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The Oxidation of Hindered Amine Light Stabilizers to Nitroxy Radicals in Solution and in Polymers

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ABSTRACT

Cyclohexane and three polyolefins (PE, PP and EPM) have been oxidized by γ-irradiation, and the concentration of nitroxy radicals derived from a typical HALS added either before or after irradiation has been studied by ESR spectroscopy. The results indicate that HALS is rapidly oxidized by peroxy radicals under irradiation and that afterwards it can be oxidized more slowly by hydroperoxides. This last reaction is, however, very limited.

INTRODUCTION

Nitroxy radicals derived from hindered amine light stabilizers (HALS) are assumed to be the active species responsible for the inhibition of the photo-oxidation of polymers.[1–4] It is not yet clearly understood how they are produced and whether stable oxidation products generated in the polymer (hydroperoxides or peroxy-acids) or free radicals (alkyl or peroxy) are involved in the oxidation of HALS. The aim of the present paper is to provide additional experimental evidence to support either of those possibilities.

EXPERIMENTAL

Cyclohexane (Aldrich HPLC Grade) was used without further purification. Polyethylene (low density) was supplied by DSM Belgium as STAMYLAN

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LD 2810. Polypropylene used in the present work was NOVOLEN from BASF. The ethylene–propylene copolymer was supplied by Essochem Europe as VISTALON 404. It contains 40 weight % ethylene units (50 mole %). Bis (2,2,6,6-tetramethyl-4-piperidinyl) sebacate and its bis-*N*-methyl derivative were supplied by CIBA-GEIGY as TINUVIN 770 and 292, respectively.

The polymers and the additives were mixed without further purification in a Brabender Plasticorder at 150°C (polyethylene and ethylene–propylene copolymer) or 180°C (polypropylene) for 10 min at 60 rpm. Sheets 1 mm thick were then pressed at 180°C between clean aluminum foils at a pressure of 180 kg cm^{-2} for 3 min and cooled in the press to 65°C by water circulation.

For ESR measurements small pieces cut from those 1 mm thick sheets were used; for IR measurements films about 80 μm thick were obtained by further pressing the previous sheets (before irradiation).

Irradiations were performed in a Gammacell 220 (Atomic Energy of Canada Ltd) with an intensity of about 0·1 Mrad h^{-1}.

The ESR spectra were recorded by means of an AEG 20X spectrometer employing 125 kHz modulation and first derivative presentation. The microwave power entering the cavity was attenuated to about 0·1 mW. For quantitative measurements the signal was recorded as the absorption curve using an electronic integrator and the area under the curve was measured with a planimeter. The number of spins in the sample was determined by comparison with the signal of a calibrated ruby fixed in the cavity.

The IR spectra were recorded with a Perkin-Elmer 257 spectrometer in the range 4000 to 625 cm^{-1}.

The hydroperoxides present in the samples were analyzed by spectrophotometric determination of I_3^- formed in the reaction

$$\mathrm{ROOH} + 3\mathrm{I}^- + 2\mathrm{H}^+ \longrightarrow \mathrm{I}_3^- + \mathrm{H_2O} + \mathrm{ROH}$$

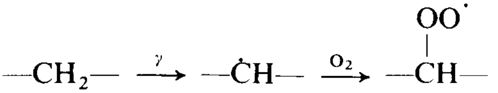
The molar decadic extinction coefficient of I_3^- at 362 nm is 25 280 M^{-1} cm^{-1}. The spectrophotometer used for that purpose was a Perkin-Elmer 124.

RESULTS AND DISCUSSION

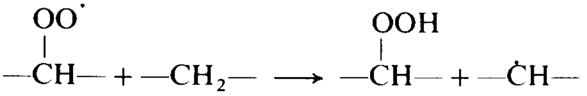
Cyclohexane and three polyolefins (polyethylene, polypropylene and an ethylene–propylene copolymer) have been oxidized under gamma irradiation and the concentration of nitroxy radicals derived from bis (2,2,6,6,-tetramethyl-4-piperidinyl) sebacate (simply referred to in the rest of this paper as HALS) added either before or after irradiation has been measured by ESR spectroscopy.

