

POLYMER STABILIZATION BY HINDERED AMINES*

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Abstract - The mechanisms by which various hindered amines and their products stabilize photo-oxidizing polypropylene films have been investigated. Tertiary amines were found to be efficiently converted to secondary amines in oxidizing systems. Effective secondary amines were found to be converted to both nitroxides and grafted substituted hydroxylamines in the polymer matrix. The latter were directly identified by infrared spectroscopy and shown to be the dominant reservoir of piperidyl species during the bulk of the photo-oxidation. Secondary amines decompose the sequences of intra-molecularly bonded hydroperoxide groups in oxidized polypropylene whereas tertiary amines do not. These tertiary amines do however act as thermal antioxidants at moderate temperatures (<80°C). The role of association between piperidyl species and polypropylene oxidation products is discussed.

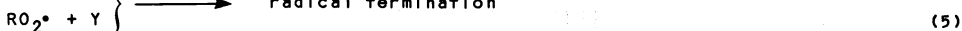
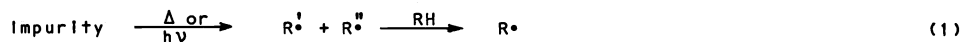
INTRODUCTION

All polymer degradation processes comprise an initiation event which may be followed by a sequence of propagation reactions if the initial event involves the generation of free radicals. Propagation ends upon radical deactivation or termination. Degradation normally implies loss of mechanical properties which stems from scission of the polymer backbone. Scission may occur during initiation, propagation or termination. In general degradation can be reduced by a) prevention of the initial event, b) interruption of the propagation reaction(s), c) introduction of a new termination process and/or d) reactive combination of polymer chains.

The above concepts apply to degradation initiated by heat, radiation, hydrolysis etc. Degradation which results solely or predominantly from the initial event is the most difficult to prevent, requiring a highly efficient interference with the initial event or a polymer chain combination process to retard degradation. Examples in this category include polyester hydrolysis and aramid photo-oxidation. Polyester hydrolysis can be retarded by reduction of catalyst levels (such as H⁺) or use of additives such as epoxides or carbodiimides (1) to promote chain recombination.

Aramid chain scission is a direct result of the absorption of an ultra-violet (UV) photon when the back combination of the primary radicals is hindered by oxygen interception of the radicals (2). Degradation can be prevented by reducing the incident UV flux with the use of a UV screen or possibly by deactivating the excited chromophores prior to scission.

The photo-oxidative and thermo-oxidative deterioration of polymers such as polyolefins, aliphatic polyamides, polyethers etc. are more complex. In all cases initiation involves the scission of an impurity (reaction 1), an impurity which is often present at a very low initial concentration.



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Direct or indirect attack by the primary radicals on the polymer matrix (RH) produces a macro radical R^* . Initiation is followed by consecutive propagation reactions (2 and 3) which may lead to the production of tens or even thousands of hydroperoxide groups (ROOH) before the propagation cycle is interrupted by a radical termination process (4 and 5). Termination may involve reaction with another radical or a compound which itself yields a stable radical. Hydroperoxide groups can themselves undergo thermal or photocleavage to reinitiate via reaction 1, and hydroperoxide quickly becomes the dominant initiator for several polymers even if it is not dominant at the onset of oxidation. Backbone scission results from the β -scission of alkoxy radicals produced both by cleavage of the hydroperoxide groups and by peroxy self-termination reactions (3).

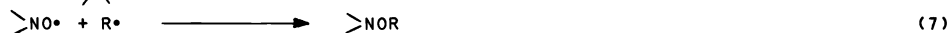
Based upon the reactions 1 to 5, it **should** be possible to inhibit these oxidative deteriorations by:

- destruction or deactivation of the dominant initiator (ROOH)
- prevention of propagation by scavenging R^* or RO_2^*
- combination of macro radicals.

Polypropylene (PPH) is one of the most photosensitive polymers in large scale use. Without stabilizers, embrittlement of films or fibres occurs after only a few months exposure to terrestrial sunlight. The photo-oxidation of PPH is consistent with reactions 1 to 5 with the macro-hydroperoxide (PPOOH) as the dominant photo-initiator (3). Several families of UV-stabilizers have been developed to protect PPH, the most successful of these being the hindered amines developed during the early 1970's. Low concentrations of these additives can extend the outdoor life of PPH articles by well over an order of magnitude when compared to unstabilized polymer. From our investigations of model and commercially important hindered amines in both model liquid-phase and polymer systems (PPH) we will present evidence that all of the above stabilization mechanisms (a-c) can operate with hindered amines based on 2,2,6,6-tetramethylpiperidine.

