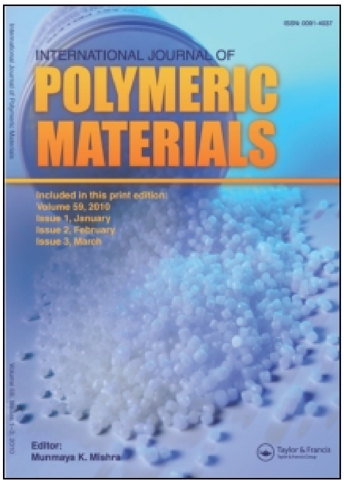

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A Comparative Study of the Efficiency of a Typical Hindered Amine Stabilizer in Different Hydrocarbon Polymers

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Inhibition of the photo-oxidation of three different polymers by the same HALS has been studied: an ethylene-propylene random copolymer (EPM), a styrene-butadiene-styrene block copolymer (SBS) and the same block copolymer previously hydroperoxidized by reaction with singlet oxygen. Two techniques have been used and compared: oxygen absorption measurements and infra-red spectroscopy in the carbonyl region. The results indicate that HALS inhibits more efficiently the propagation of the photo-oxidation in the unsaturated polymers studied. However, it also catalyses a new type of termination that in EPM delays and in SBS promotes the production of ketones. It is suggested that the practical efficiency of HALS could be mainly dependent of that last effect.

KEY WORDS Stabilization, hydrocarbon polymers, hindered amines

1. INTRODUCTION

Hindered amine light stabilizers (HALS) are efficient inhibitors of the photo-oxidation of hydrocarbon polymers and mainly of polypropylene. This is commonly ascribed to a fortunate combination of several factors:

- —first, as polar additives they tend to concentrate in oxidized regions of hydrocarbon polymers where *initiation* of the photo-oxidation is most likely to occur as a consequence of the photolysis of hydroperoxides and (or) ketones;
- —secondly, HALS are oxidized there to stable nitroxy radicals.

A general mechanism has been proposed for secondary and tertiary amines[1]:

$$>NX + ROO^{\cdot} \rightarrow >NO^{\cdot} + ROX \tag{1}$$

The stable nitroxy radicals formed act as scavengers of alkyl radicals:

$$>NO^{\cdot} + P^{\cdot} \rightarrow >NOP \tag{2}$$

Formation of N-alkyloxy derivatives of HALS thus competes with *propagation* of the photo-oxidation:

$$P^{\cdot} + O_2 \rightarrow POO^{\cdot} \tag{3}$$

$$POO^{\cdot} + PH \rightarrow POOH + P^{\cdot} \tag{4}$$

- last but not least, nitroxy radicals are regenerated from the N-alkyloxy derivatives by reaction with peroxy radicals. Several mechanisms have been proposed depending on the nature of the polymer[2,3,4]:

$$>\mathrm{NOP} + \mathrm{POO}^{\cdot} \rightarrow >\mathrm{NO}^{\cdot} + \mathrm{POOP} \tag{5}$$

$$>\mathrm{NOP} + \mathrm{POO}^{\cdot} \rightarrow >\mathrm{NO}^{\cdot} + >\mathrm{C{=}C}< + \mathrm{POOH} \tag{6}$$

$$>\mathrm{NOP} + \mathrm{POO}^{\cdot} \rightarrow >\mathrm{NO}^{\cdot} + \mathrm{P{=}O} + \mathrm{POH} \tag{7}$$

The high efficiency of HALS, even at a very low steady state concentration of nitroxy radicals, is thus also associated with the catalysis of a new type of *termination* involving alkyl and peroxy radicals:

$$(2) + (5) \qquad \mathrm{P}^{\cdot} + \mathrm{POO}^{\cdot} \rightarrow \mathrm{POOP} \tag{8}$$

$$(2) + (6) \qquad \mathrm{P}^{\cdot} + \mathrm{POO}^{\cdot} \rightarrow >\mathrm{C{=}C}< + \mathrm{POOH} \tag{9}$$

$$(2) + (7) \qquad \mathrm{P}^{\cdot} + \mathrm{POO}^{\cdot} \rightarrow \mathrm{P{=}O} + \mathrm{POH} \tag{10}$$

The aim of the present paper is to discuss the regenerative mechanism of nitroxy radicals in different polymers together with the nature of oxidation products formed. For that purpose we have studied three polymers:

- an ethylene-propylene random copolymer (EPM) as a model for saturated hydrocarbon polymers,
- a styrene-butadiene-styrene block copolymer (SBS) as a model for unsaturated polymers and
- the same SBS previously hydroperoxidized in a controlled way to investigate the influence of well defined oxidized regions on the behaviour of HALS.

