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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 ($^1O_2$ 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] >C=O from carbon monoxide impurities[3]), during melting and extrusion (OOH, -O-O-, and >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 >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 ~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 ~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 (~1×10^{-3} M naphthalene, ~1×10^{-4} M phenanthrene and ~1×10^{-5} M anthracene[7]).

The effects of Ti residues on PPH photooxidation were investigated by compounding various Ti derivatives with unstabilized isotacic PPH powder (Monticatini Moplen, 20 ppm Ti itself) which was then pressed into ~30 μm films under an atmosphere of nitrogen.

Results

Initial Stages of PPH Photooxidation. For practical purposes, 25 μm PPH films are mechanically useless at hydroperoxide (PPOOH) levels of $\geqslant 0.1$ M[4] and most published measurements of hydroperoxide formation have been restricted to this level. The effects of extraneous initiation processes (other than hydroperoxide photolysis) will however only be apparent in the very early stages of photooxidation. Thus it is essential that reliable experimental data be obtained for the low hydroperoxide yields from the first 10–20 h of degradation. Iodometry on relatively large film areas allows meaningful PPOOH determinations down to $\sim 1 \times 10^{-4}$ M. At this level, the reliability is $\pm 0.3 \times 10^{-4}$ M, determined by the reagents blank and systematic contamination resulting from film handling. Data determined in the early stages of photooxidation of a freshly extracted, PNA free PPH film are shown in Figure 1. Up to ~60 h $[\mathrm{PPOOH}]_t{}^{1/2}$ is apparently linear in time (t).

The photooxidations of other commercial film samples also gave data for PPOOH build-up which fitted the half-order kinetics in the early stages. The initial hydroperoxide level in commercial PPH samples varied quite widely from 1 to 20×10^{-4} M, the level roughly correlating with the number of years since extrusion.

Effects of Ti Compounds. Although Ti can have several oxidation states and give compounds absorbing strongly in the near uv and visible, the published literature on the sensitizing effectiveness of Ti compounds is contradictory.[11-13] In our own work additional Ti compounds ($TiCl_4$, isopropyl titanate, or a $TiCl_4/AlEt_3$ catalyst mixture) were incorporated into PPH, either by compounding with PPH powders (initially 20 ppm Ti) which were then pressed into films or by diffusion into films ($TiCl_4$ vapor). However, up to 100 ppm of these Ti compounds, or their atmospheric reaction products, caused negligible increase (only 10 h advancement) in the photosensitivity of these films. Higher levels of Ti did sensitize, especially when the $TiCl_4/AlEt_3$ mixture was used, but the concentrations were then well beyond the normal Ti levels (5–100 ppm) residual in commercial PPH samples. Furthermore the photooxidation sensitivity of several different commercial films ranging from 20 to 95 ppm Ti showed no correlation with Ti content.

Discussion

Speculation on the Importance of Photoinitiation Processes. (i) Oxidation Products and Trace Metals. In an attempt to establish the relative importance of the various chromophores found in commercial PPH samples (but excluding the PNA compounds for the moment), values for the quantum yield (ϕ) for radical generation, estimated concentration (C), and calculated rate of free radical generation for a series of important chromophores are collected in Table I. The ϕ values are drawn from the literature cited, although concentrations were determined experimentally by x-ray fluorescence (Ti), iodometry (OOH, peroxide), ir spectroscopy (>C=O), or uv spectroscopy (charge transfer absorptions[9]). Upper limit values on concentrations indicate that the species were below the detection limit of the technique. The rate of radical generation under noon summer sunlight (d[X·]/dt) for each species was calculated from the respective values of ϕ, C, the known uv extinction coefficients (ϵ_λ) of the chromophore, and the spectral intensity of noon summer sunlight (I_λ)[14] from expression 1.[4,5]

$$d[X\cdot]/dt = 2.303[C]\,\phi \int_{290\mathrm{nm}}^{\lambda_{\max}} I_\lambda \epsilon_\lambda \qquad (1)$$

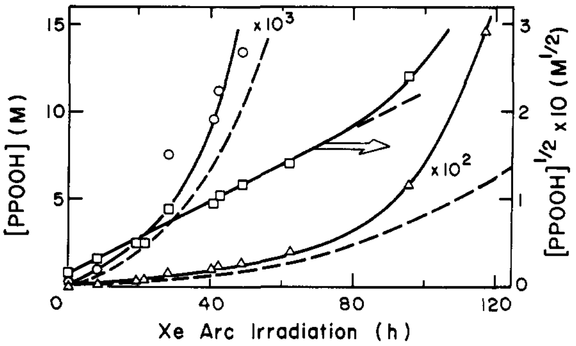


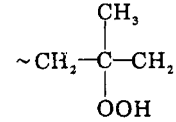
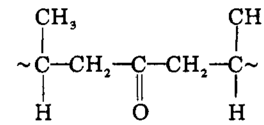
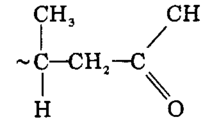
Figure 1. The photooxidation of PPH film. Freshly extracted 25 μm Enjay film, stabilizer free. Hydroperoxide concentrations by iodometry: (○) hydroperoxide concentrations times 10^3; (△) hydroperoxide concentrations times 10^2; (- - -) calculated base photooxidation curve for very low rates of photoinitiation by initial impurities; (□) half-order dependence of [PPOOH] build-up on irradiation time.

