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PHOTO-OXIDATIVE DEGRADATION OF POLYPROPYLENE AND STABILIZATION BY HINDERED AMINES

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Abstract - From a consideration of oxidative free radical reactions in solid polypropylene, it is concluded that only a small fraction of the peroxy radicals is expected to cause the bulk of the oxidation and need be scavenged for effective photo-stabilization. Most peroxy radicals terminate after only a few propagation steps with another peroxy radical descended from the same initiation event. The few that escape this "secondary cage" recombination produce long lived chains of very high kinetic length, which are easily scavenged. Tetramethylpiperidines and their products (nitroxides and substituted hydroxylamines) appear to photo-stabilize polypropylene by acting as inefficient scavengers of macroalkyl and macroperoxy radicals. In addition nitroxide association with oxidized domains is possible, together with decomposition of the grafted, substituted hydroxylamines in these oxidized regions.

INTRODUCTION

Certain hindered amines can confer outstanding resistance to sunlight on several classes of polymers.(1) These stabilizers and their products are largely non-absorbing in both the near ultra violet (UV) and visible regions. Effective hindered amines are secondary amines, which have no oxidizable hydrogens α to the amine group and produce nitroxides which do not self react. Currently the best known examples are based on 2,2,6,6-tetramethylpiperidine. A clear understanding of the mechanism(s) by which hindered amines photo-protect polymers is of obvious relevance to the optimization of these additives, as well as developing new generic classes of UV stabilizers. However before discussing stabilization mechanisms, it is essential to appreciate the complexities of solid state polymer oxidations.

The chain propagation reactions in polyolefins are mechanistically identical to the classical processes in liquid hydrocarbons (reactions 1 and 2 for polypropylene, PPH)(2,3,4). Reaction 1 is expected to be fast, and occur as

$$\mathrm{PP.} + \mathrm{O_2} \xrightarrow{k_1} \mathrm{PPO_2.} \qquad (1)$$

$$\mathrm{PPO_2.} + \mathrm{PPH} \xrightarrow{k_p} \mathrm{PPOOH} + \mathrm{PP.} \qquad (2)$$

rapidly as O_2 can diffuse to the macroalkyl radical (PP.)(4). The peroxy radical (PPO_2.) is expected to preferentially attack the tertiary C-H sites (3), at least in the early stages of oxidation, and reaction 2 is very slow [$k_p \sim 1 \times 10^{-3} M^{-1} s^{-1}$ at 25°C](4,5). Reaction 2 is in fact a composite of inter and α,γ-intra-molecular propagation steps, with the former expected to be ~ 3 times the slower of these processes(3). Although the propagation reactions are generally accepted, controversy still exists over the photo-initiation and radical termination reactions (2,5,6) and these processes will now be discussed in detail.

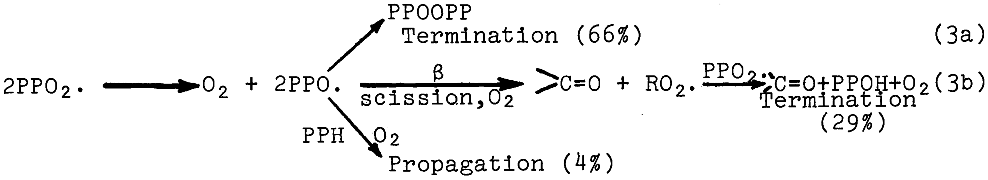
Initiation and Termination of Photo-oxidation

Pure polyolefins do not absorb beyond 200-220 nm. Absorption of solar near UV (>290 nm) results from impurities introduced into the polymer during synthesis, processing, and storage(6). The situation is complicated by the deliberate addition of thermal stabilizers, dyes, pigments, processing aids, etc. which may be or may become UV absorbing sensitizers of photo-oxidation. Ignoring these latter additives, photo-initiation is primarily from oxidation products resulting from processing. Based upon their concentrations in commercial PPH, their photochemistry and UV absorptions, these initiators may be ranked in order of decreasing importance(6,7):

$$-OOH > \rangle C{=}O > \text{polynuclear aromatics} \gg \text{polymer} - O_2 \text{ complexes.}$$

Although some Ti compounds can photo-generate free radicals(6,8), catalyst residues do not appear to be a major contributor at <100 ppm. Recently the $\rangle C{=}O$ sensitized decomposition of -OOH groups has been suggested to be an important initiation route for some polymers from liquid phase data(9,10). This process could be of increasing importance as carbonyl products accumulate during the oxidation, but has yet to be confirmed in the solid polymer. The importance of -OOH groups results not only from their production during processing by thermal or mechanical effects(11) but also from their production during the oxidative propagation step (reaction 2) following any initiation route which generates alkyl radicals.