As a typical HALS we have selected bis[2,2,6,6-tetramethyl-4-piperidinyl] sebacate simply referred to, in the text, as HALS.

2. EXPERIMENTAL PART

2.1 Polymers and Additives

The polymers used are an EPM containing 40 weight % ethylene units supplied by Exxon as Vistalon 404 and a SBS containing 28 weight % styrene supplied by Shell as Cariflex TR 1102. Both polymers were used without further purification. Thin films (about 80 μm thick) were cast from solutions (also containing additives when required) on clean glass windows. After drying they are detached and fixed on cylindrical stainless steel frames 3 cm in diameter (surface of the film 7 cm^2).

As additives, we have used bis[2,2,6,6-tetramethyl-4-piperidinyl] sebacate supplied by Ciba-Geigy as Tinuvin 770 and anthracene p.a. from Janssen Chimica.

2.2 Light Sources

The light sources were a Westinghouse FS 20 Sunlamp with a maximum of intensity at 310 nm and a half-intensity bandwidth of about 35 nm and a Philips TL 20 lamp with a maximum of intensity at 350 nm and the same half-intensity bandwidth. The incident intensity on the surface of the films was, in all cases, of the order of 10^{-7} E cm^{-2} min^{-1}.

2.3 Analytical Techniques

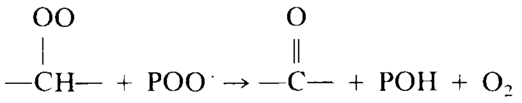
The IR spectra were recorded on films with a Perkin-Elmer 257 spectrometer in the range 4000–625 cm^{-1}.

Oxygen absorption measurements were performed according to a differential manometric technique described earlier.[5]

3. RESULTS AND DISCUSSION

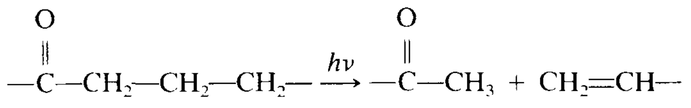
We have measured the rate of oxygen absorption by EPM, SBS and hydroperoxidized SBS irradiated under oxygen at a pressure of 600 Torr and the increase of the carbonyl absorbance in the IR spectrum of the same polymers irradiated in air. Oxygen absorption provides a true measure of the rate of propagation of the photo-oxidation whereas the intensity of the carbonyl band is related to the concentration of various compounds, mainly ketones and carboxylic acids, produced as a consequence of some types of termination step.

a) Photo-oxidation of EPM at 310 nm. The mechanism of the photo-oxidation of EPM has already been discussed in details.[6–9] It is a very short chain reaction initiated by the sensitized decomposition of hydroperoxides present as impurities and the predominant termination step involves the formation of ketones:



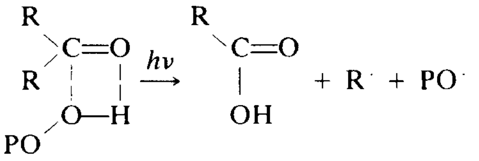
$$-\overset{\overset{\displaystyle OO}{|}}{C}H- + POO^{\cdot} \rightarrow -\overset{\overset{\displaystyle O}{\|}}{C}- + POH + O_2 \tag{11}$$

Degradation mainly results from chain scission that initially proceeds by the Norrish Type II reaction of ketones:



$$-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_2-CH_2- \xrightarrow{h\nu} -\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + CH_2{=}CH- \tag{12}$$

However, as the local concentration of oxidation products increases, hydroperoxides and ketones tend to become hydrogen bonded and a new chain scission process, involving the production of carboxylic acids, becomes operative:



(13)

Because of the high absorption coefficient of ketones and the efficient energy transfer to hydroperoxides in such a complex the rate of oxygen absorption increases dramatically. That moment coincides with a fast increase of the carbonyl absorption in the IR spectrum due to the production of carboxylic acids with an absorption coefficient about twice that of ketones.[7]