The sample thickness (l) was chosen to be 20 μm (a common film or fiber thickness) and the integration was made numerically at 10-nm intervals from 290 nm up to a wavelength $\lambda_{\max}$ at which the absorption of the chromophore became negligible (<5% of the maximum value above 290 nm). Expression 1 is an approximation but is valid for the chromophores considered here, where the absorptions (i.e., $\epsilon_\lambda[C]l$) are all below 0.01.

Before speculating on the importance of the calculated rates of radical generation listed in Table I, it must be emphasized first that these are order of magnitude calculations and second that no account has been taken of the efficiency with which the cited radical produced by the chromophore can initiate the oxidation of PPH by generating free (i.e., noncage) polypropylene peroxy ($PPO_2\cdot$) radicals. $PPO_2\cdot$ radicals are key intermediates in the chain oxidation of PPH and propagate to give *tert*-hydroperoxide groups along the backbone.[14,15] Free $PPO_2\cdot$ radicals may propagate over 100 times or more before termination.[15,16] All of the photoinitiation processes will generate radical pairs which may recombine (as expected for the products from ketone A, Table I) or combine with macroalkyl radicals (generated from attack on PPH) so that any initiation of photooxidation will be inefficient. Scissions producing mobile fragments (·OH, $CH_3\cdot$) will be more efficient sources of free $PPO_2\cdot$ than scissions yielding macroradicals. In addition some ϕ values were derived from model liquid phase systems and could be significantly reduced (by recombination for example) in the solid polymer.

Despite the reservations cited above, it is possible to draw some meaningful conclusions from Table I. In calculating the rate of radical production from the $PPH–O_2$ charge transfer complex, the maximum literature[9] ϕ and uv absorption vaues for alkane–O_2 charge transfer complexes were used. Nevertheless, the rate of radical generation is three to four orders of magnitude below those of other chromophores and can be regarded as unimportant in commercial PPH articles. The low rates of radical production from the Norrish Type I cleavage of macroketones in PPH[5] together with the anticipated facile recombination of macroradicals and efficient oxygen quenching of excited ketones[17] (section ii) indicate that >C=O photocleavage should be of low importance in the initiation of polyolefin photooxidation. This conclusion is now supported by a growing volume of experimental data which has been recently reviewed.[18] The photocleavage of the macroketones by the Norrish Type II process which gives molecular products is quite efficient for terminal methyl ketones (B)[5] but can result in only a slight drop in molecular weight with the elimination of acetone.[5,18] Various carbonyl species

Table I
Photoinitiating Chromophores in Polypropylene (PPH) Articles

Chromophore/ reactive species	ϕ,[a] mol Einstein^{-1}	Estimated concn, M[b]	Rate of photolysis product formation,[c] M s^{-1}
C.T. complexes			
$\text{+}CH_2-CH(CH_3)\text{+} \ldots O_2$	$\sim 0.02^{9}$ (liquid)		3×10^{-11} (free R·)
Catalyst residues			
$Ti(OBu^t)_4$	$\sim 0.02^{28}$ (liquid)	$3–30 \times 10^{-4}$	$1.4–14 \times 10^{-8}$ (free Bu-O·)
TiO_2	0.4^{27} (liquid) suspension		$2–20 \times 10^{-8}$ (free R·)
Oxidation products			
 $\sim CH_2-C(CH_3)(OOH)-CH_2\sim$	$\geqslant 2^{4}$ (solid)	$1–20 \times 10^{-4}$	$0.7–14 \times 10^{-9}$ (caged PPO· + ·OH)
PP—O—O—PP	2^{41} (liquid)	$<1 \times 10^{-4}$	$<2 \times 10^{-10}$ (caged PPO·)
 $\sim CH(CH_3)-CH_2-C(=O)-CH_2-CH(CH_3)\sim$ (A)	0.16^{5} (solid)	$<1 \times 10^{-4}$[d]	$<7 \times 10^{-10}$ (caged PP·)
 $\sim CH(CH_3)-CH_2-C(=O)CH_3$ (B)	0.02^{5} (solid)	$<1 \times 10^{-4}$[d]	$<7 \times 10^{-11}$ (caged PP· + CH_3·)