Cyclohexane

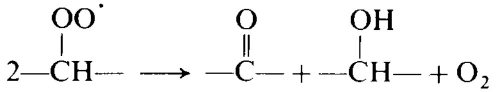
Cyclohexane has already been used as a model system to study the reactivity of HALS derivatives.[5] It is a suitable molecule containing only methylene groups which can be easily oxidized under gamma irradiation. In those conditions no subsequent decomposition of reactive oxidation products such as hydroperoxides is expected, unlike the photo- or thermal oxidation. It can be reasonably assumed that at low intensity the radiolytic oxidation of cyclohexane proceeds by the following mechanism:



$$\mathrm{-CH_2-} \xrightarrow{\gamma} \mathrm{-\dot{C}H-} \xrightarrow{O_2} \mathrm{-\overset{\overset{OO^{\cdot}}{|}}{C}H-} \qquad (1)$$

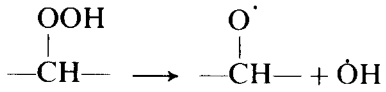


$$\mathrm{-\overset{\overset{OO^{\cdot}}{|}}{C}H- + -CH_2-} \longrightarrow \mathrm{-\overset{\overset{OOH}{|}}{C}H- + -\dot{C}H-} \qquad (2)$$



$$\mathrm{2-\overset{\overset{OO^{\cdot}}{|}}{C}H-} \longrightarrow \mathrm{-\overset{\overset{O}{\|}}{C}- + -\overset{\overset{OH}{|}}{C}H- + O_2} \qquad (3)$$

This is a chain-reaction with (3) as the termination step. No evidence for other oxidation products could be obtained by infra-red spectroscopy. The decomposition of hydroperoxides according to reaction (4) can be discarded



$$\mathrm{-\overset{\overset{OOH}{|}}{C}H-} \longrightarrow \mathrm{-\overset{\overset{O^{\cdot}}{|}}{C}H- + \dot{O}H} \qquad (4)$$

since their concentration is much lower than that of cyclohexane and γ rays are not selectively absorbed.

HALS added after irradiation

When HALS is added to cyclohexane pre-oxidized by γ-irradiation with a dose of 10·5 Mrad (105 kGy), nitroxy radicals are produced. If the solution is prepared 0·25% by weight (4·5 10^{-3} M) in HALS, 1·2 10^{16} nitroxy radicals per gram of solution can be detected by ESR spectroscopy 24 h after mixing. This corresponds to only 0·3% conversion of the initial amount of HALS. Substituted hydroxylamine ($>$NOR) can also be detected by infra-red spectroscopy at 1140 $\mathrm{cm^{-1}}$,[4] but its concentration could not be measured.

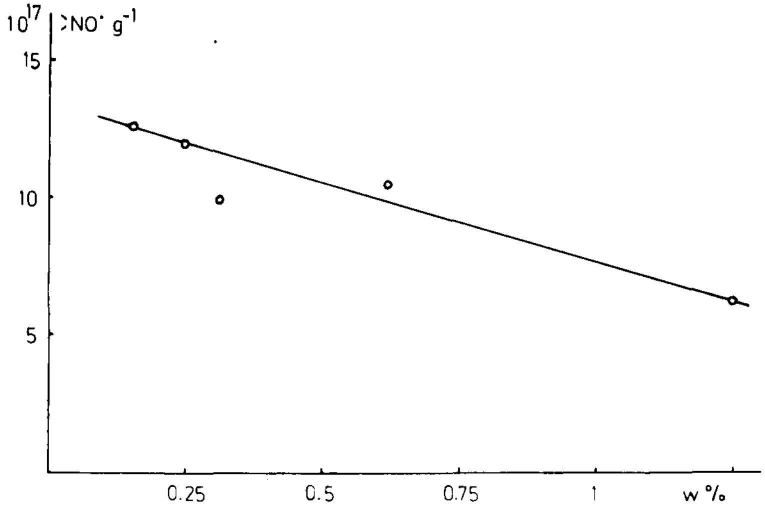


Fig. 1. Nitroxy radicals produced by addition of HALS (in various amounts) to cyclohexane pre-oxidized by γ-irradiation (10·5 Mrad).