Termination in hydrocarbon oxidations usually involves peroxy radical self-reactions at O_2 partial pressures above ∿200 torr(3,4). Self reactions of tertiary peroxy radicals are very slow and complex, giving a proportion of non-terminating products [reaction 3,(3)]. Additional fast termination results from the β scission of the macroalkoxy to give a primary macro-peroxy radical (RO_2. reaction 3b). The percentages are taken from ref. (3) and are for atactic PPH at 45°C with a thermal initiator.



Although the above-mentioned free radical processes in polypropylene are very similar to those observed in the oxidation of liquid alkanes, the solid state imposes constraints which complicate the application of simple liquid phase kinetic treatments to the photo-oxidation of the solid polymer. Several Russian workers have emphasized the importance of restricted segmental motion on radical propagation and termination(4,12,13,14). In particular Denisov(4) has proposed that radical transport through the polymer results from a combination of segmental motion, movement as a result of the peroxy propagation step (reaction 2) itself, and alkyl radical site migration by a hydrogen hopping mechanism. Treatments of peroxy self termination have stressed the restricted migration of radicals to encounter one another, which should lead to a time dependent $2k_t$ (reaction 3) based on an assumption of an initially random distribution of PPO_2.(12). In addition the behaviour of two peroxy radicals in close proximity in the encounter cage has been discussed(12). However these treatments ignore the important fact that radicals are always generated in pairs by the initiation processes. The progressive separation of a pair deserves very careful consideration, because of its important consequences on both initiation efficiency and termination.

If -OOH photocleavage is considered as the initiation event (reaction 4),(15) the primary radicals (PPO., .OH) from the efficient photo-scission of the O-O bond must largely attack the adjacent polymer matrix to generate macro-alkyl radicals (with PPOH and water). Although potentially mobile the .OH radical reacts at the encounter frequency(16) and so will attack the adjacent polymer immediately. Oxygen interception of a macro-alkyl radical (PP.) will produce a macro tertiary-peroxy radical. Extensive radical combination must take place within this initial polymer cage, before the first propagation step (reaction 2) occurs. This radical combination will greatly reduce the yield of peroxy radicals(3). Even after the escape of a PPO_2. pair from the initial polymer cage, the radicals cannot be considered as being randomly distributed throughout the polymer as assumed in conventional kinetic schemes. For the initial propagative cycles, there is a very high probability of self termination between the descendents from a given pair(17) because of their close proximity. This phenomenon which is known as the secondary cage effect has been recognized in the liquid phase, although it is of very short duration because of the rapid diffusive averaging of the radical population(18,19). In the highly viscous polymer matrix, separation of the radical pair is very restricted and the probability of secondary cage recombination (reaction 4b) remains high for long periods(17). It must be emphasized that scheme 4 is not intended to show stoichiometric processes but rather product sequences, and for simplicity ignores the complexities of reaction 3.

From a treatment of interpenetrating random walks originating from a common point (the initiation event), the probability of a propagating peroxy radical terminating with a descendent from the same initiation event may be calculated as a function of the total number of propagations of the radical pair(17). This dependence is a function of the probability of reaction (K) of a peroxy pair when their encounter spheres completely overlap. For simplicity the encounter sphere is defined as a sphere of radius equal to the displacement of the radical site within the duration of one propagative cycle (reactions 1 and 2)(17). Radical site displacement results from a combination of segmental diffusion, oxidative propagation and radical transfer reactions(4,13,14). Calculated probabilities of pair termination are shown in Figure 1 for K=0.8.