Figure 1 shows that the time required for such a situation to occur is extended in the presence of HALS. A concentration of 0.5 weight % HALS results in an increase of the apparent induction period by a factor 18. Actually, there is no induction period as Figure 2 shows since oxygen absorption starts from the very beginning of irradiation and only the rate is reduced in the presence of HALS. It is reduced by a factor 1.5 in the pressence of 0.5 weight % HALS. (The time scales of Figures 1 and 2 are not directly comparable because the incident light intensities and the oxygen pressures are different but the time required for a given effect to be observed is about three times longer in the experimental conditions used for oxygen absorption measurements.)

If only the rate of propagation was affected by the presence of HALS, without any change in nature of the termination step, the apparent induction period for

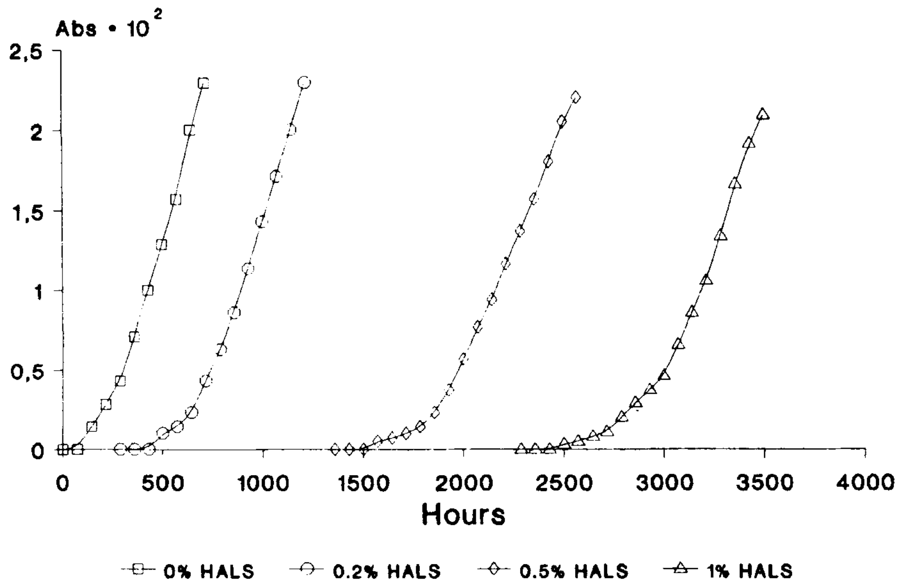


FIGURE 1 Absorbance measured at 1710 cm^{-1} on EPM films irradiated in air at 310 nm.

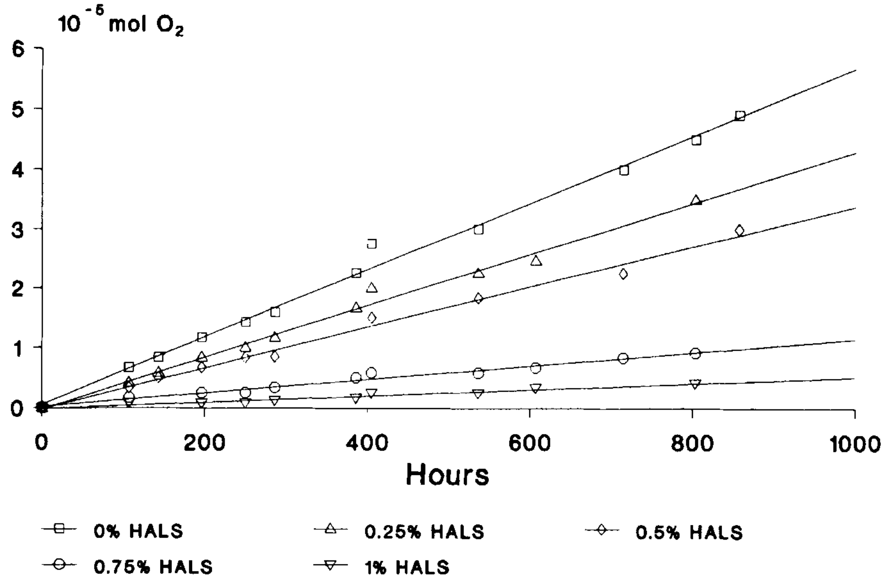


FIGURE 2 Oxygen absorption by EPM films irradiated at 310 nm (oxygen pressure 600 Torr).