Since hydroperoxides are the only possible oxidizing agent in those conditions the following mechanism can be suggested which has already been proposed by other authors.[1-5]

$$>\mathrm{NH} + \mathrm{ROOH} \longrightarrow\ >\mathrm{NOR} + \mathrm{H_2O} \qquad (5)$$

$$>\mathrm{NOR} + \mathrm{ROOH} \longrightarrow\ >\mathrm{NO}^{\cdot} + \mathrm{RO}^{\cdot} + \mathrm{ROH} \qquad (6)$$

Reaction (5) is facilitated by hydrogen bonding of HALS to one hydroperoxide.[6] It has been proposed that a complex of HALS with two (or more) hydroperoxide groups could also be involved in the oxidation process since HALS are more readily transformed into nitroxy radicals by polymeric hydroperoxides than by low molecular weight hydroperoxides.[7] The reaction could then proceed in one step (7) through a concerted mechanism:

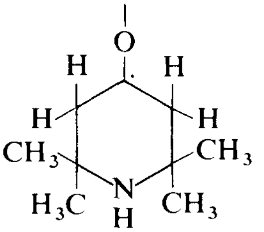
$$>\mathrm{NH} + 2\mathrm{ROOH} \longrightarrow\ >\mathrm{NO}^{\cdot} + \mathrm{RO}^{\cdot} + \mathrm{H_2O} + \mathrm{ROH} \qquad (7)$$

The net result is identical to the sequence (5) and (6) except that no substituted hydroxylamine is produced as an intermediate. Such a reaction is facilitated by a high local concentration of hydroperoxides in oxidized polymers. The occurrence of different kinds of complexes corresponding to different degrees of association of HALS with hydroperoxides is supported by our experimental results. Indeed, Fig. 1 indicates that as the amount of HALS added to pre-oxidized cyclohexane increases the concentration of nitroxy radicals decreases. This can be explained if, at low HALS concentration, tri (or poly) molecular complexes are favoured which generate nitroxy radicals more efficiently by reaction (7) whereas, at high HALS concentration, more stable bimolecular complexes predominate which result in less efficient production of nitroxy radicals, by the sequence of reactions (5) and (6). However, reaction (5) always occurs to some extent since $\gt$NOR groups are always detected by infra-red spectroscopy.

It is important to point out that no nitroxy radicals are produced under the same experimental conditions if the bis-*N*-methyl derivative of HALS is used instead of HALS itself. Tertiary amines are thus not (or much less readily) oxidized by hydroperoxides. In that case indeed the same type of complex cannot be expected.

HALS added before irradiation

When a solution of HALS in cyclohexane is irradiated with γ rays, nitroxy radicals are produced. Their concentration increases linearly with dose as shown in Fig. 2, and for a dose of 15 Mrad, 9% conversion is reached starting from a solution of HALS 0·25% by weight. This corresponds with a linear increase in the production of oxidizing agents with dose (hydroperoxides or transient free radicals). It is unlikely that nitroxy radicals result from the direct interaction of γ rays with HALS because they are not selectively absorbed and the concentration of HALS is quite low. Moreover, if this were to happen, another type of radical could be expected. Indeed, when pure HALS is irradiated in the solid state in the presence of air a symmetrical five line spectrum is observed by ESR spectroscopy with a coupling of 20*G*. This can be assigned to the radical produced by abstraction of a tertiary hydrogen atom:



in which the unpaired electron is coupled with four identical hydrogens.

For a given dose, the concentration of nitroxy radicals first increases with the concentration of HALS and then remains constant (Fig. 3) as if a limit had been reached for the scavenging of some reactive intermediates.

With a dose of 10·5 Mrad and a HALS concentration of 0·25% by weight ($4{\cdot}5 \times 10^{-3}$ M) 4×10^{17} nitroxy radicals per gram are detected. This value, which corresponds to 11% conversion (5×10^{-4} M), is 33 times larger than that measured when HALS is added *after* irradiation at the same dose and suggests that HALS is not only oxidized by hydroperoxides but also by reactive intermediates which are most likely peroxy radicals. It should thus