SECONDARY HINDERED AMINES: PHOTO-OXIDATION PRODUCTS

From studies of 2,2,6,6-tetramethylpiperidines in liquid phase systems the following key processes have been suggested (4-9)



Reactions (7) and (8) complement the oxidative propagation reactions 2 and 3. Reaction 8 is not well documented and may be a summary of a more complex sequence of reactions (see below). Model secondary piperidines ($>\text{NH}$), nitroxides ($>\text{NO}^*$) and substituted hydroxylamines ($>\text{NOR}$) have all been shown to stabilize photo-oxidizing PPH (4). Our recent aim has been to show the intermediacy of $>\text{NO}^*$ and $>\text{NOPP}$ species in photo-oxidizing PPH films stabilized by the commercially important, bifunctional amine bis (2,2,6,6-tetramethyl-4-piperidyl) decanedioate (HN--NH).

The generation of nitroxyl radicals from hindered amines has frequently been detected in photo-oxidizing systems by electron spin resonance spectroscopy (e.s.r.). The unambiguous detection of the substituted hydroxylamine species from PPH ($>\text{NOPP}$) is much more difficult. Its presence has usually been implied by indirect methods such as the chemical regeneration of $>\text{NO}^*$ after exhaustive extraction (7,8) although the chemical reactions are seldom definitive. Only spectroscopic techniques have the selectivity to identify a grafted species in a solid polymer matrix. We have combined the technique of Fourier Transform Infrared Spectroscopy (FTIR) with e.s.r. and liquid chromatography (HPLC) to identify and quantify extractable and grafted species produced from HN--NH during the photo-oxidation of PPH film. To allow the FTIR quantification of HN--NH conversion products it was found to be necessary to start with a quite high initial amine concentration (~ 0.7 wt%). This in turn leads to enormous film lifetimes ($>10,000$ h) under the xenon arc weatherometer exposure conditions used in all of our work. To enhance the rate of HN--NH reaction, PPH films were pre-oxidized to ~ 0.1 mol kg^{-1} in $-\text{OOH}$ groups by xenon arc exposure prior to diffusing the hindered amine into the films from hexane solution.

During irradiation of these pre-oxidized films, the following functional groups were quantified: $>\text{NH}$ (by FTIR at 1237 cm^{-1}), $>\text{NO}^*$ (e.s.r. on hexane extracts and on ex-

tracted film), $>NO-\dot{C}-$ (by FTIR, 1140 cm^{-1}), PPOOH (by FTIR, 3400 cm^{-1}) $-C(=O)-O-$ (by FTIR, 1738 cm^{-1}) $>NO-C(=O)-\dot{C}-$ (by FTIR, 1772 cm^{-1}). Species were quantified from FTIR spectra after the subtraction of the initial, PPH spectrum. Band assignments were made by comparison with known compounds dispersed in PPH or dissolved in hexane. (Recording IR spectra of compounds dispersed in KBr discs was found to be highly misleading because of large shifts in piperidyl absorptions caused by the salt matrix). The $>NO\cdot$ species in the film extracts were found to be the mono-nitroxide (HN-- $NO\cdot$) by HPLC. Grafted nitroxide (PPON-- $NO\cdot$) was detected by e.s.r. but was always at a very low level ($< 2\%$ of the initial $>NH$ level). The 1140 cm^{-1} assignment of the critical $>NO-\dot{C}-$ groups came from both the model compound formed by nitroxyl trapping of butyronitrile radicals and from the grafted product resulting from the γ -irradiation under nitrogen of a nitroxide dispersed in PPH film. The $>NO-C(=O)-\dot{C}-$ species were modeled by reacting acetyl chloride with the bis-hydroxylamine (HON--NOH).