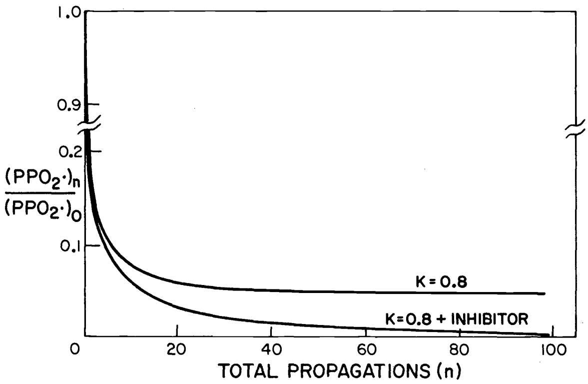
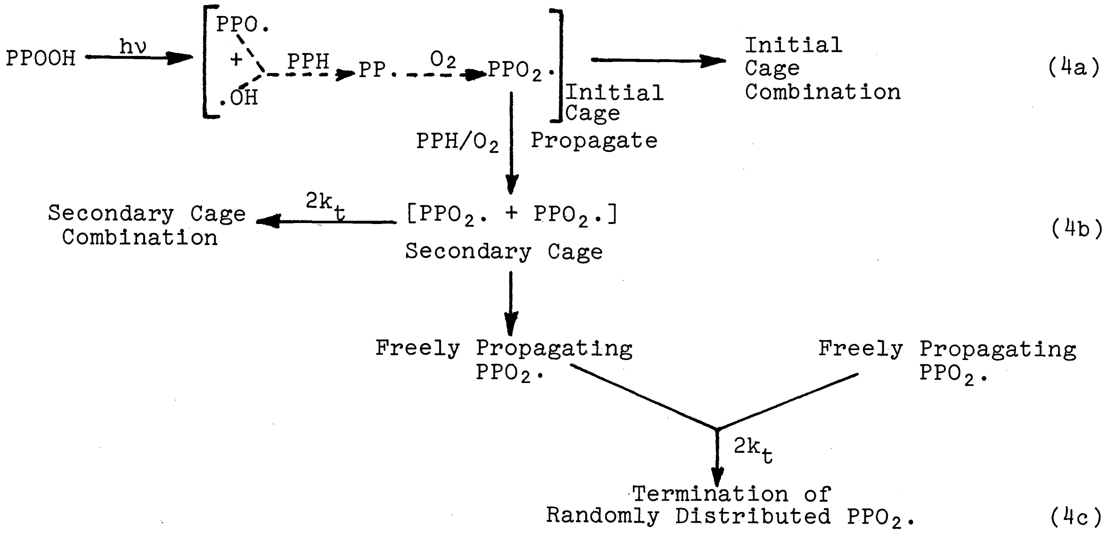


Fig. 1. Theoretical radical population during secondary cage combination. Peroxy concentrations based on the number which emerge from the initial cage process. Stabilizer assumed to scavenge at 1/40 of the rate of propagation.

Two important conclusions can be drawn from this figure. Firstly over 90% of the radical pairs will terminate within the secondary cage after <10 total propagations. Secondly a small fraction of radicals (∿4%) completely escape combination in the secondary cage. This small group of radicals will then propagate as completely "free" peroxy radicals for many thousands of steps before terminating with another peroxy radical (reaction 4c) and so be the major contributors to the formation of hydroperoxide groups.



Experimental support for the concept of secondary cage recombination is provided by electron spin resonance (e.s.r.) spectroscopy(17). A PPH film sample was pre-oxidized to 0.08M in -OOH groups by xenon arc irradiation in air. Samples of this PPOOH film were irradiated (λ>280nm) in air in the cavity of an e.s.r. spectrometer, with continuous rotation of the e.s.r. tube to improve the uniformity of radical generation within the film. The well characterized(3,20) PPO_2. signal was the only radical observed. Radical decay was then followed on interrupting irradation, essentially as described by Roginskii et al(14,20). After quite extensive irradiation (>10 min.) at 25°C, the observed radical concentration decayed slowly, following approximately second order kinetics (Figure 2), as expected for the recombination of randomly distributed PPO_2. If PPO_2. radicals are generated by only a brief irradiation (∿90 sec.) at -80°C, the radicals are stable for long periods. On quickly (<5 sec.) warming this sample to 25°C, PPO_2. decay is initially very rapid, with the rate then decreasing to a value similar to that of the extended irradiation at 25°C(Figure 2)(17).

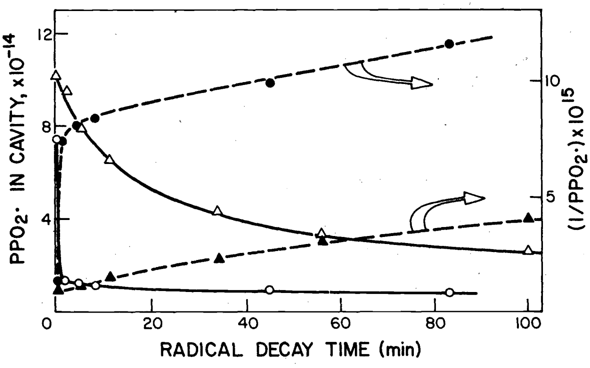


Fig. 2. PPO_2. decay at 25°C by e.s.r. spectroscopy. Isotactic PPH film irradiated directly in the cavity. Radical levels by double integration, and comparison with a nitroxide standard. Absolute concentrations not quoted because of some uncertainty in the uniformity of radical generation in the film. O● PPO_2. from 90s irradiation at -80°C; decay at 25°C. Δ▲ PPO_2. from >10 min. irradiation at 25°C.

The difference in the decay behaviour results from the fact that irradiation at -80°C will generate PPO_2. pairs, each radical being in close proximity to its partner as the rigidity of the polymer precludes PPO_2. propagation or termination. On warming to 25°C, the mobilized radicals tend to predominantly combine within the secondary cage, a fast process. Roginskii et al(14,20) have reported a similar departure from simple second order PPO_2. decay after a very brief light pulse, but have not explained its origin. Extended irradiation at 25°C will give a radical population dominated by the long lived PPO_2. which have already escaped secondary combination to become randomly distributed.