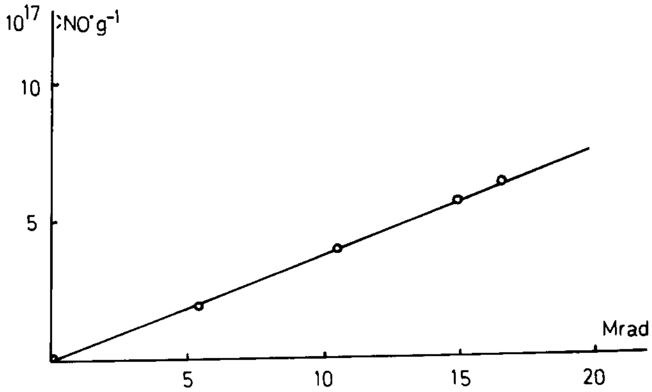


Fig. 2. Nitroxy radicals produced by γ-irradiation of a 0·25 weight % HALS solution in cyclohexane as a function of dose.

interfere with the oxidation mechanism of cyclohexane. Indeed, this is inhibited, as judged from the reduced intensity of carbonyl absorption in the infra-red spectrum.

In an air saturated cyclohexane solution of HALS in which the oxygen concentration is 3 10^{-3} M,[8] it is quite unlikely that cyclohexyl radicals could be trapped by any additive at a similar concentration before they react with oxygen according to reaction (1). It can be calculated on the basis of the data of reference 5 that the probability of alkyl radicals reacting with oxygen is about 100 times larger than their reaction with nitroxy radicals even at the highest measured concentration. On the other hand, it is difficult to believe that peroxy radicals generated that way could preferentially abstract

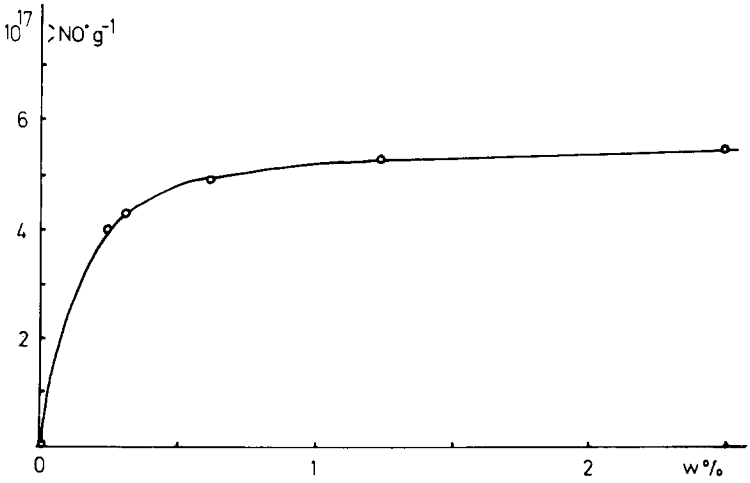
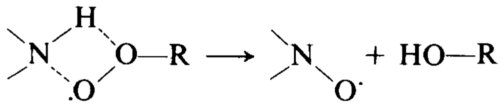


Fig. 3. Nitroxy radicals produced by γ-irradiation (10·5 Mrad) of HALS solutions in cyclohexane as a function of concentration.

hydrogen atoms from the amino group of HALS (reaction (8)) rather than from the methylene groups of cyclohexane (reaction (2)) which are about 10^4 times more abundant.

$$>NH + ROO^{\bullet} \longrightarrow >N^{\bullet} + ROOH \qquad (8)$$

Moreover, if hydrogen abstraction from HALS was to occur, the tertiary hydrogen atom would be a better choice (see above). The amino radical being an unlikely intermediate in the production of nitroxy radicals by the reaction of peroxy radicals with HALS, one has to assume that a specific interaction leading to direct oxidation can occur:



(9)

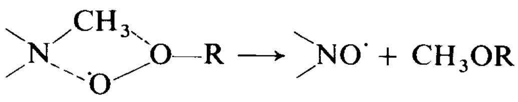
Because of the stability of nitroxy radicals such a reaction is not reversible (unlike (8)) and it could account for the inhibition of the production of ketones by reaction (3) in agreement with the experimental results. It is similar to reaction (10):

$$>NOR + ROO^{\bullet} \longrightarrow >NO^{\bullet} + ROOR \qquad (10)$$

which has been shown[5] to be about 10^3 times faster than hydrogen abstraction from cyclohexane (reaction (2)).