The loss of $>NH$ end groups and PPOOH groups are shown in Fig. 1 together with the accumulation of other piperidyl species and the overall ester concentration. From this figure it is clear that the original $>NH$ groups are progressively destroyed with the formation of some $>NO\cdot$ and the grafted $>NOPP$ species which become the dominant piperidyl species. The approximate constancy of the ester level indicates that the inhibitor backbone is not destroyed or lost from the film by volatilisation. The total piperidyl ends accounted for (i.e. $>NH + >NO\cdot + >NOPP$) are less than the initial $>NH$ level. Part of this difference can be attributed to the formation of $>NO-C(=O)-\dot{C}-$ species based on the 1772 cm^{-1} absorption. This species may result from the nitroxyl scavenging of fragments from the photocleavage of ketonic species (reaction 9),

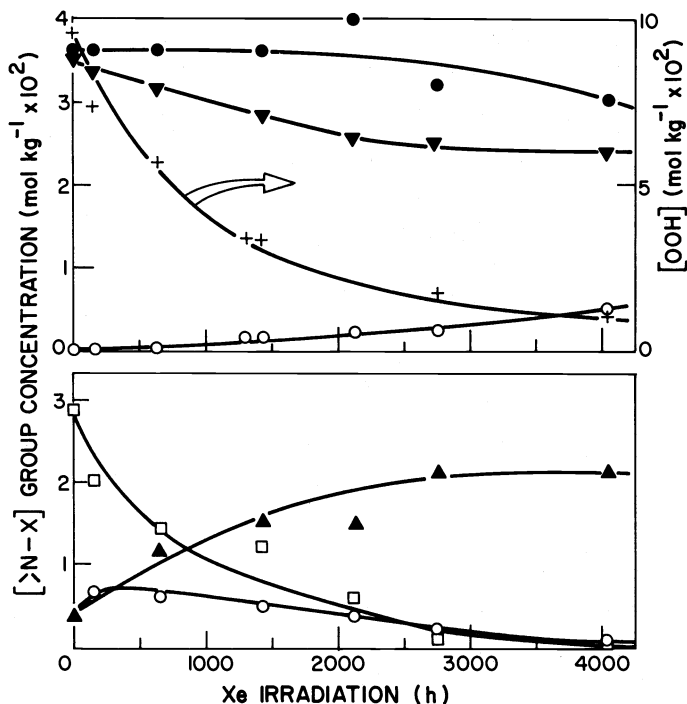
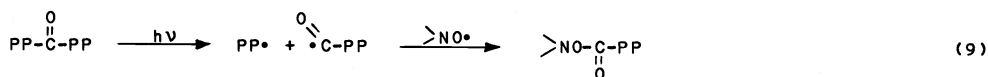


Fig. 1 Products from photo-oxidation in the presence of HN--NH
Pre-oxidized PPH film ($25\ \mu\text{m}$), $[PPOOH]_0 = 0.09\text{ mol kg}^{-1}$

Upper Fig. + PPOOH (from iodometry and FTIR at 3400 cm^{-1})
 0 $>N-O-C(=O)-\dot{C}-$ (from FTIR at 1772 cm^{-1})
 ▼ Total piperidyl end groups ($>NH + >NO\cdot + NOPP$)
 ● Total $-C(=O)O-$ (from FTIR at 1738 cm^{-1} concentrations given by $>N-X$ axis).

Lower Fig. □ $>NH$ ends (from FTIR at 1237 cm^{-1})
 0 $>NO\cdot$ ends (from e.s.r.)
 ▲ $>NOPP$ groups (from FTIR at 1140 cm^{-1})
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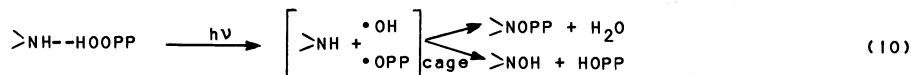
species which always accompany PPOOH formation and progressively accumulate as photo-oxidation of the polymer proceeds. Sitek *et al* have proposed that N-acyloxy species



are stable and cannot radical trap, so that they represent inactive piperidyl species (9).

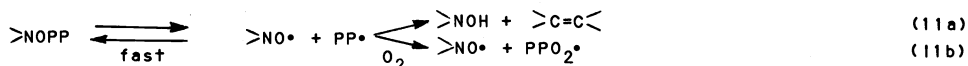
Another product detected by FTIR absorbed at 570 cm^{-1} and accumulated steadily during irradiation. This absorption is consistent with the formation of a nitroso or nitro-containing species which would imply scission of the piperidyl ring and formation of a sensitizer. However, further confirmation of this assignment is required.