[a] Quantum yield for radical generation from chromophore, with associated reference. Solid and liquid refer to conditions employed in ϕ determination. [b] In commercial PPH film and fiber. [c] During noon outdoor exposure, calculated from ϕ values in column 2, uv extinction coefficients of the chromophores, and the spectral distribution of terrestrial sunlight. Rates for free species equivalent to the expected oxidation rates. Efficiency of oxidation chain initiation from the caged photolysis products not known. [d] From ir on multiple layers of commercial film.

do accumulate during the course of the PPH photooxidation. However, the carbonyl concentration is always less than 10% of the PPOOH level, up to the point of brittle failure.[4,15,16]

Hydroperoxide and Ti species appear to be potentially the most important sources of free radicals in the initial stages of the uv irradiation of PPH from the data shown in Table I. The photolysis of solid PPH containing OOH groups has been found to result in efficient cleavage to give ·OH and a tertiary macroalkoxy radical.[4] β scission of the macroalkoxy (PPO·) group causes extensive carbonyl group formation together with backbone scission.[4] The practical importance of OOH groups in the photodegradation will in fact be even greater than that indicated in Table I. All of the potential sources of initiation will produce OOH groups, either by the direct attack of the primary radicals on the polymer and O_2 interception of radicals or by ${}^1O_2$ generation followed by >C=C< attack (section ii), so that OOH must rapidly become the dominant chromophore in the photooxidizing polymer even if it is initially present at a negligible level. The dominant importance of OOH groups is discussed in detail in section iii. Peroxide groups appear to be present at a much lower concentration than OOH groups and consequently contribute less to radical generation.

Both Ti and Al residues occur in commercial PPH films and fibers in concentrations of 5–100 ppm (Ti) and 10–100 ppm (Al). Only Ti compounds absorb intensely above 290 nm, and Al contributions have been neglected. Table I suggests that both tetraalkyl orthotitanates and titanum dioxide can generate radicals extremely efficiently on sunlight exposure. Both of these compounds may result from the termination of the Ti–Al catalyst system by the addition of an alcohol followed by reaction with atmospheric moisture. Irich[11] has shown that there is a good correlation between the efficiency with which TiO_2 suspensions initiate the photooxidation of 2-propanol and the photosensitizing ability of the TiO_2 in polypropylene. However, the importance of orthotitanates in photoinitiating PPH oxidation is less well established. Cicchetti et al.[12] have found that tetrabutyl orthotitanate can generate butoxy radicals quite efficiently in the liquid phase and produces Ti^{3+} compounds which absorb even more intensely in the near uv than do Ti^{4+} compounds and can further initiate. In contradiction to these findings, Balaban et al.[13] have found that the termination of a Ziegler–Natta polymerized PPH with 2-propanol, which was suggested to produce tetraisopropyl titanate, gave a relatively photoinactive catalyst reside.

In contradiction to our previous conclusions[40] which were based on literature data, our experimental results now indicate Ti compounds (orthotitanates, tetrachloride, catalyst mixture or their hydrolysis products) are insignificant contributors to photoinstability at the 100 ppm level. However, the importance of Ti(II), -(III), and -(IV) residues on the photooxidation of PPH requires further investigation before their true importance can be firmly established.

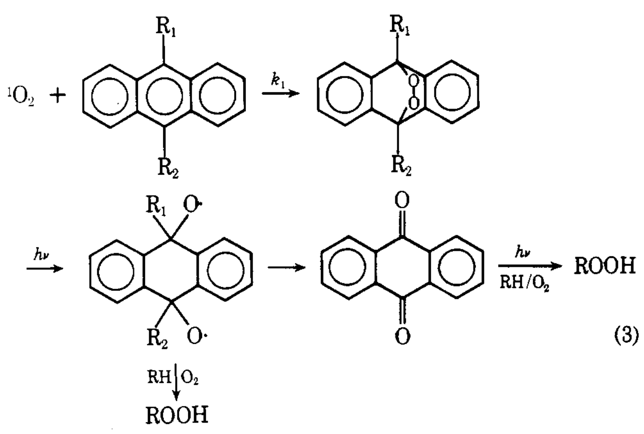
(ii) Polynuclear Aromatics and ${}^1O_2$ Generation. We have previously shown that anthracene, and to a lesser extent naphthalene, can sensitize PPH photooxidation, whereas phenanthrene is ineffective.[2a,19] These compounds are apparently absorbed by polyolefins from the urban atmosphere[7,19,20] to concentrations of $\sim 1 \times 10^{-3}$ M (naphthalene), $\sim 1 \times 10^{-4}$ M (phenanthrene), and $\sim 1 \times 10^{-5}$ M (anthracenes).[7] All three PNA compounds can generate singlet oxygen (${}^1\Delta_g$, ${}^1O_2$) on excitation (reaction 2),[21,22,23] and anthracenes can themselves rapidly react with ${}^1O_2$ to give first endoperoxides which in turn photolyze to give anthraquinone probably via a reactive biradical (reaction 3).[2a] k_1 for anthracene and 9,10-dimethylanthracene are 1.5×10^5 and 2.1