the onset of the carbonyl absorption should also be extended by a factor 1.5 in the presence of 0.5 weight % HALS. Comparison of Figures 1 and 2 clearly shows that, in EPM, HALS not only reduces the rate of propagation of the photo-oxidation but also catalyses a new type of termination not involving ketones but most likely peroxides, as expected if the regenerative mechanism of nitroxy radicals is (2) + (5) that is equivalent to (8). Indeed, evidence for the presence of peroxide groups after 1000 to 2000 h irradiation is obtained from the IR spectrum of EPM samples containing 1 weight % HALS in the region 1000–1200 cm^{-1}.[10] At that moment, no carbonyl containing oxidation product can be detected yet (Figure 1).

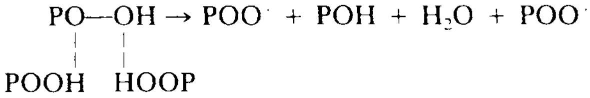
Figure 2 indicates that nitroxy radicals do not compete efficiently with oxygen for reaction with alkyl radicals in EPM. About 0.6 weight % HALS ($1.25\ 10^{-2}$ mol l^{-1}) is required to reduce the rate of oxygen absorption by a factor 2. In those conditions, the rates of reactions (2) and (3) are equal and the stationary concentration of nitroxy radicals is 0.4% of the initial piperidine groups,[9] i.e. $5\ 10^{-5}$ mol l^{-1}. Since the rate constant of reaction (2) can be estimated to be 20 times lower than that of reaction (3)[11] the *local* concentration of nitroxy radicals has to be 20 times larger than the oxygen solubility (about 10^{-3} mol l^{-1} in air[15]) thus $2\ 10^{-2}$ mol l^{-1} or 400 times the *average* concentration.

Finally, the practical efficiency of HALS in preventing chain scission by reactions (12) and (13) is mainly the consequence of a change in the nature of the termination step (now preventing the formation of ketones) and to a minor extent only to a decrease of the rate of propagation of the photo-oxidation.

b) Photo-oxidation of SBS at 350 nm. Some aspects of the photo-oxidation of SBS have already been discussed[9] and compared to that of EPM. The reaction is also initiated by the sensitized decomposition of hydroperoxides present as impurities and proceeds as a very short chain reaction. Initially, the termination step does not result in the production of ketones:

$$\mathrm{POO^{\cdot} + —CH{=}CH—CH_2—\dot{C}H—CH{=}CH— \rightarrow}$$
$$\mathrm{POOH + —CH{=}CH—CH{=}CH—CH{=}CH—} \qquad (14)$$

In those conditions, hydroperoxides are the only oxidation products detectable and, as their local concentration increases, they tend to form clusters. Photodecomposition of clustered hydroperoxides results in the production of geminate peroxy radicals by reaction (15):



$$\begin{array}{l} \mathrm{PO—OH \rightarrow POO^{\cdot} + POH + H_2O + POO^{\cdot}} \\ \;\;\;\;| \quad\;\; | \\ \mathrm{POOH \;\; HOOP} \end{array} \qquad (15)$$

Most of them react according to (11) and produce ketones that soon are hydrogen bonded with hydroperoxides and induce the production of carboxylic acids (reaction (13)). That process is associated with cross-linking by recombination of allyl radicals and with a fast increase of the carbonyl absorption in the IR spectrum.[9] An irradiation period 4.5 times longer is required to reach the same stage in the presence of 0.5 weight % HALS (Figure 3). The same amount of HALS, however, reduces the rate of oxygen absorption much more efficiently by a factor 18 (Figure 4). As with EPM (Figures 1 and 2), comparison of Figures 3 and 4 indicates that HALS not only inhibits the propagation of the photo-oxidation but also changes the nature of the termination step. In the present case, because the protective effect measured