The loss of PPOOH was not accompanied by alcohol formation. This is consistent with the mechanism suggested by Sedlar *et al* (reaction 10) involving photocleavage of PPOOH

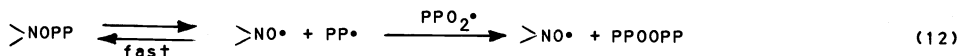


groups associated with secondary amines by hydrogen bonding (5). Cage reaction with the hydroperoxide fragments can be expected to favour $>\text{NOPP}$ formation. However, the rate of PPOOH loss is much slower than the rate of PPOOH photocleavage expected under xenon arc irradiation [$\sim 25\text{h}$ (3)]. This must mean that the piperidyl species are stopping only some of the initiation events and propagating chains, and that an appreciable amount of PPOOH is regenerated by chain oxidation.

The data shown in Fig. 1 substantiate and confirm our previous conclusions that $>\text{NOPP}$ is the dominant piperidyl species present during PPH photo-oxidation (8). Its dominance implies that reaction 8 is a key process but gives no information as to the precise mechanism of this process. We have previously shown that $>\text{NOPP}$ species slowly rearrange at ambient temperatures, possibly by an initial back dissociation to $>\text{NO}\cdot$ and $\text{PP}\cdot$ (4). In the absence of O_2 , a hydroxylamine ($>\text{NOH}$) is formed together with



unsaturation (reaction 11a). No increase in $>\text{C}=\text{C}<$ was detected by FTIR (at 1645 cm^{-1}) during the 4000h duration of our measurements. In the presence of O_2 , $>\text{NO}\cdot$ is slowly reformed from $>\text{NOPP}$ groups possibly by O_2 competition with the fast back recombination of $>\text{NO}\cdot$ and $\text{PP}\cdot$ (reaction 11b). However, the propagation of an oxidation chain in the close proximity to a $>\text{NOPP}$ site could allow reaction 12 rather than direct $\text{PPO}_2\cdot$



attack on $>\text{NOPP}$ (reaction 8). The formation of the peroxide crosslink which can photocleave to re-initiate photo-oxidation is a negative aspect of reactions 8 and 12 but quite trivial in comparison with the formation of 10^2 or even 10^3 PPOOH groups which would have occurred in the absence of the $\text{PPO}_2\cdot$ scavenging process.(3)

TERTIARY HINDERED AMINES: PHOTO-OXIDATION PRODUCTS

In practice, tertiary amines have been found to be almost as effective as secondary amines in the stabilization of photo-oxidizing polymers. Various tertiary types are commercially available (6). It is obviously of interest to investigate the stabilization mechanisms of the tertiary amines in comparison with their secondary analogues. To simplify the analytical problems we have studied a monofunctional tertiary amine 1,2,2,6,6-pentamethyl-4-piperidyl octadecanoate (St--NCH₃). This amine contains a long aliphatic chain to improve its compatibility with polyolefins and to reduce its volatility. Products from this amine were identified both from model, liquid-phase photo-oxidation (e.g. in hexane with *tert*-butyl hydroperoxide as photo-initiator) and during xenon-arc irradiation of PPH films. Both systems gave very similar results and only the solid state data are presented here. The tertiary amine was diffused into 25 μm , additive-free PPH films which were then irradiated with the xenon arc. Irradiated film samples were periodically extracted with hexane/2-propanol mixtures and products quantified by HPLC, e.s.r. and mass spectrometry. Grafted species remaining in the film after extraction were estimated by treating the films with hexane solutions of *m*-chloroperoxybenzoic acid which we have shown to quantitatively decompose $>\text{NO}-\text{C}-$ species to nitroxide. The nitroxide (St--NO \cdot) yield was quantified by e.s.r. and assumed to originate entirely from the substituted hydroxylamine (St--NOPP).

HINDERED AMINES AND HYDROPEROXIDES

Destruction of a potential initiator to give inactive products is a proven mechanism for stabilization. For example, phosphites or thio-compounds are frequently added to polyolefin formulations to improve thermal stability by hydroperoxide decomposition. We believe that secondary amines can destroy hydroperoxide groups in PPH by a dark reaction at ambient temperatures, albeit by a slow process. For example, when HN--NH was diffused into a pre-oxidized PPH film, nitroxide generation was detected by e.s.r. on the dry film, with a half life of ~ 10 days for $>NH$ loss. This process was investigated further using the simpler mono-functional amine St--NH in pre-oxidized films at 64°C under N_2 to eliminate the complication of continued oxidation (13). Product data are shown in Fig. 3. In the absence of the amine, PPOOH is unstable at 64°C but decays only $\sim 5\%$ in 20 h. In the presence of St--NH, PPOOH loss was very much faster and was accompanied by the destruction of the amine to give first a free hydroxylamine, St--NOH (estimated by indirect e.s.r. and by colourimetry based on $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ reduction) and then the nitroxide St--NO \cdot (by e.s.r.).