The shape of the PPO_2. decay curve after irradiation at -80°C and then warming to 25°C (Figure 2) is quite similar to the theoretical curve for K=0.8 (∿15% of the radicals decay very slowly by e.s.r., Figure 2, whereas ∿4% escaped secondary recombination, Figure 1). Further support for the choice of a K value in this range comes from the data of Mayo et al(3) who have reported that of the PPO_2. generated in a cage in atactic PPH, ∿84% recombine without propagation.

Measurement of PPO_2. decay after irradiation of a PPOOH sample as exploited by Roginskii et al(14,20,21) offers one of the most direct methods for estimating the apparent rate constants for PPO_2. decay in a system identical to the weathering polymer without the presence of additives. Complications inherent in previous work involving the use of low molecular weight thermal initiators [at 0.1 - 1.0M leading to segregation and plasticization problems (2,3,5)] and free radical scavengers [which may segregate from the polymer and/or associate with the initiator(2,3)] are avoided. The decay method does however require controlled irradiation of the sample to ensure uniform radical production. This necessitates irradiation of flat film samples outside the cavity in a machine such as a xenon arc Weather-Ometer (reproducing noon summer sunlight), or outdoor exposure. Isotactic PPH film samples (∿0.1g) were xenon arc irradiated to give 0.12M in -OOH groups (calculated assuming that only the amorphous phase is oxidized). When films were then quickly inserted into e.s.r. tubes, PPO_2. decay could be measured within ∿5 min of the ending of irradiation(22). A typical radical decay curve and second order plot are shown in Figure 3. The initial portion of the second order plot leads to an apparent $2k_t$ value of $8M^{-1}s^{-1}$ at 25°C. The curvature of the second order plot may result from some non-uniformity in PPO_2. concentrations or variations in the apparent $2k_t$ resulting from the dependence of PPO_2. self reaction on a diffusive process(12). Apparent $2k_t$ values derived from the later stages of the curves in Figure 3 should be essentially time independent, but unfortunately the very low PPO_2. levels at long times cannot be measured accurately enought to give reliable $2k_t$ values.

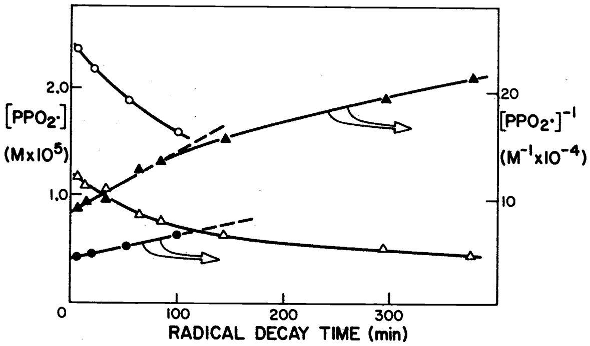


Fig. 3. PPO_2. decay at 25°C by e.s.r. spectroscopy. Δ▲ Isotactic PPH film. Decay immediately after irradiation in a xenon arc Weather-Ometer for ∿60h to 0.12M in -OOH groups. O● Atactic PPH powder. Decay immediately after γ-irradiation in air (30 min at 8000 rad. min^{-1}).

A similar procedure for the determination of "$2k_t$" can employ γ-irradiation. Peroxy decay following γ-irradiation of a low molecular weight, unoxidized atactic PPH powder in air is shown in Figure 3, and leads to "$2k_t$" ≃$3M^{-1}s^{-1}$. This "$2k_t$"value for the atactic PPH indicates that the low value observed in the isotactic film (∿$8M^{-1}s^{-1}$) did not depend on PPO_2. becoming trapped in or around crystalline domains(2). When a pre-oxidized isotactic film (identical to the xenon arc irradiated sample) was γ-irradated in air, PPO_2. decay was slower than observed after photo-oxidation ("$2k_t$"∿$1M^{-1}s^{-1}$). This difference between γ and UV irradiated isotactic films could result from localized radical concentrations in the UV irradiated film (resulting from highly localized chromophoric groups) whereas γ initiation is largely random throughout the polymer.