Since substituted hydroxylamine is also detected when HALS is added to cyclohexane prior to irradiation, it can be concluded that the mechanism previously assumed also occurs under irradiation. Moreover, it contributes to a very small increase of the nitroxy radical concentration in the 24 h following the irradiation.

It is important to notice that if the bis-*N*-methyl derivative of HALS is used instead of HALS, 0·15% conversion to nitroxy radicals is observed when a 0·5 weight per cent solution is irradiated to 10·5 Mrad whereas the conversion is 5% from HALS itself in the same conditions. This indicates that though the tertiary amine is not oxidized by hydroperoxides (see above) it can react with peroxy radicals, probably in a way similar to the secondary amine (11):



(11)

Polyolefins

When polyethylene (PE), polypropylene (PP) and an ethylene–propylene copolymer (EPM), each containing 0·25% HALS by weight, are irradiated

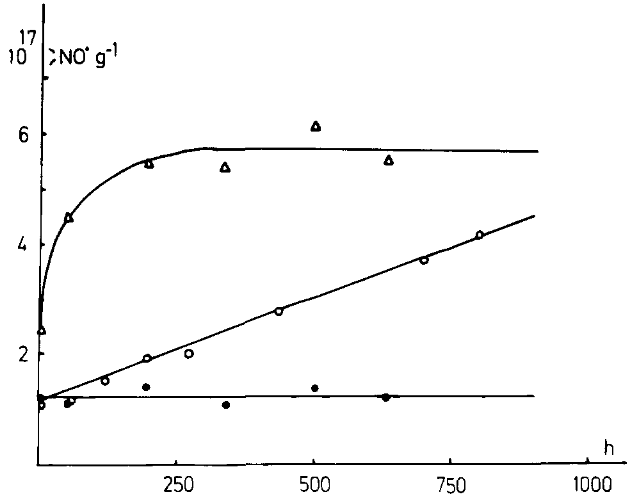


Fig. 4. Nitroxy radicals produced by γ-irradiation (2·5 Mrad) of PE (●), PP (○) and EPM (△) each containing 0·25 weight % HALS as a function of time after irradiation.

to a dose of 2·5 Mrad, nitroxy radicals can be detected in all cases (Fig. 4). When the irradiated samples are kept in the dark at room temperature, the radical concentration does not change in PE whereas it increases almost linearly with time in PP and in EPM it increases until a plateau is reached. If the same polymers containing no HALS are irradiated under the same conditions, no trapped radicals can be detected in EPM (as expected since the glass transition temperature is −50°C), a tiny signal typical of only alkyl radicals is observed in PE, but the spectrum of peroxy radicals is clearly visible in PP. Therefore no (or a negligible) overlap occurs between the signal of nitroxy radicals and that of any other radical in EPM and PE but a distinction between nitroxy and peroxy radicals should be made in PP. This is relatively easy since band 1 (Fig. 5A) is typical of the peroxy radical, the spectrum of which can be obtained separately with γ-irradiated PP and band 2 is due to nitroxy radicals, the spectrum of which can be measured in γ-irradiated EPM containing HALS. From these individual spectra it can be calculated that band 1 (Fig. 5B) corresponds to 13% of the total peroxy radical spectrum and band 2 to 21% of the nitroxy radical spectrum. In this way the relative contributions of both radicals to the total spectrum (Fig. 5B) can be deduced. The results are plotted in Figs 6 and 7.

Polyethylene

Qualitatively the radiolytic oxidation of PE is similar to that of cyclohexane (reactions (1) to (3)) but the probability of termination (3) is now much larger than in solution. Therefore, the oxidation of PE in the solid state at room temperature is a very short chain reaction:[9] few hydroperoxides are

