Phase. Hindering the 9 and 10 positions of anthracene prevents dimerization[18,19] and simplifies the photooxidation scheme. Product build-up for various irradiation conditions is shown in Figure 4. In air saturated Freon 113, for long wavelength irradiation (>340 nm), 9,10-dimethylanthracene is rapidly destroyed to give a quantitative yield of endoperoxide. Full arc irradiation of the endoperoxide caused its rapid destruction, with the formation of an ~80% yield of anthraquinone (after 15 h). This was confirmed by HPLC, with mass spectrometric identification of the eluted main

Scheme II

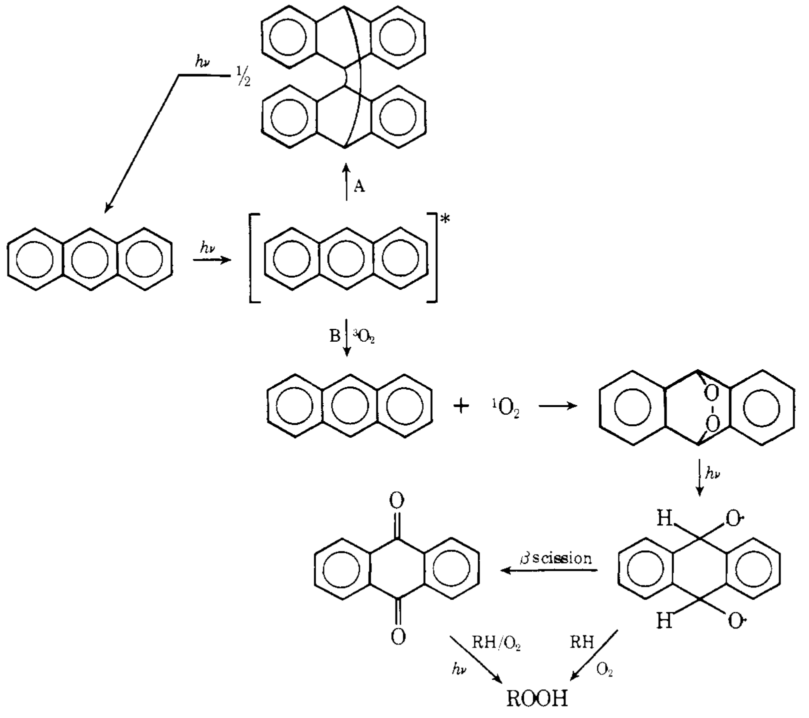


Table I
Quantum Yields for the Photolysis of Polynuclear Aromatic Compounds

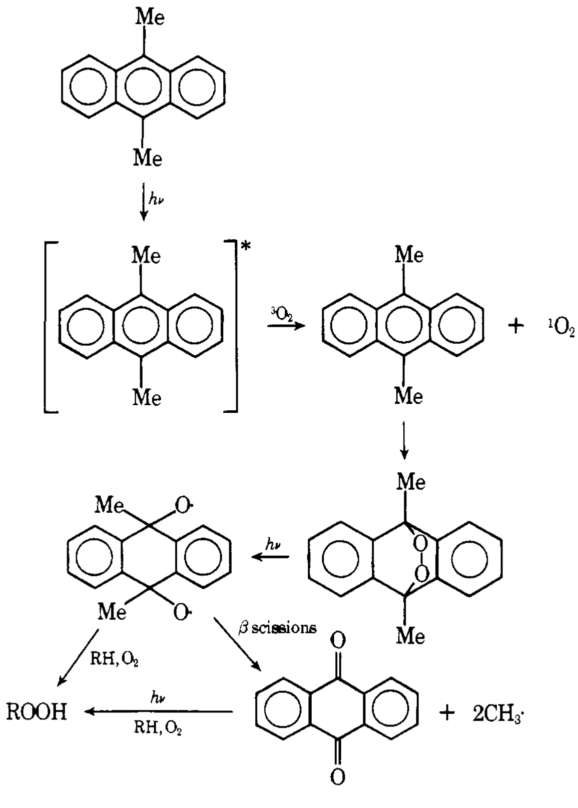
Compd	ϕ_{loss}, mol Einstein^{-1}	Solvent
Anthracene	~0.019	Isooctane, Freon 113
9,10-Dimethylanthracene (DMA)	~0.021	Isooctane, Freon 113
DMA endoperoxide	~2[a]	Freon 113
Anthraquinone	~0.004	Isooctane

[a] Probably greater than unity because of an underestimation of the extinction coefficients above 290 nm for this very weak absorber.

product. In isooctane the rapid 9,10-dimethylanthracene loss is accompanied by a rapid build-up in peroxides (presumably largely endoperoxide, plus some octylhydroperoxides) on long wavelength irradiation. Subsequent full arc irradiation causes a further rapid build-up in a peroxidic product, most likely a hydroperoxide resulting from attack on the isooctane by the alkoxy biradical produced by cleavage of the endoperoxide. Only ~10% anthraquinone was found after full arc irradiation.