Various rate constants for PPH oxidation are collected in Table 1. Our

TABLE 1. Experimental Rate Constants^a (in Ms units) and f values^b for PPO_2. reactions in PPH

Parameter	Values (temperature, °C)			
	Ref(5)^c	Ref(2)^c	Ref(4,14,20)^d	This work^{c,d}
10^2k_p	0.4(45°)	8.3^e	0.05(25°)	-
$2k_t$	50(45°)	$1.2X10^{5e}$	5-170(25°)	1-8(25°)
$10^4k_p/(2k_t)^{½}$	5.7(45°)	2.3^e	>2.2(25°)	-
f^b	∿0.01(45°) DBPO	0.14(71°) BP	0.043(65°) PPOOH	0.0014(25°) PPOOH

a) Per tertiary C-H
b) Efficiency of generating propagating PPO_2. DBPO is di-tert-butyl peroxyoxalate BP in dibenzoyl peroxide
c) Atactic PPH
d) Isotactic PPH
e) Extrapolated to 45°C from 70-130°C data

apparent $2k_t$ values are smaller than those of Mayo(3,5) and Chien and Wang (2), possibly because of their use of low molecular weight thermal initiators and radical scavengers as well as their assumption of a statistical distribution of all radicals, as in the liquid phase. There is fair agreement between our values and those of Roginskii et al ($2k_t$=5M^{-1}s^{-1} for 0.1M PPOOH) (14) although they proposed that $2k_t$ decreases with increasing -OOH concentration.

Buchachenko(13) has proposed that experimentally derived $2k_t$ values have little firm mechanistic meaning because termination is largely determined by the diffusive-reactive migration of radical sites. Our own conclusions on primary and secondary cage processes support this proposal. Any observed $2k_t$ value will be highly dependent on the history of the radical population and the precise composition of the sample. The rapid termination of PPO_2. in the secondary cage will lead to high apparent $2k_t$ values, if $2k_t$ were estimated from the overall PPO_2. concentration. The propagation of oxidative chains in localized domains, followed by photo-initiation by -OOH photolysis in these domains will cause primary and secondary oxidation products to influence the rate and mechanism of photo-oxidation by, for example, introducing mobile low molecular weight peroxy radicals and/or primary and secondary peroxy radicals which terminate $\sim10^4$ times faster than tertiary peroxy radicals in the liquid phase(3). Thus a wide range of apparent $2k_t$ values must be expected, depending on the precise oxidation conditions, all values being "valid" within the context of the specific experimental conditions employed. In addition, $2k_t$ must always be a composite of values for all types of PPO_2. in the polymer system, including tertiary sites on the backbone, at chain ends, and on low molecular weight fractions, as well as contributions from all non-tertiary peroxy radicals and other terminating species. Thus the search for a "true" $2k_t$ value which rigorously defines the peroxy termination process in a semi-rigid polymer would appear to be futile, although the experimental values are of use if cautiously interpreted.

In irradiated, pre-oxidized PPH film samples, the overall rate of peroxy radical production following PPOOH photolysis (reaction 4) by xenon arc Weather-Ometer irradiation is given by

$$d[PPO_2.]/dt=0.6\text{X}10^{-6}[PPOOH]f \qquad (5)$$

The constant ($0.6\text{X}10^{-6}s^{-1}$) is derived from the spectral distribution of the arc and filters, the UV absorption of PPOOH and a primary quantum yield for radical production of 2(15). From expression 5 and the PPO_2. level at the end of irradiation (i.e. $[PPO_2]_o$ in Figure 3), the efficiency of formation of propagating PPO_2. radicals (f) following PPOOH photolysis may be calculated. For the photo-oxidizing film, the data in Figure 3 lead to f $\approx1.4\text{X}10^{-3}$. This value is appreciably lower than some other literature values collected in Table 1. The different f values may well result from the differing methods of determination. Our kinetic method of f determination will give a value approximating to the efficiency of production of PPO_2. radicals which result from radical escape from <u>both</u> the initial and secondary cages. In addition to the initial and <u>secondary</u> cage events shown in reaction 4(a,b) other radical destruction reactions may contribute to our low f value. For example radical attack on an adjacent oxidation site within an oxidized domain might also suppress f(4,14). Techniques employing moderate concentrations of radical scavengers(2,3) should approximate the f values for overall PPO_2. production from the <u>initial</u> cage. However it must be emphasized that it is the PPO_2. population <u>which</u> escapes <u>both</u> the initial and secondary cage self termination which propagates <u>extensively</u> and carry the bulk of the oxidation.

