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The oxidation of hindered amine light stabilisers to nitroxy radicals in solution and in polymers. Part II

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Different types of hindered amine light stabilisers (HALS) have been oxidised by peroxy radicals generated by gamma irradiation of air saturated cyclohexane solutions. In all cases the concentration of nitroxy radicals, measured by EPR spectroscopy, increases linearly with absorbed dose. The sequence of reactivity observed is:

amino ether > sec. amine > tert. amine

The same HALS have been oxidised in a hydroperoxidised styrene–butadiene–styrene block copolymer by peroxy radicals resulting from the decomposition of clustered hydroperoxides. At room temperature the nitroxy radical concentration slowly increases with time and tends to a limit corresponding to the fraction of HALS molecules that are in a suitable environment to be oxidised. The sequence of reactivity observed is the reverse of that mentioned above. In this case, it reflects the ability of the different HALS to catalyse the decomposition of clustered hydroperoxides.

1 INTRODUCTION

In a previous paper[1] we showed that bis (2,2,6,6-tetramethyl-4-piperidinyl) sebacate, a typical hindered amine light stabilizer (HALS), is oxidised to the corresponding nitroxy radical when air saturated cyclohexane solutions are irradiated with gamma rays. We proposed that the reaction proceeds through an intermediate resulting from addition of cyclohexyl peroxy radicals to the nitrogen centre. Subsequent breakage of the O–O bond would give nitroxy radicals and cyclohexanol as final products:

$$>NH + POO\bullet \longrightarrow >NO\bullet + POH \quad (1)$$

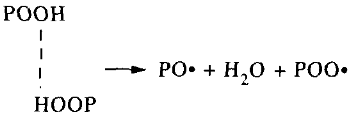
This mechanism is in agreement with results published later by other authors showing by isotopic labelling (oxygen-18) that the oxygen of the peroxy radical is incorporated into the nitroxy radical.[2] More recently the reaction of photogenerated peroxy and acylperoxy radicals with several HALS amino ethers has been studied in detail and two possible mechanisms have been discussed.[3] One is an electrophilic radical substitution at the nitrogen atom of the amino ether followed by decomposition of the amino peroxide formed:

$$>NOR + POO\bullet \longrightarrow >NOOP + RO\bullet \quad (2)$$

$$>NOOP \longrightarrow >NO\bullet + PO\bullet \quad (3)$$

As noticed by the authors the production of alkoxy radicals, which are highly reactive in hydrogen abstraction, should promote the degradation rather than the stabilisation of polymers. Though they suggest that the radicals could react in the primary cage they agree that the selective formation of harmless products is difficult to imagine. A more likely alternative mechanism is analogous to the one we proposed earlier. Of course, besides the nitroxy radicals, the products formed from an amino ether are expected to be different from those formed from a secondary amine but their nature has not yet been investigated.

In our previous paper[1] we also observed that HALS is slowly oxidised to nitroxy radicals during the post-irradiation oxidation of polypropylene and we suggested that this proceeds according to reaction (1) involving, in that case, peroxy radicals produced by the bimolecular decomposition of hydrogen-bonded hydroperoxides:[4]



$$\begin{matrix}\text{POOH}\\ \vdots\\ \text{HOOP}\end{matrix} \longrightarrow PO\bullet + H_2O + POO\bullet \quad (4)$$

In the present paper we have irradiated with gamma rays different HALS in a cyclohexane solution in order to compare their reactivity with cyclohexyl peroxy radicals. We have also studied the oxidation of those HALS by clustered hydroperoxides produced in a selective way by reaction of singlet oxygen with a styrene–butadiene–styrene (SBS) triblock copolymer. In both cases the production of nitroxy radicals was monitored by EPR spectroscopy.

2 EXPERIMENTAL

2.1 Polymer and additives

Four different HALS have been used. Bis (2,2,6,6-tetramethyl-4-piperidinyl) sebacate and bis (1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate were supplied by CIBA-GEIGY as Tinuvin 770 and 765, respectively. We shall refer to them in this paper as Bis-NH and Bis-N–CH_3, respectively. 2,2,6,6-tetramethyl-4-piperidinyl stearate and 1-*t*-butoxy-2,2,6,6-tetramethyl-4-piperidinyl stearate were obtained from Dr J. Sedlar (Research Institute of Macromolecular Chemistry, Brno, Czech Republic). We shall refer to them as Mono-NH and Mono-NO–*t*-But, respectively.

