

PHOTODEGRADATION AND PHOTOSTABILIZATION OF POLYMERS

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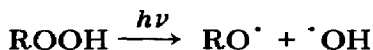
1. Introduction

The past decade has witnessed intense scientific interest in the photo-degradation of polymers [1]. This reflects the concern of the materials technologist for the durability of polymers in the outdoor environment. Two opposed trends can be observed. The first is concerned with the "weathering" behaviour of polymers for use in building and in the automotive industry where durability is essential, and the second with the persistence of some plastics articles (notably packaging) after discard and the need to control the outdoor lifetime of plastics used in agriculture.

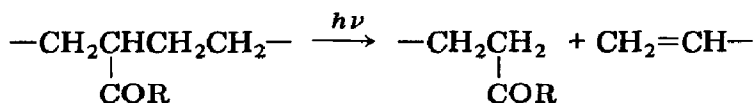
2. The origin of photosensitizing impurities in polymers

Most polymers do not absorb strongly above 285 nm. It is all the more surprising therefore that hydrocarbon polymers such as polypropylene are particularly sensitive to photo-oxidation [2]. A variety of potential chromophores have been considered and in turn discarded in the search for the weakly absorbing photoinitiating species.

Our present knowledge of the chemistry of polymer photo-oxidation is due to the pioneering studies of Bateman and Gee [3] and later of Norrish and coworkers [4, 5]. Both groups showed that hydroperoxides, the primary products of autoxidation, absorb weakly up to 350 nm with the formation of carbonyl compounds which absorb much more strongly. Subsequent work has shown [6] that hydroperoxides are formed as impurities primarily during the high temperature conversion operations used in the manufacture of polymer artefacts. High temperature thermal treatment of polyethylene or polypropylene in argon causes thermolysis of hydroperoxides to carbonyl compounds but significantly leads to a decrease, not an increase, in the initial rate of photo-oxidation. Photolysis of polypropylene in an inert atmosphere has a similar effect on the rate of photo-oxidation. This evidence indicates the primary importance of hydroperoxide photolysis



(R \equiv alkyl) both as a source of initiating radicals and as the cause of polymer chain scission during the photo-oxidation of hydrocarbon polymers. This has been confirmed by a detailed study of the rate constants of the alternative processes. Nevertheless there is also evidence that, when ketonic groups are deliberately incorporated into hydrocarbon polymers, photolysis is the major cause of chain scission. This procedure has been adapted by Guillet to the production of light-sensitive polymers which are particularly useful for the "natural" disposal of short-lived articles such as plastic cups abandoned in the countryside. However, this process has to be clearly distinguished from photo-oxidation, since the primary process involved is the Norrish type II process



which does not give rise to free radicals.

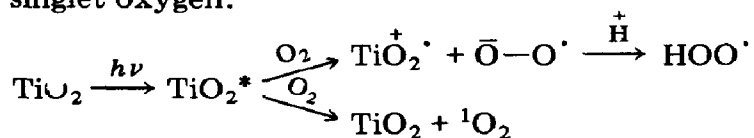
2.1. *The role of carbonyl impurities as sensitizers of photo-oxidation*

Much debate has centred round the question of whether carbonyl impurities, which can be detected even in unprocessed polymers by the sensitive technique of photoluminescence measurement, might be involved in photoinitiation. An ingenious theory by Trozzolo and coworkers [7] proposed that carbonyl compounds might sensitize ground state dioxygen to singlet oxygen, which in turn might attack vinyl compounds resulting from the Norrish type II reaction in the polymer. Hydroperoxides so produced would then behave as described previously. However, the evidence suggests [8] that $^1\text{O}_2$ does not react readily with vinyl compounds, and that it is more likely to be quenched by other chemical species present in much higher concentration. Although $^1\text{O}_2$ does not attack saturated polymers, it does react readily with unsaturated polymers and this may be a possible sensitization process in elastomers, particularly in the presence of certain pigments (see Section 2.2). Conceptually, dioxygen sensitization by carbonyl compounds seems to be an unnecessary postulate in view of the fact that carbonyl compounds are formed from hydroperoxides through radical intermediates. The same argument applies to a more recent proposal [9] that α,β -unsaturated compounds may be responsible for the sensitization of hydrocarbon polymers. What evidence there is suggests that conjugated carbonyl compounds are photostabilizers at normal additive concentration by virtue of their ability to undergo photoisomerization in a non-radical process. It has been noted, however, that hydroperoxides quench the fluorescence of carbonyl groups in polymers, and this has been reported both to increase and to decrease the rate of chain scission of polystyrene containing carbonyl groups.