Shlyapnikov(23) has suggested that a "supercage" exists in polymer systems, where radicals have a high probability of combination. This concept is obviously similar to our concept of the secondary cage, but its implications were not explored further by Shlyapnikov. However two main conclusions from our considerations of photo-oxidation of the solid polymer are of special significance to the problem of stabilization. Firstly the efficiency of production of freely propagating PPO_2. (i.e. PPO_2. which escape the secondary cage, and carry the bulk of the photo-oxidation) is very low ($f\sim1.4\text{X}10^{-3}$) because the photolysis of a high percentage of -OOH groups produces radical pairs which terminate very quickly with little net gain in -OOH sites. A small percentage of PPO_2. escape the secondary cage and have enormous kinetic chain lengths. For example the $\sim$4% of all peroxy pairs which propagate freely (K assumed 0.8), application of conventional kinetics (assuming a random distribution) to these radicals at (say) 10^{-7}M predicts a kinetic chain length (KCL) of $5.5X10^4$ steps ($k_p \sim 2X10^{-3}$ and $2k_t \sim 8M^{-1}s^{-1}$ at 25°C). The average KCL of all $PPO_2.$ which escape the initial cage will then be ~2500 ($0.045X5.5X10^4$ + a small contribution from those $PPO_2.$ which quickly terminate within the secondary cage). It is only the freely propagating $PPO_2.$ (reaction 4) which must be scavenged in some way to prevent the acceleration of photo-oxidation. In the presence of even an inefficient $PPO_2.$ radical scavenger, this average KCL will be dramatically reduced. For example in the scavenging reaction, if k_{InH} [InH]/k_p[PPH] is only 0.025, the average KCL for -OOH production drops to 2.3. When combined with the low f value expected for

$$PPO_2. + InH \xrightarrow{k_{InH}} PPOOH + In.$$

escape from the initial cage, [~0.02(3)] this low KCL implies that the photo-oxidation cannot be self sustaining, more -OOH groups being destroyed than regenerated by the oxidative chain. The calculated effect of the weak scavenger on the proportion of $PPO_2.$ pairs remaining after a given number of propagations is shown in Figure 1(17). At each propagation step, there is a 1 in 40 probability of termination of $PPO_2.$ with the scavenger and the $PPO_2.$ level is progressively reduced (after 300 steps, 99.998% of the $PPO_2.$ have been destroyed). A lower K value will make the scavenger less effective. For example if K=0.5, the average KCL in the presence of the scavenger becomes 9.8, which again will be insufficient to replace -OOH wasted in the initial cage processes.

The combination of very low overall photo-initiation efficiency and long kinetic chain length make polyolefin photo-oxidations potentially much easier to retard by free-radical scavengers (which need only have low efficiency) than is expected from liquid phase photo-oxidation data. The migration of a peroxy site by a combination of propagation and segmental movement should allow the peroxy radical to move to a relatively immobile stabilizer(13). Although some -OOH groups must result from each propagation, those produced before peroxy encounter with the stabilizer can only represent a small fraction of the potential -OOH yield in the absence of a stabilizer. Emanuel(24) has suggested that the physical retention of a stabilizer in a polymer, and the resistance of the stabilizer to destructive side reactions is of greater importance than the effectiveness of the stabilizer in a specific stabilization reaction.

Photo-Stabilizer Reactions

Additives may inhibit the photo-oxidative degradation of polyolefins by four potential mechanisms: prevention of photo-excitation, deactivation of excited chromophores, destruction of chromophores or the scavenging of free radicals (25). The latter three mechanisms are most important for thin films and fibers, with the latter two being given progressively greater attention of late. As well as operating by one, or a combination of the above mechanisms, an effective, practical UV stabilizer, or its active products, must have adequate light stability, be non-sensitizing, have resistance to loss by volatilization, extraction and processing conditions and probably have an optimum diffusivity and compatability with the host polymer.

Most of the highly effective polyolefin photostabilizers are progressively destroyed during the lifetime of the irradiated polymer, usually as a result of peroxy and alkoxy radical attack(26). For certain UV stabilizers, the parent compound is destroyed very rapidly (within 20% of the total polymer lifetime), yet photo-oxidation is delayed for many hundreds of hours in an accelerated photodegradation test. This phenomenon is particularly marked in the case of the hindered amine family of UV stabilizers, based on 2,2,6,6-tetramethylpiperidine. Both the parent piperidine and its nitroxide when initially compounded with separate polypropylene samples are quickly destroyed by the UV irradiation of the sample and lost by volatilization. Both samples have a low, constant nitroxide level throughout most of the lifetime of the sample (about $1.5X10^{-4}$M, ~2% of the initial nitroxide or piperidine levels)(26). Stabilization by piperidine species is shown in Figure 4. The nitroxide in a freely suspended PPH film is rapidly lost in ~100h, but photo-oxidation only becomes evident at ~300h, while the unstabilized film oxidizes rapidly after ~60h.

From the well established reactions of piperidine species in model systems, reactions 6 and 7 are expected, where R. represents an alkyl radical(27,28).

$$>NH \xrightarrow[\text{or } ^1O_2]{\text{radical attack}} >NO. \qquad (6)$$

$$>NO. + R. \xrightarrow{k_7} >NOR \qquad (7)$$

In addition the substituted hydroxylamine ($>$NOR) has been suggested(29) to intercept peroxy radicals, with nitroxide regeneration (reaction 8). Photostabilization of a PPH film initially containing a nitroxide (or piperidine)

$$>NOR + R'O_2. \xrightarrow{k_8} >NO. + [R'OOR] \qquad (8)$$

must then occur in the presence of a low residual $>$NO. level and in the presence of the (grafted) substituted hydroxylamine ($>$NOPP).