Table II
Generation of Reactive Species from Polynuclear Aromatics (PNA) in Polypropylene

Chromophore	Concn in PPH, M	ϕ·loss,[a] mol Einstein^{-1}	Calcd initial rates PPH[b]	Calcd initial rates M s^{-1}
Anthracene	$\sim 1 \times 10^{-5}$	~ 0.019	$-d[\text{anthracene}]/dt$[c]	$\simeq 2 \times 10^{-8}$
			$d[\text{OOH}]/dt$[d]	$\simeq 3 \times 10^{-7}$
9,10-Dimethylanthracene (DMA)	$\sim 1 \times 10^{-5}$	~ 0.021	$-d[\text{DMA}]_0/dt$[c]	$\simeq 4 \times 10^{-8}$
			$d[\text{OOH}]/dt$[d]	$\simeq 6 \times 10^{-7}$
DMA endoperoxide	$\sim 1 \times 10^{-5}$[e]	~ 2	$d[\text{R}\cdot]/dt$[c]	$\simeq 1 \times 10^{-9}$
			$-d[\text{endoperoxide}]/dt$[c]	$\simeq 1 \times 10^{-9}$
Anthraquinone	$\sim 1 \times 10^{-5}$[e]	$\sim 4 \times 10^{-3}$	$d[\text{R}\cdot]/dt$[c]	$\simeq 2 \times 10^{-9}$
			$-d[\text{anthraquinone}]/dt$[c]	$\simeq 2 \times 10^{-9}$
Naphthalene	$\sim 1 \times 10^{-3}$		$d[\text{OOH}]/dt$[d]	$\simeq 5 \times 10^{-9}$
Phenanthrene	$\sim 1 \times 10^{-4}$		$d[\text{OOH}]/dt$[d]	$\simeq 1 \times 10^{-7}$

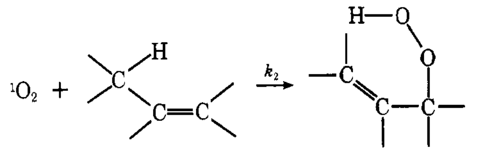
[a] Values observed in isooctane or Freon 113 from ref 2a. [b] Calculated for concentrations found in commercial PPH films for noon summer sunlight exposure. [c] From published ϕ values and rate constants in the liquid phase. [d] Calculated from quantum efficiencies for $^1O_2$ formation of ~ 0.5 (polynuclear aromatics). k_2 (reaction 1) assumed $\sim 1 \times 10^6$ M^{-1} s^{-1},[42] [C=C] $\sim$ 0.05 M, and $^1O_2$ deactivation rate constant in PPH $\sim 1 \times 10^5$ s^{-1}.[26] [e] After precursor completely converted with 100% efficiency.

$$\text{PNA} \xrightarrow{h\nu} [\text{PNA}]^* \xrightarrow{^3O_2} \text{PNA} + {}^1O_2 \qquad (2)$$



(3)

$\times 10^7$ M^{-1} s^{-1}, respectively.[24] Both the endoperoxide and anthraquinone can photolyze to give radicals[2a] and initiate hydrocarbon oxidation.[2a] Furthermore the $^1O_2$ from reaction 2 may diffuse to a >C=C< site in the polymer (residual >C=C< level in PPH ~0.05 M[19]) and react to give an allyl hydroperoxide[25] (reaction 4) before deactivating back to $^3O_2$ ($\tau_{1/2}$ for $^1O_2$ in PPH $\sim 1 \times 10^{-5}$ s[26]).



(4)

To assess the importance of the PNA impurities as photoinitiators, it is then necessary to consider both direct radical formation from the photooxidation products of anthracenes and also PPOOH formation from the unsaturation in PPH by attack of $^1O_2$ generated because of the presence of PNA compounds. The anthracene concentration ($\sim 1 \times 10^{-5}$ M) usually detected in PPH can only oxidize to give at best 1×10^{-5} M of endoperoxide, which can in turn photocleave to 1×10^{-5} M anthraquinone.[1] Table II lists the anticipated rates of radical formation from eithe of these products ($1\text{–}2 \times 10^{-9}$ M s^{-1} assuming 100% yields from anthracene in each case) during exposure to sunlight. However, these rates are somewhat below those anticipated from, for example, OOH photolysis in commercial PPH samples (up to 1×10^{-8} M s^{-1}, Table I) so that photolyses of the anthracene derivatives are apparently of relatively low importance as sources of photoinitiation in most commercial PPH samples.