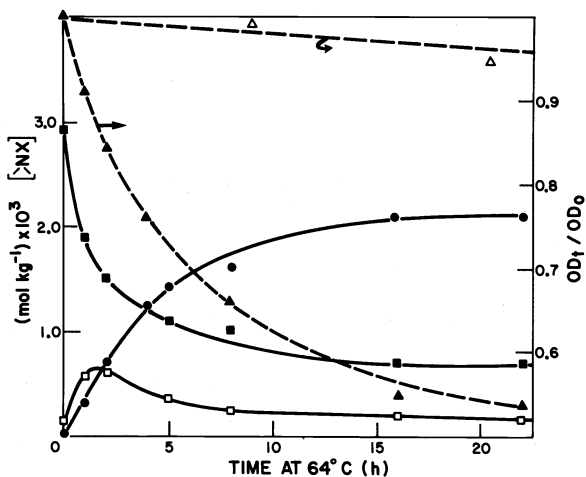


Fig. 3

PPOOH thermal decomposition by St--NH under N_2 at 64°C Pre-oxidized PPH film ($25 \mu\text{m}$, $[\text{PPOOH}]_0 = 0.03 \text{ mol kg}^{-1}$)

Δ PPOOH concentration in the ABSENCE of St--NH by FTIR and Iodometry).

\blacktriangle PPOOH concentration with St--NH present

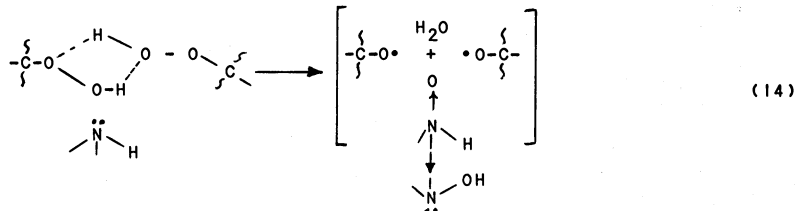
\blacksquare St--NH

\square St--NOH

\bullet St--NO \cdot Reprinted with permission from reference (13).

In model compound experiments, tert-butyl hydroperoxide did not react with the secondary amine over prolonged periods whereas the 2,4,6-trihydroperoxide from 2,4,6-trimethylheptane did, implying that adjacent -OOH sequences similar to the α , γ , ω ... sequences expected in oxidized PPH are necessary for rapid reaction.

By analogy with other known reactions of amines with activated hydroperoxides a suggested mechanism involves reaction 14 (14). This mechanism involves a hydrogen



bonded pair of -OOH groups (either intra or inter-molecularly bonded) and, to be rapid in the solid state, requires $>NH$ association with this pair. We believe that this association occurs readily as indicated for example by the 10 fold increase in secondary amine solubility upon oxidizing a PPH film to $\sim 0.06 \text{ mol/kg}$ of -OOH group (see below).

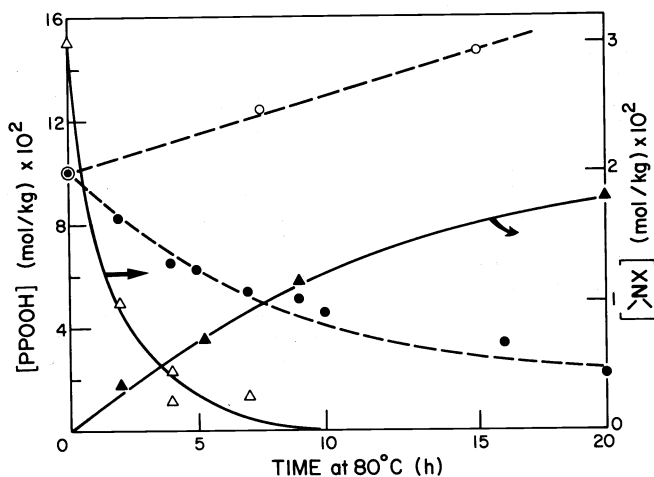


Fig. 4

PPOOH thermal decomposition at 80°C in the presence of St--NCH₃ PPH film (25 μm) pre-oxidized

- PPOOH in film heated in AIR, St--NCH₃ ABSENT.
- PPOOH in film a) heated in N₂, St--NCH₃ ABSENT and b) heated in N₂ or AIR, St--NCH₃ PRESENT.
- △ St--NCH₃ (Δ) and St--NH (▲) under N₂.