Stabilization by the $>$NOPP species is shown in Figure 4 where a quite low

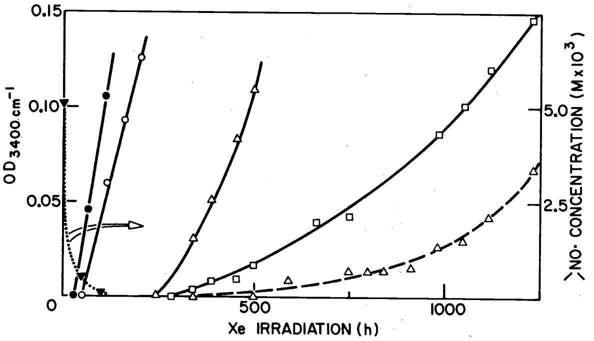


Fig. 4. Stabilization of PPH by piperidine species. Film samples (25 µm) irradiated in a xenon arc Weather-Ometer. Oxidation measured by -OH+-OOH accumulation in the infrared at 3400 cm^{-1}.

1) ○ Unstabilized PPH.
2) ● Unstabilized PPH, after 32h γ-irradiation under N_2 at 300 rad. min^{-1}.
3) -△- PPH with (initially) 5.0X10^{-3}M 4-oxo-2,2,6,6-tetramethylpiperidine-N-oxyl. Film irradiated uncovered.
4) □ PPH with 2.4X10^{-3}M 4-oxo-2,2,6,6-tetramethylpiperidine-N-oxyl. This nitroxide containing film was γ-irradiated (32h at 300 rad. min^{-1}) under N_2 before UV exposure. Nitroxide concentration after γ-exposure 5X10^{-5}M.
5) -△- As for (4), but film loosely held between quartz plates.
6) ▼ Nitroxide level in sample 3 from e.s.r. spectroscopy.

level of $>$NOPP was prepared by γ-irradiating a $>$NO. containing PPH film under N_2(30). After virtually complete loss of $>$NO. (by e.s.r.), the presence of the piperidyl groups in the polymer was confirmed by IR spectroscopy(30). In comparison when a similarly stabilized pre-γ-irradiated PPH film is placed between loose-fitting quartz covers, this sandwiched film only begins to oxidize rapidly at above $\sim$1000h(30). The difference between "free" and "sandwiched" $>$NOPP stabilized films must result from loss of $>$NO. and other piperidine intermediates by volatilization from the free film. The photo-oxidative lifetime of an unstabilized PPH film is little changed by being sandwiched between quartz plates, as compared to a free film. The γ-irradiation of a $>$NO.-free control film under N_2 caused a marked increase in light sensitivity (Figure 4). This appeared to correlate with the presence of long lived radicals in the γ-irradiated polymer which combine with O_2 when air was admitted to the sample.

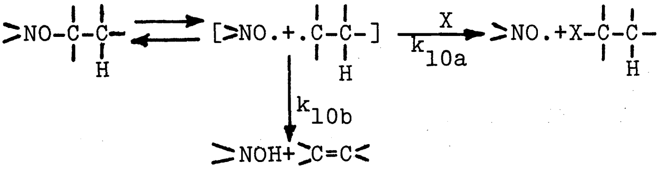
Reactions 7 and 8 complement the PPH oxidative propagation steps (reactions 1 and 2 respectively). However stabilization will depend on the values of the ratios $k_p[PPH]/k_8[>NOR]$ and $k_1[O_2]/k_7[>NO.]$, the lower each value the more effective being stabilization. From work on model, liquid-phase systems, lower limits for these ratios are $k_p[PPH]/k_8[>NOPP] > 22$ ($[>NOPP] < 5X10^{-3}M$, $[PPH]=25M$) and $k_1[O_2]/k_7[>NO.] > 140$ ($[>NO.] \sim 1.5X10^{-4}M$ $[O_2] \approx 8X10^{-4}M$)(28). From these ratios, $>$NO. and $>$NOPP can be expected to operate as only very weak radical scavengers in PPH oxidation. However from the secondary cage considerations, only a weak scavenger is needed to markedly reduce the very high kinetic chain lengths of freely propagating (i.e. randomly distributed) PPO_2.

The eventual grafting of the hindered amine to the PPH backbone by the reaction sequence 6→7→8 must compete with loss of the volatile amine and its intermediates from the irradiated polymer. This conclusion is supported by the observation that piperidine species appear to be very effective in photostabilizing partially oxidized polyolefins(26,31) in contrast to other classes of UV stabilizers such as the 2-hydroxybenzophenones and nickel chelates which have poorer UV stabilizing ability in oxidized as compared to unoxidized PPH samples.