The rates of OOH group formation via $^1O_2$ attack on residual polyolefin unsaturation may be estimated if the quantum efficiency of $^1O_2$ generation from the sensitizers is known. Stevens and Algar[21] have shown that $^1O_2$ only results from $^3O_2$ quenching triplet PNA states. Oxygen quenching of these triplets occurs at close to the diffusion-controlled rate in the liquid phase[22] and will represent the major deactivation route for these aromatic triplets in the air saturated, rigid polymer matrix.[27] Thus the efficiencies of $^1O_2$ formation from the anthracenes, phenanthrene, and naphthalene in air saturated PPH can be taken as the quantum efficiencies of intersystem crossing (~0.5 mol Einstein^{-1} in all cases[28]). Published quantum yield values for $^1O_2$ generation from air saturated PNA solutions are within ~50% of this value.[29,30]

Calculated rates of OOH formation from PNA compound generated $^1O_2$ attack on >C=C< are collected in Table II. Hydroperoxide formation from naphthalene and phenanthrene (which are destroyed relatively slowly during irradiation of PPH films) will continue for many hours. Over 10–20 h exposure, both naphthalene and phenanthrene may yield appreciable OOH concentrations ($\sim 2 \times 10^{-4}$ and 4×10^{-3} M, respectively). However, these concentrations are an order of magnitude below the OOH yield ($\sim 3 \times 10^{-2}$ M) from the photolysis for a comparable period of time of the initially present OOH itself (assuming an average kinetic chain length of 10 for peroxy radical propagation[16] and the upper initial rate of radical generation from OOH shown in Table I). In contrast, the anthracenes can only produce $^1O_2$ for 1–2 h before being themselves completely oxidized. Nevertheless anthracene could theoretically yield $\sim 1 \times 10^{-3}$ M of hydroperoxide in this time, within the range of hydroperoxide concentrations found experimentally in unirradiated PPH samples ($1\text{–}20 \times 10^{-4}$ M).

Ketonic groups were only previously considered as radical sources in PPH (Table I, section i) but can also act as $^1O_2$ sources within the polymer.[25,30] An upper limit on the rate of hydroperoxide generation from the molecular process involving $^1O_2$ (from $^3O_2$ deactivation of >C=O*) and >C=C< can be calculated if the quantum efficiency of $^1O_2$ generation from an excited macroketone is assumed. $^1O_2$ probably only results from ketone triplet quenching.[31] Oxygen quenching of the phosphorescence from macroketones is reported[32] to be very effective, even at low O_2 partial pressures, and oxygen has been found to quench the photocleavage reactions of ketones in solution at approximately the encounter frequency.[17] Yang and Feit[33] have found that product formation from the triplet state dominates in 2-hexanone photolysis, so that a quantum efficiency for $^1O_2$ formation close to the quantum yield for macroketone photolysis (~0.1 mol Einstein^{-1} [5]) seems reasonable for air saturated PPH. However, the estimated rate of OOH production ($<3 \times 10^{-10}$ M s^{-1}) from ketone-generated $^1O_2$ (assuming $<1 \times 10^{-4}$ M $>C{=}O$, and the conditions listed for Table II) is negligibly small in comparison with the rates for the anthracenes and phenanthrene (cf. Table II).

The chalking of paints by TiO_2 pigments has been correlated with $^1O_2$ photogeneration by the TiO_2.[34] However, the relative importance of radical photogeneration from TiO_2 and $^1O_2$ generation has not yet been established.

(iii) Photooxidation Kinetics and the Photoinitiation Problem. The preceeding discussion based on quantum yields for possible initiation processes allows some meaningful semiquantitative conclusions to be reached. However, an analysis of the photooxidation kinetics in the very early stages should yield more substantial quantitative information on the photoinitiation process.

Based on a simple reaction scheme

$$? \xrightarrow{h\nu} PPO_2\cdot \qquad \text{rate} = R_i \tag{5}$$

$$PPOOH \xrightarrow{h\nu} 2PPO_2\cdot \qquad \text{rate} = 2f\phi I_a/\Delta V \tag{6}$$

$$PPO_2\cdot + PPH \xrightarrow{k_p} PPOOH + PP\cdot \tag{7}$$

$$PP\cdot + O_2 \longrightarrow PPO_2\cdot \qquad \text{fast} \tag{8}$$

$$2PPO_2\cdot \xrightarrow{k_t} \text{termination} \tag{9}$$

the observed rate of PPOOH formation (d[PPOOH]/dt) should be given by

$$\frac{1}{\Delta V}\,d[PPOOH]/dt = k_p[PPH](2\phi f I_a/\Delta V + R_i/\Delta V)^{1/2}/(2k_t)^{1/2} - \phi I_a/\Delta V \tag{10}$$

R_i and $2f\phi I_a$ are the rates of generation of free (i.e., uncaged) $PPO_2\cdot$ from extraneous initiation and from PPOOH photolysis, respectively. I_a is the total light intensity absorbed by PPOOH, and f is the efficiency with which radicals escape geminate recombination to propagate via reactions 7 and 8. ΔV is the volume fraction of sample undergoing photooxidation and corrects for the nonoxidizable crystalline content and for the effects of oxidation in for example surface layers.