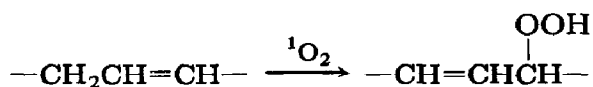
2.2. *Sensitization by contaminants*

Commercial polymers are never "pure" in the chemical sense and, even if the effects of the processing operation could be avoided, they would still

contain minor impurities (*e.g.* metallic catalyst residues) from the manufacturing process and would rapidly become contaminated by constituents of the industrial atmosphere (*e.g.* soot and other combustion products), all of which are potential sensitizers for photo-oxidation. However, extensive studies over the past decade have failed to show that these have a very significant effect on the light stabilities of polymers compared with the indigenous chromophores (hydroperoxides and carbonyl compounds) present in the polymer as a consequence of the profound effect of mechano-oxidation during processing. Other compounding ingredients, notably pigments, can modify the rate of photo-oxidation of polymers very markedly. Titanium dioxide, the most common white pigment, which is also a minor product formed from the ionic polymerization catalyst used in the manufacture of many polymers, has attracted the attention of photochemists since in its photoactive form (anatase) it is capable of sensitizing oxygen either to a radical species (superoxide ion or the related hydroperoxyl radical) or to singlet oxygen:



Singlet oxygen does not react with saturated polymers but is a potent sensitizer in polyunsaturated polymers due to its ability to react with the double bonds in an "ene" reaction:

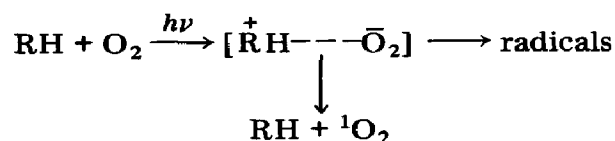


Titania pigments are normally deactivated for use in polymers. Manganese ions are particularly effective stabilizers which act by quenching the photoluminescence of anatase and markedly reduce its photocatalytic activity.

2.3. Sensitization by agents external to the polymer

A variety of photochemically formed minor components of the atmosphere are capable of abstracting hydrogen from polymers [10]. These include ozone, which is present in relatively high concentration in some industrial atmospheres, oxides of nitrogen and sulphur dioxide. Although the latter is not reactive towards polymers in the ground state, the triplet state is an effective hydrogen abstracting agent.

Another possible photoinitiation process which has been suggested on the basis of model compound studies is the formation and excitation of hydrocarbon-oxygen charge transfer complexes:



New charge transfer bands with tails absorbing above 300 nm have been identified in liquid alkanes and alkenes. No positive evidence has been put

forward for the participation of such processes during the photo-oxidation of polymers, but they continue to be invoked.

3. Photostabilization of polymers

It will be clear from the foregoing sections that polymer photodegradation under normal conditions of environmental exposure is essentially a light-initiated autoxidation process. The initiation step, however, is crucial to the length of the oxidation induction period and to the rate of formation of chain scission products, both of which determine the durability of the polymer. The primary reactions occurring are summarized in Fig. 1. The broken lines indicate the points at which the initiation and propagation reactions may in principle be interrupted.

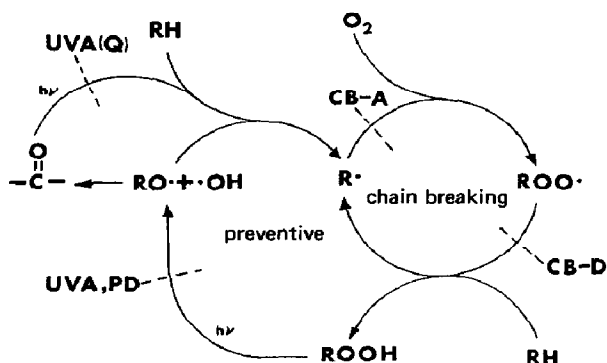
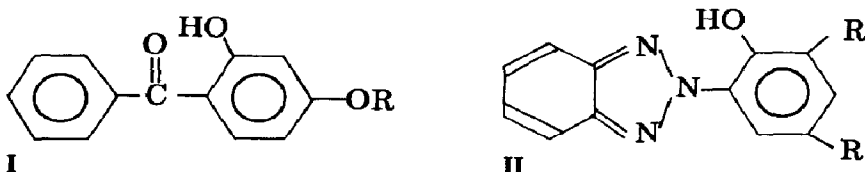


Fig. 1. Photoantioxidants (CB-A, chain-breaking-electron acceptor mechanism; CB-D, chain-breaking-electron donor mechanism; PD, peroxidolysis (peroxide decomposition); UVA, UV absorber; Q, excited state quencher).