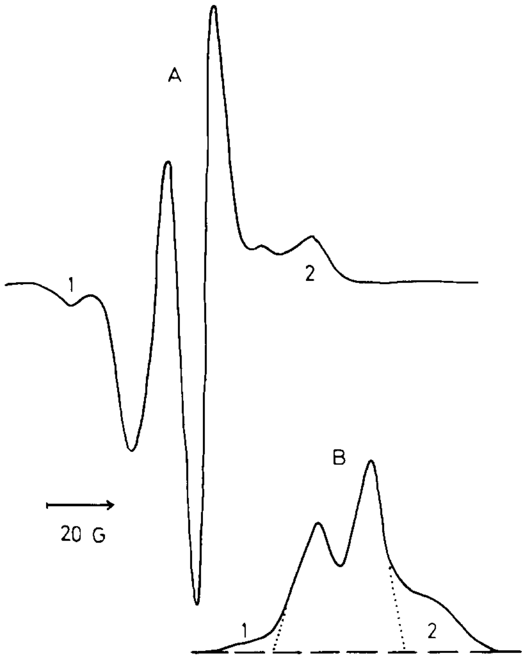


Fig. 5. ESR spectrum of PP containing 0·25 weight % HALS irradiated with γ-rays (2·5 Mrad). A, first derivative presentation; B, absorption curve (obtained by integration). Band 1 is due to peroxy radicals and band 2 to nitroxy radicals.

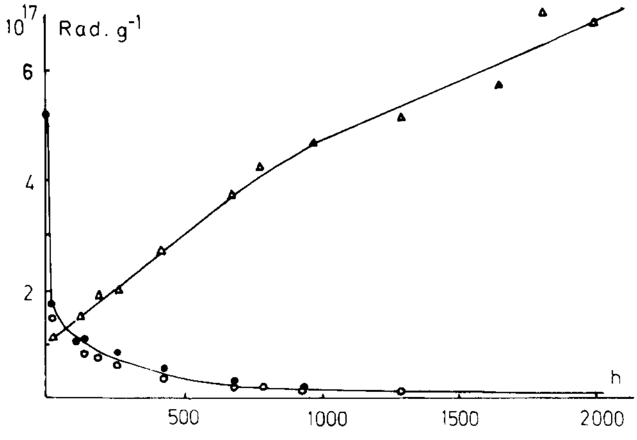


Fig. 6. Radicals produced by γ-irradiation (2·5 Mrad) as a function of time after irradiation. ○, peroxy radicals in PP containing 0·25 weight % HALS; △, nitroxy radicals in the same sample; ●, peroxy radicals in pure PP.

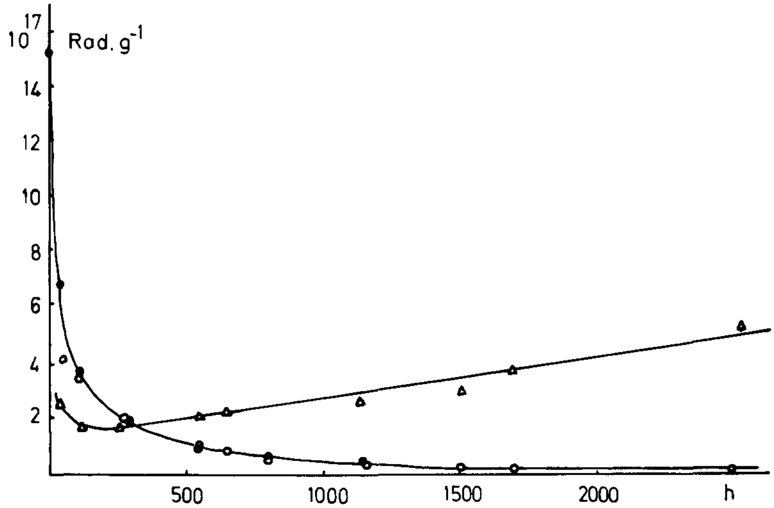


Fig. 7. Radicals produced by γ-irradiation (16 Mrad) as a function of time after irradiation. ○, peroxy radicals in PP containing 0·25 weight % HALS; △, nitroxy radicals in the same sample; ●, peroxy radicals in pure PP.

produced (less than 10^{-3} M) and the main oxidation products are ketones and alcohols. Nitroxy radicals are formed when PE containing 0·25 weight% HALS is irradiated with a dose of 2·5 Mrad but their concentration does not increase after irradiation (Fig. 4). As in cyclohexane, they most likely result from oxidation either by hydroperoxides or transient peroxy radicals (no peroxy radicals are trapped in PE after irradiation). The former being scarce in PE and no further production of nitroxy radicals occurring after irradiation, it can be suggested that under γ-irradiation, reaction (9) is responsible for the production of nitroxy radicals.