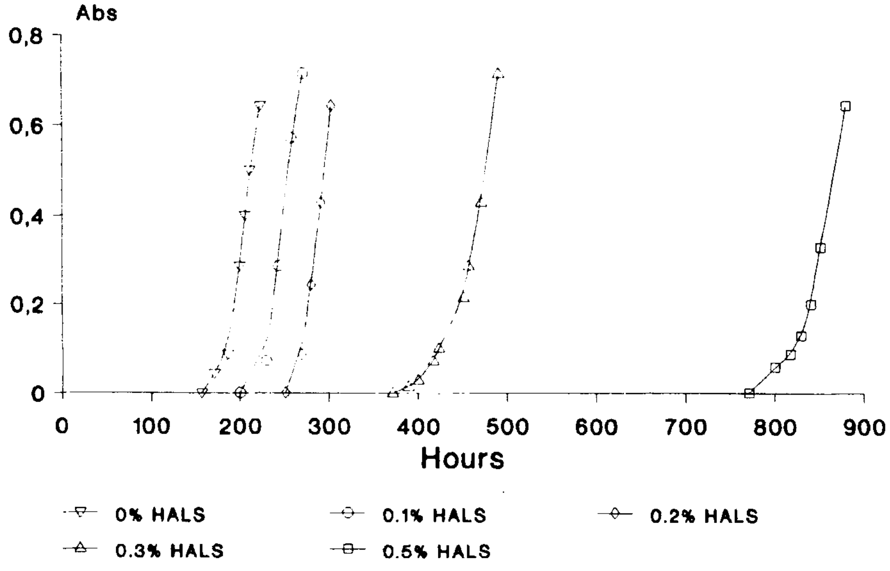


FIGURE 3 Absorbance measured at 1710 cm^{-1} on SBS films irradiated in air at 350 nm.

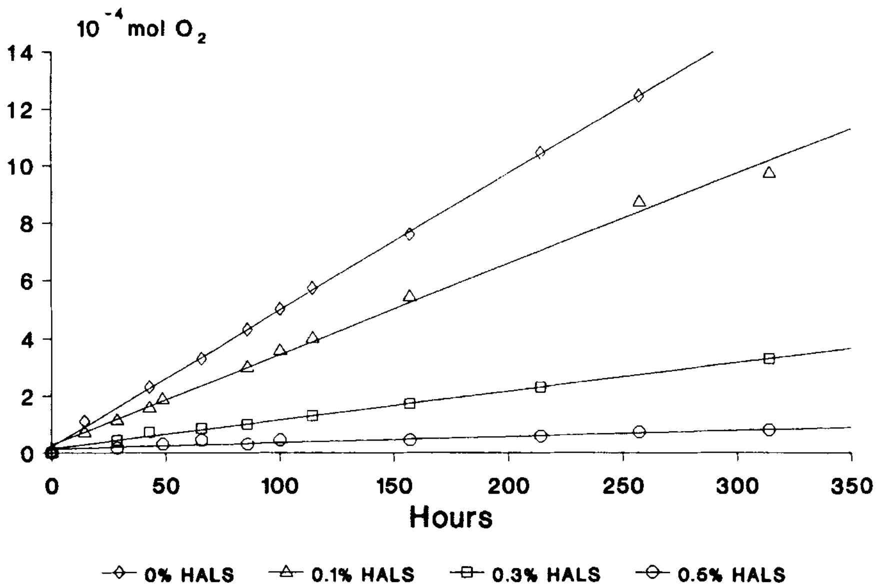
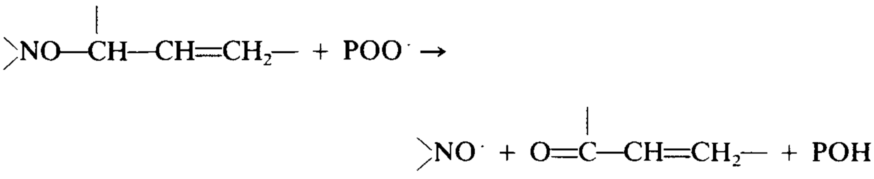


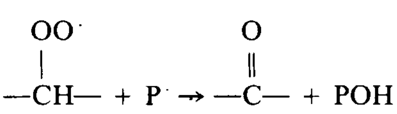
FIGURE 4 Oxygen absorption by SBS films irradiated at 350 nm (oxygen pressure 600 Torr).