For the weak PPOOH uv absorption, as in expression 1, $2f\phi I_a/\Delta V$ is given by the summation $4.606\,\phi f \Sigma I_x \epsilon_x \cdot [PPOOH]/\Delta V$ which for convenience can be reduced to $A[PPOOH]/\Delta V$. For the early stages when the kinetic chain length is long (>10) the $\phi I_a/\Delta V$ term in expression 8 becomes negligible, and (8) can be integrated to give at time t

$$\left([PPOOH]_t + \frac{R_i}{A}\right)^{1/2} - \left([PPOOH]_0 + \frac{R_i}{A}\right)^{1/2} = \frac{k_p[PPH]t}{2}\left(\frac{\Delta VA}{2k_t}\right)^{1/2} \tag{11}$$

If R_i is negligible $[PPOOH]_t^{1/2}$ will be a linear function of t, with an intercept $[PPOOH]_0^{1/2}$, which gives the PPOOH concentration initially present in the PPH sample. This behavior is clearly shown by the data in Figure 1. From regression analysis (excluding the zero time point), the half-order plot gives an intercept of 1.3×10^{-2} $M^{1/2}$, a slope of 5.78×10^{-7} $M^{1/2}\,s^{-1}$, and a correlation coefficient of 0.973. From the intercept $[PPOOH]_0$ is 1.7×10^{-4} M, in good agreement with the experimentally measured value of $(1.1 \pm 0.3) \times 10^{-4}$ M. A slope value can also be calculated from experimental constants and literature date. For solely tert C–H attack (21 M), $k_p/(2k_t)^{1/2}$ is 1.7×10^{-4} [35], ϕ is ~1[4], and the summation $2.303\Sigma I_x \epsilon_x$ is 2.7×10^{-6} einstein $M^{-1}\,cm^{-3}$ for xenon irradiation and the PPOOH chromophore whence the calculated slope is $4.1 \times 10^{-6}(f\Delta V)^{1/2}$. A value of ~0.16 for f has been reported for atactic polypropylene,[15,16] and we have found values of ~0.1.[36] Using $f = 0.1$, the experimental and calculated slope parameters lead to a ΔV of 0.2, a reasonable value considering that the film is ~60% amorphous and that we have previously shown that photooxidation is predominant in a 2 μm surface layer on each side of the film.[37] Kinetic measurements on othe commercial and laboratory PPH film and fiber samples containing a wide range of initial hydroperoxide concentrations have been made in our laboratories. These data were all consistent with expression 8, and the rates of hydroperoxide formation showed a 0.5-order dependence on the incident intensity.[36]

Niki, Decker, and Mayo[15,16] have suggested reaction sequences similar to 7 to 9 to explain PPOOH formation during atactic PPH oxidation initiated by γ rays or a thermal initiator. The overall oxidation process is greatly complicated by the fact that $PPO_2\cdot + PPO_2\cdot$ is not necessarily terminating, and a high proportion of terminations within the cage involve primary peroxy radicals which result from alkoxy β scission.[15,16] However, only $PPO_2\cdot$ radicals which escape from the cage (with efficiency f) can propagate to give PPOOH, so that the simplified scheme is adequate to describe PPOOH formation in the absence of inhibitors or of impurities causing first-order termination.

Karpukhin and Slobodetskaya[38] in their detailed review of the photochemical oxidation of polyolefins used a reaction scheme very similar to reactions 5 to 9 and derived an expression analogous to eq 10. They attempted to fit published date to their kinetic expressions but were restricted to data collected at high degrees of photooxidation.

If the linearity of the $[PPOOH]^{1/2}$–t plot at short irradiation times (<50 h) can be taken as verification of the simple reaction scheme (steps 5 to 9), these kinetics lead to some very pertinent conclusions. First the effects of extraneous photoinitiation other than by PPOOH can be predicted by the substitution of various values of R_i in expression 11. For example, the use of $R_i/A = 2 \times 10^{-4}$ M (i.e., equivalent to an extra 2×10^{-4} M PPOOH at zero time) generates a plot closely paralleling the linear plot in Figure 1 at >20 h but curving quickly to the $[PPOOH]_0^{1/2}$ value at zero time. Thus the linear plot in Figure 1 implies that the PPOOH initially present in the film can entirely account for the initiation at zero time and that the photooxidation follows the expression 11 ($R_i = 0$) up to ~60 h irradiation.