The polymer used was a SBS triblock copolymer containing 28 wt% styrene, supplied by Shell as Cariflex TR 1102. Its specific weight is 940 kg m^{-3}. Films about 100 μm thick were cast on clean glass windows from dichloromethane solutions also containing anthracene (as a photosensitizer for the production of singlet oxygen) and different HALS. After drying the polymer films were detached and fixed on cylindrical stainless steel frames 3 cm in diameter. The final concentration of anthracene was always $2.8 \cdot 10^{-3}$ mol l^{-1} and the final concentration of HALS was either $8 \cdot 10^{-3}$ or $1.6 \cdot 10^{-2}$ mol l^{-1} in piperidinyl groups in the films.

2.2 UV irradiation

SBS films containing both anthracene and HALS were irradiated at a distance of 4 cm from a Philips TL 20 fluorescent lamp. This is a polychromatic light source with an emission spectrum extending from 300 to 420 nm, a maximum of intensity at 350 nm and a half-intensity bandwidth of about 35 nm. The total intensity at the surface of the films measured with the benzophenone-benzhydrol actinometer[5] was found to be 1.73×10^{-5} E m^{-2} s^{-1}.

2.3 Gamma irradiation

Air saturated cyclohexane solutions containing different HALS at a concentration of 10^{-2} mol l^{-1} in piperidinyl groups were irradiated in a Gammacell 220 (Atomic Energy of Canada Ltd) with an intensity of 0.9 kGy h^{-1}.

2.4 Electron paramagnetic resonance

EPR 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.

3 RESULTS AND DISCUSSION

3.1 Oxidation of HALS by peroxy radicals in solution

When solutions of different HALS in cyclohexane, all at a concentration 10^{-2} mol l^{-1} in piperidinyl groups, are irradiated with gamma rays, nitroxy radicals are produced and their concentration increases linearly with dose as shown in Fig. 1. This results from reaction with cyclohexyl peroxy radicals as discussed in a

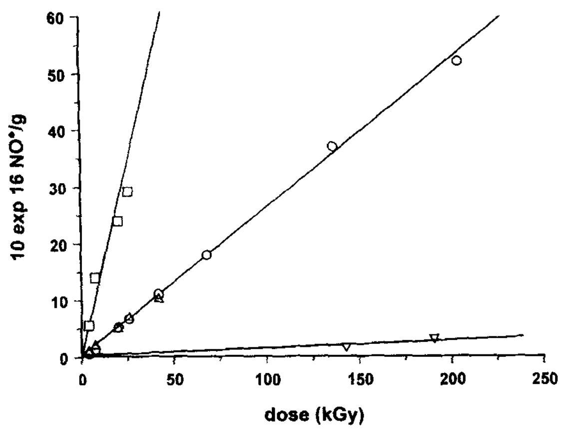


Fig. 1. Production of nitroxy radicals (spins g^{-1}) by the gamma irradiation of air saturated cyclohexane solutions of different HALS (all at the same initial concentration 10^{-2} mol l^{-1} in piperidinyl groups):(○) Bis-NH, (▽) Bis-N–CH_3, (△) Mono-NH, (□) Mono-NO-*t*-But.

previous paper.[1] Indeed, it is unlikely that gamma rays that are not selectively absorbed interact directly with HALS at their low concentration. Also in an air saturated cyclohexane solution in which the oxygen concentration is $3 \cdot 10^{-3}$ mol l^{-1} it can be calculated, on the basis of reference,[6] that the probability for cyclohexyl radicals to react with oxygen is about 100 times larger than their reaction with nitroxy radicals even at the highest concentration measured. Both secondary amines (Bis-NH and Mono-NH) are oxidised with the same yield though one contains two piperidine groups per molecule and the other only one. This indicates that in solution piperidine groups react independently of each other with cyclohexylperoxy radicals. It is important to notice that the amino ether Mono-NO-*t*-But is oxidised more easily than the corresponding secondary amine Mono-NH and that the tertiary amine Bis-N–CH_3 is oxidised with a lower yield than the corresponding secondary amine Bis-NH. The sequence of reactivity is clearly:

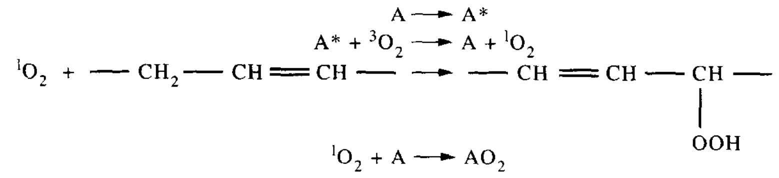
$$\text{NO-}t - \text{But} > \text{NH} > \text{N} - \text{CH}_3$$

and the reactivity ratios are approximately 120/30/1. The fact that the amino ether is more reactive than the corresponding secondary amine is in contradiction with the observation of other authors.[3] However, these also found that the reactivity of a given HALS can vary by a factor of 4 depending on the nature of the peroxy radicals and that the reactivity of different HALS amino ethers, in the same experimental conditions, can vary by a factor of 7. It thus seems difficult in the present state of knowledge to come to a general conclusion.

3.2 Oxidation of HALS in the dark, at room temperature, by clustered hydroperoxides

Our previous results indicate that the concentration of nitroxy radicals increases linearly with time after gamma irradiation of polypropylene containing Bis-NH.[1] The rates of oxygen absorption and of hydroperoxide production in polypropylene also remain constant for more than a year after irradiation.[7] Therefore the oxidation process was considered to be most probably induced by clustered hydroperoxides. However, this was not conclusively demonstrated since other potential oxidative agents could also be present, for instance peroxy acids. In the present paper we have selectively prepared clustered hydroperoxides by irradiation at 350 nm of SBS films containing anthracene and HALS. It has been shown that HALS does not inhibit the reaction of singlet oxygen with SBS at concentrations lower than $2 \cdot 10^{-2}$ mol l^{-1} in piperidinyl groups.[8]

Anthracene sensitises the production of singlet oxygen that reacts specifically with the polybutadiene phase in SBS to produce allylic hydroperoxides. The sensitiser itself reacts with oxygen and is progressively converted to the 9,10-endoperoxide. The sequence of reactions is the following:



$$\text{A} \longrightarrow \text{A}^*$$
$$\text{A}^* + {}^3\text{O}_2 \longrightarrow \text{A} + {}^1\text{O}_2$$
$${}^1\text{O}_2 + -\text{CH}_2-\text{CH}{=}\text{CH}- \longrightarrow -\text{CH}{=}\text{CH}-\underset{\text{OOH}}{\underset{|}{\text{CH}}}-$$
$${}^1\text{O}_2 + \text{A} \longrightarrow \text{AO}_2$$

That reaction has been studied quantitatively and the quantum yield of hydroperoxide formation was found to be close to one.[9] As long as anthracene conversion is low, it absorbs most of the light thus preventing hydroperoxides from being photolysed. Therefore no other oxidation products can be detected by IR spectroscopy. For prolonged irradiation periods, when anthracene absorbance becomes low, hydroperoxides themselves are photolysed and secondary oxidation products (mainly ketones and alcohols) are formed. To prevent photolysis of hydroperoxides, anthracene conversion has been limited to less than 60%. This requires about 50 min in our experimental conditions. At that moment, the hydroperoxide concentration in the film is of the order of 0.18 mol l^{-1}, i.e. about 130 times the concentration of anthracene transformed into endoperoxide. From this it can be concluded that, after irradiation, clusters of about 130 polymeric hydroperoxides are distributed in the film at a distance of about 10 nm from each other since this was initially the average distance between anthracene molecules.[9]