from the onset of the carbonyl absorption is smaller than expected from the decrease of the rate of oxygen absorption, it can be concluded that a new type of termination step, involving the production of ketones, is catalyzed by nitroxy radicals. Indeed, if the regeneration of nitroxy radicals proceeds according to (16) (equivalent to (7)):



$$\gt NO{-}\overset{|}{C}H{-}CH{=}CH_2{-} + POO^{\cdot} \rightarrow \gt NO^{\cdot} + O{=}\overset{|}{C}{-}CH{=}CH_2{-} + POH \qquad (16)$$

the new termination step combines (2) and (16) to give (17) (equivalent to (10)):



$$-\overset{\overset{\displaystyle OO^{\cdot}}{|}}{C}H- + P^{\cdot} \rightarrow -\overset{\overset{\displaystyle O}{\|}}{C}- + POH \qquad (17)$$

The fact that reaction (16) (or (7)) takes place in SBS and not noticeably in EPM can be ascribed to the presence of a more reactive allylic hydrogen in the N-allyloxy derivative, though the probability to form a transition state with a suitable geometry is probably lower in both polymers than in model compounds.[4]

Finally the poor efficienty of HALS in preventing degradation of SBS (and also probably of other unsaturated rubbers) is due to a change in the nature of the termination step (now resulting in the production of ketones) and not to a weak inhibition of the propagation of the photo-oxidation. Indeed, the rate of oxygen absorption is reduced 12 times more efficiently in SBS than in EPM by the same amount of HALS (0.5 weight %) though the stationary nitroxy radical concentration is 20 times lower in SBS than in EPM.[9]

c) Photo-oxidation of hydroperoxidized SBS at 350 nm. On irradiation of SBS containing anthracene, this sensitizes the production of singlet oxygen that specifically reacts with the polybutadiene phase in SBS to produce allylic hydroperoxides:

$$A^* + {}^3O_2 \rightarrow A + {}^1O_2 \tag{18}$$

$${}^1O_2 + \text{—CH}_2\text{—CH=CH—} \rightarrow \text{—CH=CH—}\underset{\displaystyle \text{OOH}}{\underset{|}{\text{CH}}}\text{—} \tag{19}$$

As a consequence, Figure 5 shows that the formation of carbonyl compounds starts much earlier than in pure SBS (Figure 3) because clustered hydroperoxides are now produced from the very beginning and the sequence of reactions (15) and (11) immediately ensues. The presence of HALS slows down the increase of the carbonyl absorption but no apparent induction period is observed as would be expected if a change of termination mechanism was to occur, as in SBS. After about 30 h irradiation (Figure 6), when anthracene has been converted to endoperoxide by reaction with singlet oxygen, the hydroperoxide concentration is 40 times larger in pre-oxidized SBS than in pure SBS. However, the rate of oxygen absorption is only twice higher (Figure 6) because most geminate peroxy radicals produced by photodecomposition of clustered hydroperoxides (reaction (15)) quickly disappear

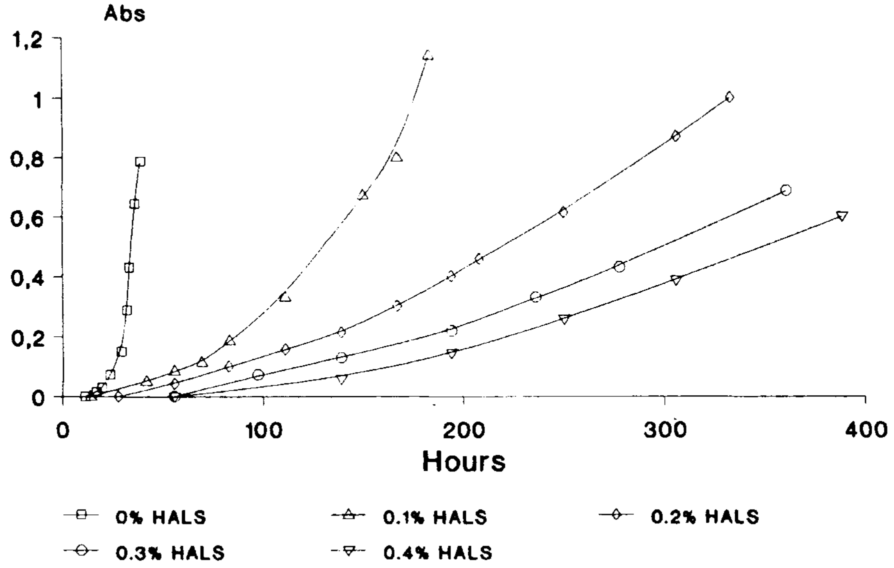


FIGURE 5 Absorbance measured at 1710 cm^{-1} on SBS films containing 0.05% anthracene irradiated in air at 350 nm.