The macro-alkoxyl pair generated in the proposed reaction 14 may directly recombine or undergo β-scission followed by radical combination within the rigid polymer cage. The free hydroxylamine is anticipated to be a highly effective stabilizer in its own right, being able to rapidly scavenge peroxy radicals as well as to decompose hydroperoxide groups (15).

The ability of secondary amines to decompose PPOOH naturally leads to the question of whether tertiary amines can play the same role. We have found that St--NCH₃ does not decompose PPOOH at 80°C, but does interact with products from PPOOH thermal cleavage (Fig. 4). Heating pre-oxidized film in air at 80°C causes an increase in the PPOOH concentration because of chain oxidation of the polymer initiated by the thermal decomposition of -OOH groups. However, in the presence of St--NCH₃, heating at 80°C in air resulted in a drop in the -OOH level. In fact the -OOH level decayed at exactly this same rate when film was heated both in the absence and presence of St--NCH₃ under N₂ when oxidative regeneration of -OOH groups is impossible (Fig. 4). The -OOH decay curve in a N₂ atmosphere is believed to represent the intrinsic thermal decay of PPOOH groups and is unaffected by the amine. The fact that PPOOH decay occurs at this intrinsic rate in air with St--NCH₃ present implies that the amine can effectively suppress the chain oxidation which results from PPOOH thermal decomposition. St--NCH₃ reacted during PPOOH decomposition in air (not shown) or under N₂ (Fig. 4) with the associated formation of St--NH. Although the precise radical scavenging mechanism has not been established it is possible that the tertiary amine efficiently intercepts alkoxyl, •OH and/or peroxy radicals resulting from PPOOH scission or induced decomposition at 80°C. This process will be aided by strong -OOH/ tertiary amine association (see below).

ASSOCIATION EFFECTS AND STABILIZATION

In many of the potential stabilization reactions involving piperidyl species, the stabilizing moiety is competing with a relatively fast propagation reaction (cf. reactions 2 v.7 and 3 v. 8) or the fast reaction of radicals from a primary event such as PPOOH photocleavage. If additive and -OOH sites are randomly distributed throughout a polymer matrix it is difficult to see how the hindered amines can ever successfully inhibit. However, both possibilities are unlikely. Oxidation of a solid polyolefin proceeds by a free radical process which feeds upon itself. This must lead to highly oxidized domains surrounded by regions which are undegraded. Furthermore there is considerable evidence that piperidyl species specifically associate with these oxidized domains. As has been briefly mentioned, the solubility of >NH as well as >NO• and >NCH₃ species can increase by over an order of magnitude on going from "unoxidized" (i.e. as extruded) to partially oxidized PPH film ([-OOH] ~ 0.06 mol/kg)

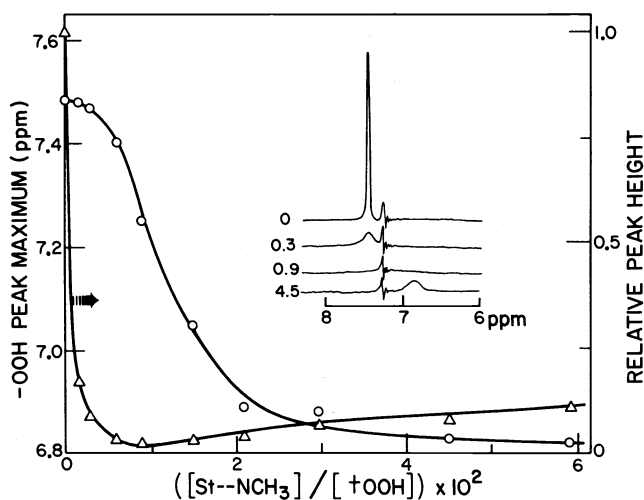


Fig. 5

Effects of St--NCH₃ on the NMR of *tert*-butyl hydroperoxide. Spectra measured at 60 MHz in CDCl₃ solutions at 22°C. All data for OOH proton (δ values).