The observed products from 9,10-dimethylanthracene can be rationalized by Scheme III. The full xenon arc irradiation of an anthraquinone solution in isooctane did in fact lead to a rapid build-up of hydroperoxide and complete loss of the quinone in ~10 h.

Scheme III



Quantum yields calculated from the initial rates in Figure 4 for the photolysis of 9,10-dimethylanthracene and its oxidation products are shown in Table I. The value for endoperoxide photolysis is surprisingly greater than unity. This anomaly probably results from an underestimate of the uv absorption of this weakly absorbing compound ($\epsilon \sim 10$ cm^{-1} M^{-1} at 310 nm).

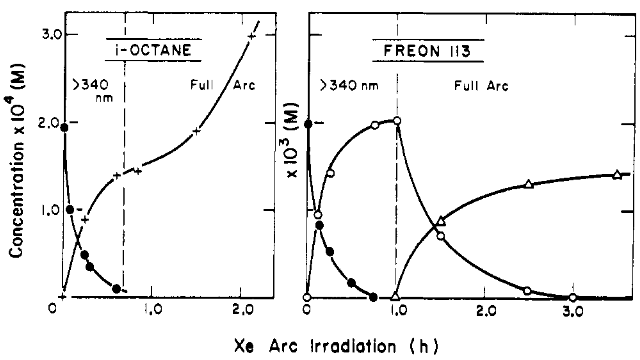


Figure 4. Photolysis of 9,10-dimethylanthracene. Conditions as in Figure 3: (+) total (OOH + endoperoxide) by iodometry; (●) 9,10-dimethylanthracene (from OD at 396 nm); (○) endoperoxide (from HPLC and iodometry); (△) anthraquinone (from HPLC).

Polynuclear Aromatics and PPH Photoinitiation. Pivovarov et al.[5] have previously reported that naphthalene and phenanthrene can photosensitize radical formation in PPH and polyoxymethylene, whereas anthracene retards radical formation. However, these results, which were attributed to biphotonic processes, were obtained for film samples at 77 K with full mercury arc irradiation in the absence of oxygen. Our film data were obtained for longer wavelength (>290 nm) irradiations at 38 °C in the presence of oxygen when biphotonic processes will be unlikely because of the shorter excited state lifetimes resulting from the faster decay at higher temperatures and the $^3O_2$ quenching of excited states.

From both the sensitized photooxidation of PPH films (Figure 1) and the liquid phase data (Figure 2) it is apparent that anthracenes and (less efficiently) naphthalene can effectively promote the photooxidation of hydrocarbons. This sensitization might result from $^1O_2$ generated by the PNA compounds (which then gives hydroperoxide by attack on unsaturation in the polymer) or from direct radical formation from the oxidation products of the PNA compounds. From the data shown in Figure 1, it is apparent that anthraquinone and especially the endoperoxide can effectively sensitize. The quinone has been previously reported to readily sensitize PPH photooxidation[22] and vinyl polymerization[23] by free radical formation.

Dimer formation from the photolysis of unsubstituted anthracene dominated in the alkane solvent. However, dimer formation can be expected to be much less important because of the low concentrations of anthracenes in PPH samples and also from the rigidity of the polymer matrix which will reduce the mobility of the PNA molecules.

Previously phenanthrene has been shown to be an inefficient sensitizer (or even a retarder) of PPH photooxidation.[3] In fact it is possible that phenanthrene and anthracene may both sensitize polymer photooxidations and scavenge radicals,[5,20,21] radical scavenging dominating for phenanthrene, sensitizing dominating for anthracene.