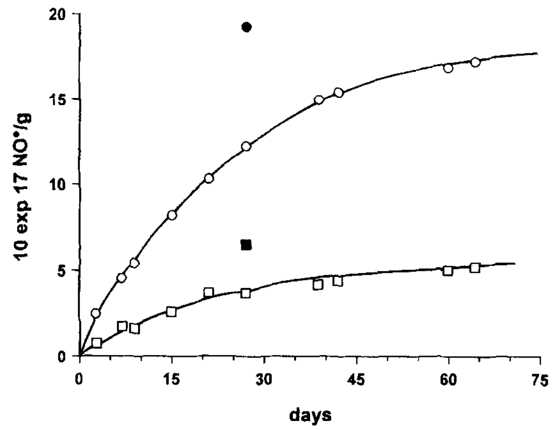


Fig. 2. Production of nitroxy radicals (spins g^{-1}) from Bis-NH in hydroperoxidised SBS kept in the dark at room temperature. Initial concentration of Bis-NH: (□) 8·10^{-3} mol l^{-1} piperidine groups, (○) 1.6·10^{-2} mol l^{-1} piperidine groups (full symbols correspond to concentration after heating for 1 h at 70°C).

In hydroperoxidised SBS films, also containing Bis-NH, nitroxy radicals are progressively formed in the dark at room temperature and detected by EPR spectroscopy (Fig. 2). Simultaneously, the intensity of the O–H stretching band of hydroperoxides at 3470 cm^{-1} decreases with no evidence in the carbonyl region for the production of oxidation products. In the absence of HALS, in the same conditions, no change can be detected in the IR spectrum of hydroperoxidised samples. From this it can be concluded that, as for other amines,[4] Bis-NH catalyses the decomposition of hydroperoxides. The thermal decomposition of clustered hydroperoxides in SBS has been shown to proceed mainly via radical induced reactions:[10]

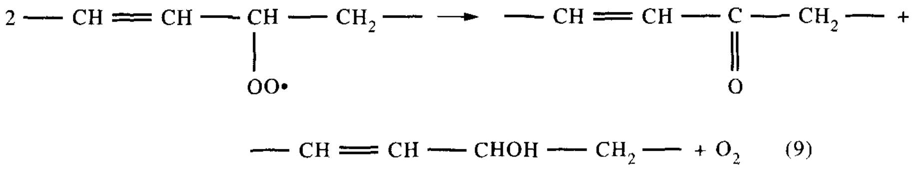
$$\mathrm{POOH} \longrightarrow \mathrm{PO\bullet} + \mathrm{\bullet OH} \tag{5}$$

$$\mathrm{HO\bullet} + \mathrm{POOH} \longrightarrow \mathrm{H_2O} + \mathrm{POO\bullet} \tag{6}$$

$$\mathrm{PO\bullet} + \mathrm{POOH} \longrightarrow \mathrm{POH} + \mathrm{POO\bullet} \tag{7}$$

$$3\ \mathrm{POOH} \longrightarrow \mathrm{POH} + \mathrm{H2O} + 2\ \mathrm{POO\bullet} \tag{8}$$

In the absence of HALS pairs of secondary peroxy radicals produced by reaction (8) undergo mutual termination by Russell's mechanism[11] to give a ketone and an alcohol:[10]



$$2\ \mathrm{-CH{=}CH-\underset{\displaystyle OO\bullet}{CH}-CH_2-} \longrightarrow \mathrm{-CH{=}CH-\underset{\displaystyle O}{\overset{}{C}}-CH_2-} + \mathrm{-CH{=}CH-CHOH-CH_2-} + \mathrm{O_2} \tag{9}$$

However, in the presence of Bis-NH and because reaction (8) is slow enough, all peroxy radicals are scavenged and no oxidation of the polymer takes place. If the catalysed decomposition of clustered hydroperoxides proceeds by the same mechanism, it is reasonable to assume that the peroxy radicals produced will oxidise Bis-NH according to reaction (1), as proposed earlier.[1] After 15 days the intensity of the O–H band decreases by 20% (i.e. 5.6·10^{-4} mol l^{-1} hydroperoxides have disappeared) in a sample containing initially 8·10^{-3} mol l^{-1} piperidine groups while 5% of those groups have been converted into nitroxy radicals (i.e. 4·10^{-4} mol l^{-1}). This corresponds approximately to the expected stoichiometry of 3 hydroperoxide groups decomposed for 2 nitroxy radicals formed if decomposition of hydroperoxides by reaction (8) is followed by scavenging of all peroxy radicals by reaction (1). This is not the case if hydroperoxidised SBS films, also containing Bis-NH, are irradiated in air at 350 nm instead of being kept in the dark.