Inset: NMR spectra at values corresponding to the shown ratios of $([St-NCH_3]/[-OOH]) \times 10^2$.

The small peak at 7.25 ppm is caused by a trace of CHCl₃ in the solvent.

Hydroperoxide concentration 0.315 mol dm⁻³ in all cases.

(13,16). The e.s.r. spectra of nitroxides show marked changes in line shape when dispersed in an oxidized polymer as compared to unoxidized polymer (16). These changes are consistent with a strong interaction between $>NO^\bullet$ and the hydroperoxide groups, interactions which restrict the rotation of the nitroxyl. Complex formation between $>NO^\bullet$ or $>NH$ and hydroperoxides has also been inferred from UV spectroscopy (17).

In a recent review of hindered amine photostabilization mechanisms, Felder *et al* briefly reported that very low concentrations of 2,2,6,6-tetramethylpiperidine dramatically altered the ¹H-NMR spectrum of the -OOH proton in *tert*-butyl hydroperoxide dissolved in toluene-d₈ (17). We have confirmed this effect and shown it to occur when $>NH$, $>NCH_3$ and $>NO^\bullet$ species were added to the hydroperoxide solution. Representative spectra and data are plotted in Fig. 5 for St--NCH₃. Very small amounts of St--NCH₃ (1 St--NCH₃/10³-OOH) cause a dramatic broadening of the -OOH proton signal as measured by the height of this peak but integration indicates the constant presence of one proton. As the St--NCH₃/-OOH ratio is increased, the -OOH peak maximum is progressively displaced from 7.45 to 6.85 ppm. For St--NCH₃ the -OOH peak begins to sharpen again at $[St-NCH_3]/[-OOH] > 0.01$ whereas this does not occur for St--NH or St--NO[•]. The parent amine and the hydroperoxide could be simply recovered by vacuum distillation from these mixtures. Although this NMR effect implies a strong piperidyl species/-OOH interaction, the precise origin of this process is unclear. However in several ways the process is analogous to the effects of traces of HCl on the NMR spectrum of a pyridine(18). In our case the hydroperoxide may act as a weak acid and the piperidyl species are certainly known to be strong bases.

CONCLUSIONS

Hindered amines (either secondary or tertiary) become involved in oxidative processes in polymers and sequentially generate a series of products most of which can stabilize the polymer by acting as weak radical traps. Their weakness is counteracted by the tendency of these species to associate with hydroperoxidized sites. Secondary amines can cause the slow thermal decomposition of polypropylene hydroperoxide groups. Although probably unimportant under accelerated weathering conditions, during natural exposure this slow decomposition process may well contribute to photoprotection by destroying the key photo-initiator sites (-OOH) during dark intervals. In photo-oxidizing polymer systems the grafted, substituted hydroxylamines appear to be the domi-

nant reservoir of stabilizer species. Nitroxyl species are key intermediates in the scavenging of many radicals by each hindered amine but do not accumulate to high levels. This is probably fortunate because the weak visible and UV absorption of these groups could lead to side reactions which would speed the wasteful fragmentation or deactivation of the piperidyl rings, whereas other important piperidyl intermediates only absorb at < 240 nm.

Multifunctional hindered amines may re-link damaged polymer chains through species such as PP-ON--NO-PP. However, it is not known whether this "healing" mechanism makes a viable contribution to stabilization. Russian workers have suggested that multifunctional additives provide most effective stabilization (19), but no clear attempt was made to eliminate other contributing factors such as changes in volatility, compatibility, ease of migration etc. Macro-hindered amines have become fashionable and are unquestionably superior to small molecules in terms of their resistance to volatilization and extraction. However, Gugumus has clearly shown that photo- and thermal stability decreases for a series of poly-(1,2,2,6,6-pentamethyl-4-piperidyl acrylates) as molecular weight increases beyond ~ 2000 (20). This result is consistent with the concept that the additive (and its non-grafted products) should be able to migrate, albeit slowly, through the polymer matrix for maximum stabilizer effectiveness. This is not meant to imply that the additive migrates to a macro-alkyl or peroxy radical site during the (brief) lifetime of that site, but that the additive can move to domains in the polymer where oxidation is being initiated, that is oxidized domains. The piperidyl group will then be optimally located to scavenge as a radical site propagates by, within the encounter volume surrounding the piperidyl group.

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