In addition the effects of extreme PPH purification on PPH photostability can be predicted. For very pure PPH film where $[PPOOH]_0 \rightarrow$ zero, the calculated oxidation curve for a film under the same irradiation conditions as the Enjay film, and with the same f and ΔV (i.e., a slope of 5.78×10^{-7} $M^{1/2}\,s^{-1}$), cannot drop below the basic curve calculated from 11, where $R_i = 0$. This curve is plotted in Figure 1 for comparison with the experimental data. The presence of $\sim 1 \times 10^{-4}$ M of initial PPOOH has advanced the experimental oxidation curve by ~7 h over the basic curve. Extreme purification of any PPH sample, to reduce $[PPOOH]_0$ or R_i from other extraneous initiators, cannot suppress the photooxidation below that of the basic curve, which is an intrinsic property of PPH under the chosen irradiation conditions, and fixed physical form of the sample. Karpukhin and Slobodetskaya[38] reached a similar theoretical conclusion but lacked the data at low degrees of photooxidation needed to substantiate their conclusion. The enhancement of uv stability by the extreme purification of PPH appears to be futile, and the cost and effort would be better spent on stabilizer additives. This conclusion is largely consistent with the reported insensitivity of PPH photostability to processing, storage, and preirradiation treatments reported by Wood and Kollman.[39]

The linearity of the $[PPOOH]^{1/2}$–t plot beyond ~50 h is probably fortuitous. For the xenon arc irradiation employed, the kinetic chain length can be calculated at each PPOOH concentration from literature values of the parameters in expression 10. Assuming $\Delta V \sim 0.2$, the kinetic chain length is >10 only at <50 h irradiation. Beyond 50 h, the neglected $\phi I_a/\Delta V$ term in expression 10 will become important and should cause deviations in $[\mathrm{PPOOH}]_t$ *below* the base curve in Figure 1. The rapid increase in the experimental $[\mathrm{PPOOH}]_t$ values *above* the base curve at >70 h could result from large changes in the kinetic scheme, perhaps due to high local concentrations of oxidation products.

(iv) Kinetic Scheme and Stabilization. The simple kinetic scheme (5 to 9) leads to some interesting conclusions regarding the anticipated effectiveness of different types of uv stabilizers which have been suggested in the literature.[40]

(a) Energy Quenchers. PPOOH excited states are dissociative and cannot be quenched.[18] Thus only the extraneous initiation R_i might be decreased by a quencher. However, the foregoing arguments lead to the conclusion that the maximum anticipated amounts of extraneous initiation should not advance the photooxidation curve by more than 10–20 h. Thus any stabilizer which *solely reduces* R_i will have only marginal effectiveness, certainly in reducing the initial rates of photooxidation and possibly also in determining the total photooxidative lifetime.

(b) $^1O_2$ Quenchers. Hydroperoxide formation via $^1O_2$ addition to allyl methylenes will increase $[\mathrm{PPOOH}]_0$ but large $[\mathrm{PPOOH}]_0$ values ($>1 \times 10^{-3}$ M) are required to significantly increase the rate of oxidation of unstabilized PPH beyond that of the base curve. A uv stabilizer which operates solely as a $^1O_2$ quencher will be only marginally effective.

(c) Hydroperoxide Decomposers. A stabilizer which reduces the initial PPOOH concentration in commercial articles but cannot significantly reduce the PPOOH formed as a result of photooxidation within the time scale of the oxidation will be only marginally effective. However, if the stabilizer can destroy the PPOOH which builds up during the photooxidation either during the irradiation period or during intermediate dark periods, PPH lifetime will be significantly enchanced. The decomposition products from stabilizer–PPOOH reaction must not of course be other effective sensitizers or the stabilizer effectiveness will be nullified.

(d) Radical Scavengers. The extreme sensitivity of PPH to photooxidation results from the long kinetic chain lengths at low rates of initiation (e.g., ~110 at 1×10^{-4} M OOH for the Xe arc irradiation conditions). Efficient radical scavenging (PPO·, PPO·, or $\mathrm{PPO_2\cdot}$) will lead to a dramatic improvement in uv stability, and in fact many of the best PPH uv stabilizers such as the tetramethylpiperidines (and their associated nitroxides) probably operate predominantly by this route.[40] However, it must be remembered that a free radical scavenger can only operate as an effective uv stabilizer when that scavenger is itself thermally and photooxidatively stable. A number of hindered phenols, for example, do not meet these criteria and it is for this reason that they fail to protect polymers from actinic degradation, rather than from a failure of the radical scavenging concept.[40]

(e) Synergism. The induction period due to a radical scavenger InH will be proportional to $[\mathrm{InH}]_0/(R_i + 2\phi f I_a)$. Thus any additional stabilizer which can reduce R_i, $[\mathrm{PPOOH}]_0$, or the incident light intensity will synergistically enhance the protection offered by a uv stabilizer package which contains an effective free-radical scavenger. For example $^1O_2$ effects may improve the effectiveness of a radical trap or OOH decomposer, so that a $^1O_2$ quencher may show synergism when used with these dominant types of uv stabilizers.