The photodecomposition of clustered hydroperoxides is now much faster than their thermal decomposition at room temperature. More nitroxy radicals are formed but not all peroxy radicals are scavenged and some can initiate the oxidation of SBS.[8]

After about two months the concentration of nitroxy radicals produced by oxidation of Bis-NH tends to level off (Fig. 2). To determine more rapidly to what limit it tends, samples kept at room temperature for 25 days were heated for 1 h at 70°C. The nitroxy radical concentration quickly increases to $6.5 \cdot 10^{17}$ spins g^{-1} (or a maximum nitroxy radical concentration $[NO^\bullet]_{max}$ of $1 \cdot 10^{-3}$ mol l^{-1}) in the sample containing initially $8 \cdot 10^{-3}$ mol l^{-1} piperidine groups and to $19.3 \cdot 10^{17}$ spins g^{-1} (or a maximum nitroxy radical concentration $[NO^\bullet]_{max}$ of $3 \cdot 10^{-3}$ mol l^{-1}) in the sample containing initially $1.6 \cdot 10^{-2}$ mol l^{-1} piperidine groups. Those values correspond respectively to 13 and 19% conversion of the initial piperidine groups to nitroxy radicals. They depend on the probability for Bis-NH to be close enough to (or inside) clusters of hydroperoxides for the sequence of reactions (8) and (1) to occur. That fraction of piperidine groups that, in hydroperoxidised SBS, are in a suitable environment to be oxidised clearly increases with the piperidine concentration.

Figure 3 shows that the concentration of piperidine groups of Bis-NH that are in that suitable environment (assumed equal to $[NO^\bullet]_{max}$) is transformed to nitroxy radicals according to a first order kinetic equation. This is easy to explain by the fact that the concentration of clustered hydroperoxides is much larger ($0.18 \cdot$mol l^{-1}) and remains practically constant. The slopes of the straight lines indicate that the apparent first order rate constant is proportional to the initial piperidine concentration to the power of 1.5. However, mechanistic information is difficult to deduce from that value because in solid polymers local concentrations can be very different from average concentrations, especially in this system where hydroperoxides are not homogeneously distributed and where Bis-NH tends to concentrate in polar oxidised regions of the non-polar hydrocarbon polymer.

A comparison of the reactivity of different HALS in the presence of clustered hydroperoxides is interesting. From the initial slopes of Fig. 4 it appears that both Mono-NH and Bis-N-CH_3 are oxidised about 1.8 times faster than Bis-NH though the nitroxy radical concentration tends to almost the same limit in all three cases. The higher reactivity of Bis-N-CH_3 compared to Bis-NH can be ascribed to the fact that tertiary amines catalyse the decomposition of hydroperoxides more efficiently than secondary amines.[4] Surprisingly Mono-NO-*t*-But is oxidised extremely slowly (about 100 times more slowly than Mono-NH) although HALS is very reactive with peroxy radicals (see above). The low rate of oxidation is due to the fact that it does not catalyse the decomposition of hydroperoxides. The rate determining step is now the slow

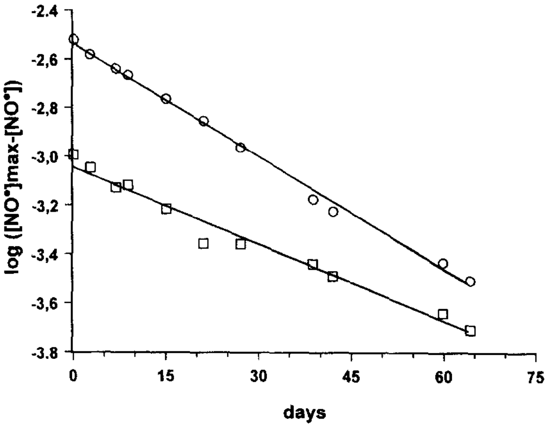


Fig. 3. Decrease of the concentration (in mol l^{-1}) of piperidine groups that are in a suitable environment in hydroperoxidised SBS to be oxidised to nitroxy radicals (data of Fig. 2). Initial concentrations: (□) $8 \cdot 10^{-3}$ mol l^{-1} piperidine groups, (○) $1.6 \cdot 10^{-2}$ mol l^{-1} piperidine groups.