Ethylene–propylene copolymer

In EPM more hydroperoxides are produced during irradiation than in PE because tertiary peroxy radicals recombine less readily than secondary peroxy radicals and are thus more likely to abstract hydrogen atoms.[9] After absorption of 2·5 Mrad the concentration of hydroperoxides in an EPM film is 4·8 10^{-3} M in the absence of HALS. The amount of nitroxy radicals detected just after irradiation in an EPM sample containing HALS is twice the amount measured in PE in the same conditions. Moreover, it still increases by a factor two during the first 200 h following irradiation (Fig. 4). This can be explained by the fact that under irradiation HALS has more opportunity to react with peroxy radicals in rubbery EPM than in semi-crystalline PE and the yield of reaction (9) is larger. After irradiation, reaction (7) (or (5) and (6)) occurs to a measurable extent because more hydroperoxides are present in EPM than in PE. The formation of nitroxy

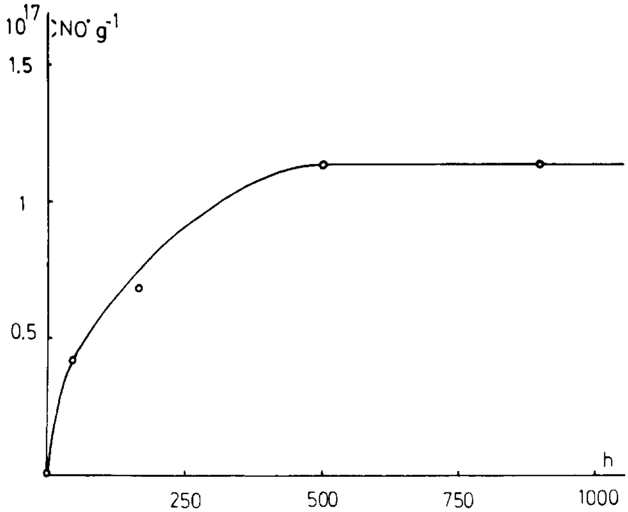


Fig. 8. Nitroxy radicals produced as a function of time in γ-irradiated EPM (2·5 Mrad) to which HALS has been added after irradiation.

radicals is slow either because the reaction itself is slow or because it is limited by the diffusion of HALS to oxidized regions of the polymer where it can react with hydroperoxides. The former explanation seems the more likely, however, for the following reason. When an EPM film containing no HALS but pre-oxidized with a dose of 2·5 Mrad is dipped for 24 h in a 0·46 weight% (8·24 10^{-3} M) HALS solution in octane, the hindered amine is soaked from the solution. After washing and drying the film the HALS concentration can be estimated from the absorption of the ester group at 1740 cm^{-1} to be 1·6 10^{-2} M, thus about twice the concentration of HALS in the starting solution. This can be ascribed to the higher affinity of HALS for the more polar oxidized regions of the polymer.[4] ESR shows (Fig. 8) that in the dry film in which an equilibrium situation has been reached and where HALS can be expected to be hydrogen bonded to hydroperoxides, the production of nitroxy radicals is nevertheless quite slow. In Fig. 8 it can be seen that only 1% conversion of HALS is reached after 500 h though this is far from exhaustion of the hydroperoxides available. The rate of oxidation of HALS by hydroperoxides in a polymer is thus rather slow even if it is not limited by diffusion.

Polypropylene

Just after irradiation with a dose of 2·5 Mrad of a PP film containing no HALS, trapped peroxy radicals can be detected. Their concentration decreases very quickly during the first 24 h and is reduced to about 20% of the initial value within 100 h. Afterwards the decrease slows down and an almost stationary concentration is reached (Fig. 6). A similar behaviour is observed after absorption of 16 Mrad but in that case some alkyl radicals can also be detected together with peroxy radicals during the fast initial decay period (Fig. 7). When PP films containing 0·25 weight% HALS are irradiated in the same conditions, peroxy *and* nitroxy radicals are present initially (together with some alkyl radicals for a dose of 16 Mrad). The total initial concentration is only 20% lower in the presence of HALS and the decay of peroxy radicals is *not* affected by the presence of HALS (Figs 6 and 7). However, the nitroxy radical concentration slowly increases almost linearly with time. This has been monitored up to about 4 months. From this it can be deduced that the additional nitroxy radicals formed *after* irradiation do not result from a reaction with peroxy radicals but rather with hydroperoxides, the concentration of which also increases linearly with time in pure PP[10] as a consequence of the post-irradiation oxidation that is known to occur in PP.[11] In Fig. 7 it can be seen that before starting to increase, the nitroxy radical concentration first decreases. This is most probably due to trapping of some alkyl radicals present after irradiation to 16 Mrad:

$$>\!\mathrm{NO}^{\bullet} + \mathrm{R}^{\bullet} \longrightarrow\ >\!\mathrm{NOR} \qquad (12)$$

The trapped peroxy radicals detected in PP *after* irradiation are most likely located in semi-crystalline regions of the polymer not accessible to HALS and they do not contribute to its oxidation though some of those formed *during* irradiation can react according to (9) as in PE and EPM. The peroxy radicals being generated randomly by γ-irradiation (unlike uv irradiation) the efficiency of their trapping by HALS, also randomly distributed, is rather low and the inhibition of the radiolytic oxidation of PP is not larger than 30% in the presence of 0·25 weight% HALS, as judged from the carbonyl absorption.[10] The post-irradiation oxidation of PP is, however, almost completely inhibited by HALS at the same concentration level.[10] Detailed discussion of those results falls beyond the aim of the present paper and will be presented later.

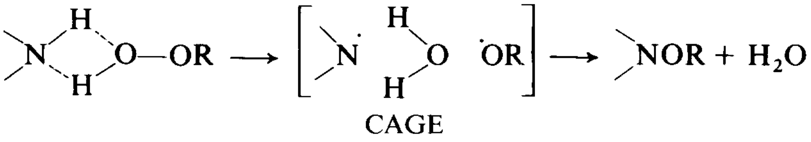
CONCLUSION

The main conclusion of the present work that fits all experimental results obtained so far is that HALS are quickly oxidized by peroxy radicals and more slowly by hydroperoxides. The first possibility is only one example of a general type of reaction that can be schematized as:

$$>\!\mathrm{N}\text{—}X + \mathrm{ROO}^{\bullet} \longrightarrow\ >\!\mathrm{N}\text{—}\mathrm{O}^{\bullet} + \mathrm{RO}X$$

where X could be a hydrogen atom or an alkyl group as suggested in the present paper or an alkoxy group as in substituted hydroxylamines.[5] In a solid polymer the yield of such a reaction is strongly dependent on the probability for a macro peroxy radical to be generated close to HALS or to the probability for such a radical to migrate until an encounter with HALS takes place.

The efficiency of HALS oxidation by hydroperoxides is related to the association of the reagents probably by hydrogen bonding. If a well defined bimolecular complex is formed, Sedlar's mechanism is most likely to occur:[6]



The substituted hydroxylamine produced as an intermediate then has to be oxidized itself by peroxy radicals (reaction (10)). Higher degrees of association can also be expected.[7] In that case a well defined complex is difficult to figure out but it is known that hydrogen bonded hydroperoxides decompose by a bimolecular mechanism[12] and this could be facilitated by additional interaction with HALS:

$$\begin{array}{l} \text{R—O—OH} \\ \quad\vdots \\ \quad\text{H—OOR} \end{array} \longrightarrow \text{RO}^{\bullet} + \text{H}_2\text{O} + \text{ROO}^{\bullet}$$

The peroxy radical thus formed close to a HALS molecule could easily react according to reaction (9) in such a way that the net result is reaction (7).

It is striking that hydroperoxides and peroxy radicals are common oxidation products or intermediates in most types of polymer oxidation: thermal, photochemical, radiolytic and post-radiolytic and that indeed nitroxy radicals are generated from HALS in all those conditions though with different efficiencies that are dependent on local concentration and mobility of the reagents. This, of course, also has an influence on the ability of HALS to inhibit the oxidation that is very low or nil in thermal oxidation,[13] usually high in photo-oxidation,[1-4] low in radiolytic oxidation[10] and quite high in post-radiolytic oxidation.[10]

The conclusions of the present paper do not exclude the possibility of HALS oxidation by other reagents (peracids, for instance) in some specific conditions less usual for polymers.

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