An appraisal of the relative importance of polynuclear aromatic photoinitiation by $^1O_2$ generation compared to that by radical formation from oxidation products can be made based on quantum yields reported in this work and literature values, combined with calculated light absorption parameters. The relative importances of these initiation modes and those from several other potential initiators are compared in detail in part 2 of this two part series.[24] However, it is of interest to note at this stage that several very effective PPH uv stabilizers such as Ni(II) oximes, substituted benzotriazoles, 2-hydroxybenzophenones, and nitroxides are known to efficiently quench excited states of PNA compounds.[25]

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Initiation of Polypropylene Photooxidation. 2. Potential Processes and Their Relevance to Stability[1a,2a]

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ABSTRACT: The relative importance of various potential photoinitiation processes in commercial polypropylene articles is examined, based on literature values for impurity concentrations and quantum yields and on a study of the photooxidation kinetics in the early stages of degradation. The low hydroperoxide levels detected in polypropylene films and fibers were estimated to adequately account for the observed photosensitivity, although polynuclear aromatic compounds ($^{1}\mathrm{O}_2$ sources) and Ti residues may contribute to a limited extent. From a simple kinetic analysis of the early stages of photooxidation, it is apparent that extreme purification of polypropylene to enhance uv stability is futile and that uv stabilizer packages must include either a radical scavenger or a hydroperoxide decomposer.

Despite an intensive study during the past 20 years of the photodegradation of polyolefins by sunlight, the key photoinitiation processes have yet to be firmly established. A knowledge of these processes is of obvious relevance to the development of uv stabilizers for the polyolefins. However, the photoinitiation question is complicated by the fact that "pure" polyethylene and polypropylene (PPH) (i.e., free of dyes, pigments, and other deliberately or adventitiously incorporated additives) do not themselves absorb terrestrial sunlight ($\gtrsim$290 nm).

Chromophoric impurities can be introduced during many steps in the manufacture of polyolefin articles: during polymerization (Ti, Al from the Ziegler–Natta catalyst,[2b] $>\mathrm{C{=}O}$ from carbon monoxide impurities[3]), during melting and extrusion (OOH, -O-O-, and $>\mathrm{C{=}O}$ from thermal oxidation[4–6]), and during the storage of the polymer at ambient temperatures [polynuclear aromatic (PNA) compounds absorbed from the urban atmosphere[7] or OOH, O-O, and $>\mathrm{C{=}O}$ from O_3 attack on residual unsaturation[8]]. In addition the charge transfer complex formed between oxygen and the saturated polymer can weakly absorb ultraviolet (uv) wavelengths and it has been suggested that this absorption results in the generation of free radicals directly[9] or from a photosensitive hydroperoxide intermediate.[10] All of these species reputedly can absorb at wavelengths >290 nm, generate macroalkyl radicals either directly or indirectly, and so potentially initiate the photooxidative degradation.

In this paper, quantum yields from our own work and other published data are combined to give estimated rates of initiation from several key potential initiators in the commercial polymer. Kinetic measurements made in the early stages of photooxidation are also combined with these estimated values in an attempt to give an overall view of the importance of different initiators and the importance of the initiation step in determining the lifetime of uv stabilized and unstabilized PPH articles under outdoor exposure conditions.

Experimental Section

Commercial isotactic PPH film (Enjay, 25 μm) was Soxhlet extracted with acetone for 48 h immediately before vacuum drying and use to remove processing antioxidants and absorbed PNA compounds. After vacuum drying, acetone residues were undetectable by ir at $\sim$1720 cm^{-1} on a 64-layer thickness of film (i.e., below 1×10^{-4} M). Film samples were photooxidized with a xenon arc Weather-Ometer (Atlas 6000 W, Pyrex inner and outer filters). Hydroperoxide build-up in the irradiated films was monitored by iodometry[4] on up to 0.2-g samples which were initially dissolved in peroxide free decahydronaphthalene (2.0 ml) at 130 °C for 30 s and then rapidly cooled to $\sim$25 °C, to give an extended precipitate of the polymer.

The PPH film examined contained 80 ppm Ti (by x-ray fluorescence analysis) and $(1.1 \pm 0.3) \times 10^{-4}$ M hydroperoxide. After Soxhlet extraction, PNA impurities were undetectable by fluorescence analysis, indicating less than 1/100 of their normal level from atmospheric exposure ($\sim 1 \times 10^{-3}$ M naphthalene, $\sim 1 \times 10^{-4}$ M phenanthrene and $\sim 1 \times 10^{-5}$ M anthracene[7]).

The effects of Ti residues on PPH photooxidation were investigated