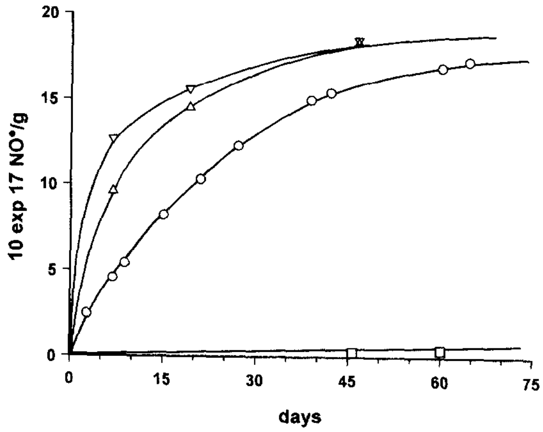


Fig. 4. Production of nitroxy radicals (spins g^{-1}) from different HALS in hydroperoxidised SBS kept in the dark at room temperature (all at the same initial concentration $1.6 \cdot 10^{-2}$ mol l^{-1} in piperidinyl groups): (○) Bis-NH, (▽) Bis-N-CH_3, (△) Mono-NH, (□) Mono-NO-*t*-But.

generation of peroxy radicals by decomposition of clustered hydroperoxide at room temperature and the sequence of catalytic activity of different HALS for the decomposition of hydroperoxides is:

$$\mathrm{NO} - t - \mathrm{But} < \mathrm{NH} < \mathrm{N} - \mathrm{CH_3}$$

i.e. just the reverse of that observed for their reactivity with cyclohexyl peroxy radicals. If the reactivity ratios with cyclohexyl peroxy radicals are still valid in the present case, the relative catalytic efficiencies would be approximately in the ratios 1/200/10 000.

It is interesting to notice that in hydroperoxidised SBS, Mono-NH is more easily oxidised than Bis-NH though they exhibit the same reactivity in solution (see above). This could be due to the higher probability for Mono-NH to diffuse to clusters of hydroperoxides where it can be oxidised. From that viewpoint, the lower molecular weight of the additive could play a role (368 compared to 480) but also the fact that Bis-NH could be immobilised by one end if, after oxidation of one piperidine group, the nitroxy radical formed reacts with a radical of the polymer. Also the reactivity of both piperidine groups could not be independent of each other if an appropriate geometry is required for the oxidation to proceed in clusters of hydroperoxides.

4 CONCLUSION

The high efficiency of HALS as inhibitors of the photo-oxidation of polymers, and especially of polyolefins, is considered to be determined by a complex set of reactions involving the scavenging of alkyl and peroxy radicals formed during oxidation. The primary active species being the nitroxy radicals derived from HALS it can be expected that, if the formation of those radicals by reaction (1) is the rate determining step, the sequence of efficiency would be:

$$\mathrm{NO} - t - \mathrm{But} > \mathrm{NH} > \mathrm{N} - \mathrm{CH_3}$$

However, if the peroxy radicals involved in reaction (1) are produced by the catalysed decomposition of clustered hydroperoxides (reaction (8)) and if that is the rate determining step, the expected sequence of efficiency would be:

$$\mathrm{NO} - t - \mathrm{But} < \mathrm{NH} < \mathrm{N} - \mathrm{CH_3}$$

The rate determining step could well depend on the nature of the polymer (saturated or unsaturated[8] for instance, or more or less oxidised[12]). Therefore, the prediction of the relative efficiency of different HALS is still highly speculative at the moment. Moreover, other factors can also have an influence on the efficiency of HALS such as their tendency to concentrate in oxidised regions of the polymer where the photo-oxidation is most likely to be initiated (by the photolysis of ketones or hydroperoxides) and their ability to diffuse to those oxidised regions. Some of these factors are presently being actively investigated in our laboratory and the results of a comparative study of the efficiency of different HALS, will be published soon.[13]

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