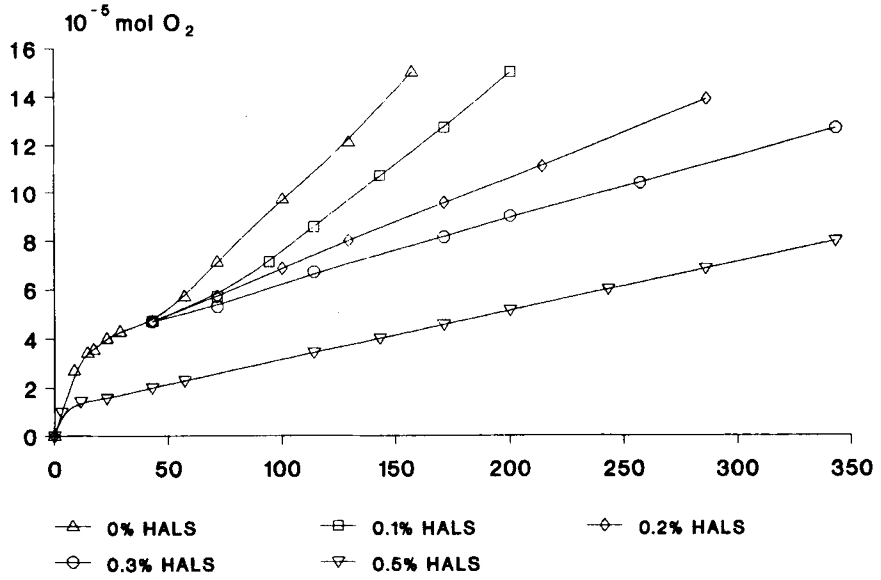


FIGURE 6 Oxygen absorption by SBS films containing 0.05% anthracene irradiated at 350 nm (oxygen pressure 600 Torr).

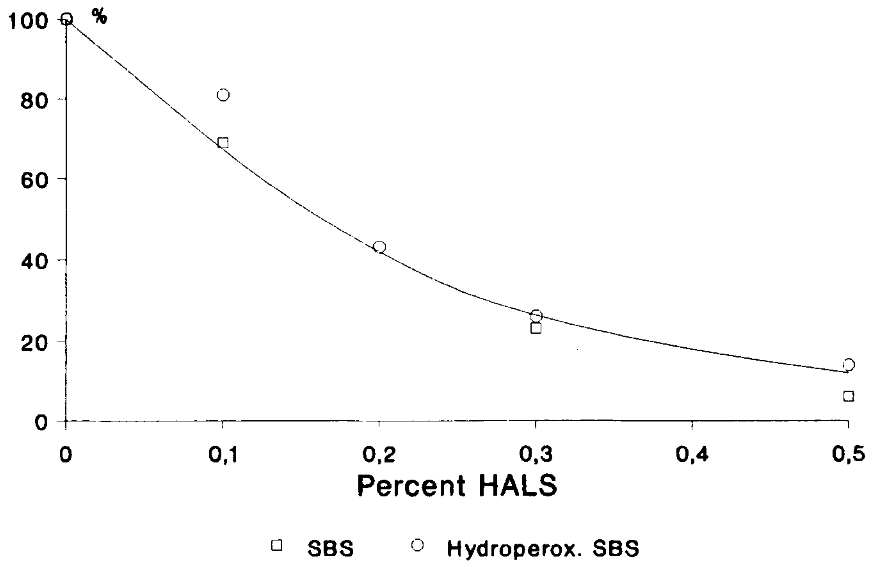


FIGURE 7 Relative rate of oxygen absorption as a function of HALS concentration.

by reaction (11) without initiating the photo-oxidation. The first 30 h of irradiation on Figure 6 correspond to the reaction of singlet oxygen and it can be seen that it is not affected by the presence of HALS except at the highest concentration. It should be reminded also that the experimental conditions of Figures 5 and 6 are different and that 30 h on Figure 6 are equivalent to about 10 h on Figure 5.