Several other factors of piperidine chemistry may play a role in hindered amine photo-protection of polypropylene. For example a study of the N^{14} hyperfine coupling constant of nitroxides in liquids has shown that nitroxides at room temperature associate quite strongly with hydroperoxides as compared to alkanes (RH, reaction 9) (32). An association constant (K=[>NO....HOOR'][RH]/[>NO....RH][R'OOH]) of 26 was found with tert-butyl hydroperoxide and iso-octane. Thus if this same equilibrium persists in the solid polymer, up to 96% of the >NO. groups will associate with highly oxidized domains in the polymer. These >NO. will then be at a high local concentration in the zones where radicals will be generated by hydroperoxide photocleavage, and so much more likely to successfully compete with O_2 for the PP. than expected from the low, overall >NO. level.

$$[{>}\mathrm{NO....RH}] + \mathrm{R'OOH} \rightleftharpoons [{>}\mathrm{NO....HOOR'}] + \mathrm{RH} \qquad (9)$$

As well as the suggested reaction 8 between >NOPP and PPO_2., the substituted hydroxylamines have other important properties. We have extensively studied the thermal stability of model and macromolecular substituted hydroxylamines (33), and have confirmed both the decomposition to the hydroxylamine and olefin as reported by Bolsman et al(34) and the decomposition to reform nitroxide in the presence of an alkyl radical scavenger as reported by Kovtun et al(35). These reactions are shown in process 10 where X is an alkyl radical scavenger. In the absence of a scavenger only products from 10b are detected whereas in the presence of a scavenger such as O_2, reaction 10a dominates. For example $k_{10a} \simeq 40\ k_{10b}$ in a given solvent for the decomposition of 1-(2'-cyano-2'-propoxy)-4-oxo-2,2,6,6-tetramethylpiperidine(33). Both reactions 10a and 10b are strongly solvent dependent, rate constants increasing by a factor of about ten on going from cyclohexane to methanol or tert-butyl hydroperoxide. For example $k_{10a}=0.8\mathrm{X}10^{-4}s^{-1}$ and $k_{10b}=0.021\mathrm{X}10^{-4}s^{-1}$ in cyclohexane at 82°C in the absence and presence of dissolved air respectively; $k_{10a}=1.5\mathrm{X}10^{-7}s^{-1}$ in cyclohexane and $9\mathrm{X}10^{-7}s^{-1}$ in methanol at 23°C with both solvents air saturated(33).



$$\begin{aligned} &{>}\mathrm{NO}{-}\underset{|}{\overset{|}{\mathrm{C}}}{-}\underset{\mathrm{H}}{\overset{|}{\mathrm{C}}}{-} \rightleftharpoons [{>}\mathrm{NO.}+\mathrm{.}\underset{|}{\overset{|}{\mathrm{C}}}{-}\underset{\mathrm{H}}{\overset{|}{\mathrm{C}}}{-}] \xrightarrow[k_{10a}]{X} {>}\mathrm{NO.}+\mathrm{X}{-}\underset{|}{\overset{|}{\mathrm{C}}}{-}\underset{\mathrm{H}}{\overset{|}{\mathrm{C}}}{-} && (10a)\\ &\qquad\qquad\qquad \downarrow k_{10b} \\ &\qquad\qquad\qquad {>}\mathrm{NOH}+{>}\mathrm{C}{=}\mathrm{C}{<} && (10b)\end{aligned}$$

The dependence of the decomposition rate of substituted hydroxylamines on the polarity of the environment implies that >NOPP decomposition should be most rapid in highly oxidized domains in the polymer. We have observed the progressive reformation of >NO. from >NOPP (prepared by γ-irradiation of >NO. in PPH in the absence of O_2) when the film samples were immersed in tert.-butyl hydroperoxide(30). The half life for >NO. generation was ∿15 days. For >NOPP films stored in air or immersed in air saturated iso-octane, >NO. reformation was over ten times slower. However the formation of >NO. from >NOPP in the hydroperoxide is consistent with either reaction 10a or 10b because of the rapid reaction between hydroxylamines and hydroperoxides to form nitroxides(36). Thus further work is required to clarify the precise nature of the decomposition of >NOPP at ambient temperatures.

In conclusion, the hindered amines act as precursors to generate >NO. and grafted >NOPP species in the irradiated polymer. These products together can terminate many propagating chains. Association of the nitroxide with the oxidized domains of the polymer and >NOR decomposition in these polar domains may also play roles in hindered amine photo-stabilization processes. Although the >NO. and >NOPP species can be expected to act as only inefficient PP. and PPO_2. radical scavengers respectively, the role of secondary cage recombination of peroxy radicals in the solid polymer leads to the conclusion that only weak scavenging is adequate for effective photo-stabilization of polypropylene.

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