Conclusions

(1) The low hydroperoxide level detectable in a commercial unstabilized PPH sample is alone adequate to account for the photoinitiation kinetics.

(2) Other extraneous impurities which can contribute (but to a lesser extent than OOH) to the photoinitiation processes in unstabilized, commercial PPH samples, include PNA compounds (as $^1O_2$ sources) and possibly Ti compounds.

(3) Initiation by O_2–PPH charge transfer complexes, carbonyl impurities, and peroxide groups is probably insignificant.

(4) The early stages of photooxidation can be explained in terms of a simple kinetic scheme, which indicates that the practical levels of initiators found in commercial PPH do not drastically enchance the photoinstability of PPH beyond its intrinsic level of instability.

(5) The kinetic scheme leads to the conclusion that only free radical scavengers or hydroperoxide decomposers can effectively photostabilize; the contributions by chromophore quenchers and $^1O_2$ deactivators are significant only in the presence of a radical scavenger.

(6) Although initiation by the various chromophoric impurities in unstabilized commercial PPH will not drastically enhance the photosensitivity, all of the extraneous photoinitiation processes *will* be important in reducing the lifetime of PPH samples protected by radical scavenging or hydroperoxide decomposing uv stabilizers.

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Cyclodextrin-Containing Polymers.
1. Preparation of Polymers

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ABSTRACT: The synthesis of polymers containing cyclodextrin residues on the side chain is described. Four monofunctional monomers, acryloyl-α-cyclodextrin (α-CD-A), acryloyl-β-cyclodextrin (β-CD-A), *N*-acrylyl-6-aminocaproyl-α-cyclodextrin (α-CD-NAC), and *N*-acrylyl-6-aminocaproyl-β-cyclodextrin (β-CD-NAC), were prepared by the reaction of *m*-nitrophenyl acrylate or its derivative and cyclodextrin. Acryloyl and *N*-acrylyl-6-aminocaproyl groups were found to be attached at one of the secondary hydroxyl groups of cyclodextrin. These monomers were polymerized in high yields except α-CD-A by a radical initiator to give water soluble polymers, which were purified by gel chromatography or dialysis. These monomers were also copolymerized with other water soluble monomers to give water soluble copolymers.

Cyclodextrins (cycloamyloses which are cyclic α-1,4-linked D-glucose oligomers[1]) display various characteristic chemical and physical properties[2] due to their cyclic nature when compared to the flexible open-chain analogues. The most specific property is their ability to form inclusion complexes in aqueous solution[3] as well as in the crystalline state.[4] The inclusion properties of cyclodextrins have been studied extensively to clarify the nature of the cavity, i.e., the driving force[5] for binding and the binding specificity. Cyclodextrins have also been studied as an enzyme model,[6] the results having disclosed the substrate specificities in the binding step as well as in the catalytic step based on the size of their hydrophobic cavities.

In order to obtain polymers equipped with substrate specificity caused by inclusion, it seems advantageous to study the behavior of cyclodextrins when incorporated into a polymer as a definite structural unit. In this paper we wish to report the preparation of cyclodextrin-containing polymers. To obtain linear polymers, it is necessary to prepare monovinyl derivatives of cyclodextrin. Since cyclodextrin has many primary and secondary hydroxyl groups, we used Bender's acylation technique,[6f] in which the reaction proceeds by way of inclusion and the acylation occurs selectively at one of the secondary hydroxyl groups under mild conditions.

Results and Discussion

Preparation of Monomers. Cyclodextrin-containing monomers were newly synthesized by the reactions shown in Scheme I. The main feature of this synthesis is the reaction of *m*-nitrophenyl esters and cyclodextrins. This procedure, first found by Bender et al.,[6f] was used because this reaction proceeds by way of inclusion, which would permit selective transesterification of cyclodextrin at one of the secondary hydroxyl groups under mild conditions, minimize multifunctional products, and suppress thermal polymerization.

In a typical synthesis, cyclodextrin was allowed to react with an equimolecular amount of *m*-nitrophenyl ester in carbonate buffer, pH 11, at room temperature for 5 min. The product was purified by gel chromatography on a Sephadex G-15 column[7] and, if necessary, was subjected to ultrafiltration using an Amicon UM-05 UF-membrane to remove sodium chloride. In the case of β-cyclodextrin monomers, final purification was carried out by a Sephadex G-15 column (2.5 × 200 cm). Elution diagrams were obtained by following cyclodextrin and monomer concentrations as shown in Figure 1. Small amounts of multifunctional products with higher extinction coefficients were eluted at the beginning of the main fraction. The extent of the reaction was limited by solubilities of the reactants to about 40% and the yield of the pure monomer was about 20%. All monomers except α-CD-A were chromatographically pure, giving satisfactory results in the elemental analysis as monofunctional products. α-CD-A was found to contain a small

Scheme I