The efficiency of HALS as inhibitor of the oxygen absorption is practically the same in SBS and in hydroperoxidized SBS, as revealed by Figure 7. This reflects identical situations at the local molecular level in both polymers: the hydroperoxide concentration is 40 times higher in hydroperoxidized SBS but also the nitroxy radical concentration. Therefore, the fraction of radicals scavenged is the same in both polymers and the rates of oxygen absorption are reduced in the same proportion. However, the time required to reach a given carbonyl absorbance, say 0.1, is extended by a factor 4 when 0.3 weight % HALS is added to hydroperoxidized SBS (Figure 5) and only 2 when SBS contains the same amount of stabilizer (Figure 3). Again, this depends on the nature of the termination step and it should be noticed that in hydroperoxidized SBS, contrary to SBS and EPM, the efficiency of HALS is the same whether it is measured from oxygen absorption or carbonyl absorbance (for instance, 0.3 weight % HALS also reduces the rate of oxygen absorption by a factor 4 as shown of Figure 7). This peculiarity is due to the fact that in hydroperoxidized SBS, termination involves the production of ketones both in the absence (reaction (11)) and in the presence of HALS (reaction (17)). Therefore, inhibition appears likewise on the rates of termination and propagation.

The results discussed above show that the efficiency of HALS as inhibitor of the *propagation* of the photo-oxidation of polymers can be estimated from the decrease of the rate of oxygen absorption. From that view point, HALS is more efficient in SBS than in EPM, probably because of the more efficient scavenging of allyl as compared to alkyl radicals. On the other hand, extension of the time to reach a given carbonyl absorbance depends not only on a decrease of the rate of propagation but also on a possible change in the nature of the *termination* step catalyzed by nitroxy radicals. We have been fortunate enough to observe the three possible situations:

—in EPM, HALS catalyses a termination not producing ketone (reaction (8)) whereas the normal termination involves a ketone (reactions (3) + (11), equivalent to (10)),
—in SBS, we have the reverse situation (reaction (10) instead of (14) identical to (9)) and
—in hydroperoxidized SBS, ketones are produced both in the absence and in the presence of HALS (by reaction (11) or reactions (2) + (7) equivalent to (10)).

This explains why, based on IR spectroscopy in the carbonyl region, HALS looks more efficient in EPM than in SBS while actually the reverse is true, as shown by oxygen absorption measurements.

4. CONCLUSION

The efficiency of HALS as inhibitor of the propagation of the photo-oxidation of different polymers varies considerably. It is based on the competition between reactions (2) and (3) and also between (4) and (5), (6) or (7). In the oxidation of cyclohexane, where cyclohexyl and cyclohexylperoxy radicals are involved,[11] $k_{[2]}/$

$k_{[3]} = 0.05$, what does not favor inhibition of oxygen absorption, but $k_{[4]}/k_{[5]} = 0.01$, what reduces the rate of propagation of the oxidation accordingly. Similar reactivity ratios can be postulated in the photo-oxidation of EPM whereas in SBS the former is probably larger (because of the longer lifetime of allyl radicals) but the latter also (because of the higher reactivity of allylic hydrogen atoms). The final balance is not easy to predict but experimental results show that HALS is more efficient in SBS than in EPM as inhibitor of the propagation of the photo-oxidation.

From a practical viewpoint, however, what really matters in the degradation of polymers is a change of their molecular weight (due to chain scission or cross-linking) whatever the amount of oxygen absorbed. Experimental evidence accumulated not only with EPM and SBS but also with polystyrene,[12] styrene-acrylonitrile copolymers[13] and other polymers indicates that failure of the material is often coincident with the appearance of ketones, even if not the consequence thereof. Now ketones usually result from a termination step that can either be promoted or delayed by the presence of HALS, as we have seen. Prediction of the practical efficiency of HALS in different polymers thus requires a detailed knowledge of the mechanism of the photo-oxidation, namely the nature of the termination step, both in the presence and in the absence of the stabilizer.

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