3.1. UV absorbers

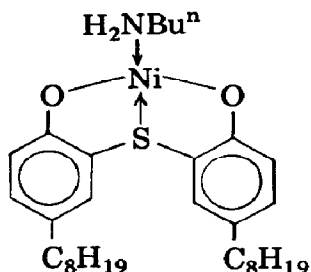
The earliest class of UV stabilizers to be developed commercially was based on the principle of screening the polymer from the damaging influence of UV light. Carbon black, the most effective UV absorber, is still widely used in polyethylene for long-term outdoor applications. Two major classes of colourless light absorbers (I and II)



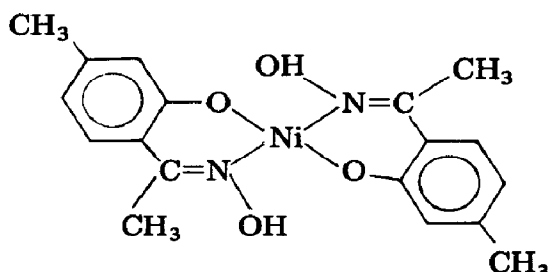
with high extinction coefficients in the region 300 - 350 nm were subsequently developed [11]. It has also been suggested that these compounds may act as "quenchers" for excited states of polymer chromophores. The evidence suggests that I and II do indeed react with photolysis products but by a sacrificial rather than a catalytic process.

3.2. Excited state quenchers

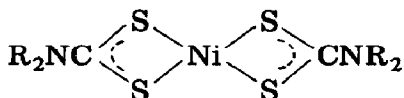
A variety of nickel complex UV stabilizers (e.g. III - V) ($\text{Bu}^n \equiv n\text{-butyl}$)



III



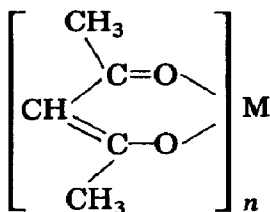
IV



V

have been known for many years to be more effective than the UV absorbers described in Section 3.1. In common with I and II, III - V function at least in part by UV screening; however, their activity cannot be accounted for by UV screening alone. The well-known ability of many metal chelates to quench excited states of molecules led to intense speculation among photochemists in the early 1970s that the stabilizing activity of these compounds might be associated with their quenching ability. No direct correlation has in fact been unequivocally demonstrated under experimental conditions, but the term "quencher" is now part of the vocabulary of polymer photostabilization. It is also used indiscriminately by polymer technologists to explain the mechanism of any UV stabilizer which does not act simply by absorbing UV light.

There is no question that many nickel complex UV stabilizers do have the ability to quench excited states, particularly triplet carbonyl and singlet oxygen, but so do many other metal compounds which are not UV stabilizers. For example, the transition metal acetylacetonates VI

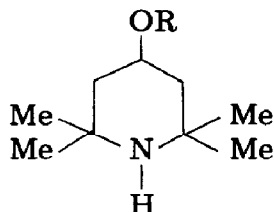


VI

which are effective quenchers of triplet carbonyl, are among the most powerful photoinitiators for the photo-oxidation of polyethylene known. The iron(III) complex is particularly potent. Other studies have shown that the nickel complexes III - V are photostable antioxidants [11].

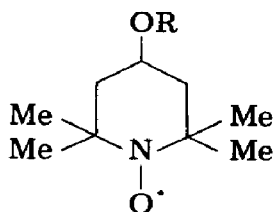
3.3. Chain-breaking photoantioxidants

Most antioxidants acting by the chain-breaking–electron donor mechanism are substituted aromatic compounds, arylamines or phenols and their oxidation products. These are generally unstable to light and behave as photosensitizers for polymers. An interesting recent addition to the range of commercially available UV stabilizers are the hindered piperidines VII [12, 13] (Me \equiv methyl):

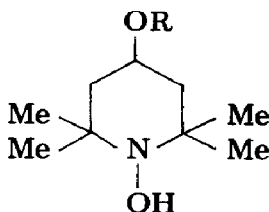


VII

They do not absorb UV light and are transformed in the polymer to the corresponding nitroxyl VIII and hydroxylamine IX



VIII



IX

which are even more effective as photoantioxidants than the piperidine. Attempts to explain the activity of VII - IX in terms of photophysical quenching processes have been largely unsuccessful and the antioxidant mechanism which has emerged as a result of the investigations of a number of research groups is summarized in Fig. 2. The same regenerative cycle involving a nitroxyl–hydroxylamine couple has been observed under other oxidative conditions in polymers [10, 11].

3.4. Synergism involving photoantioxidants

There is an important trend in UV stabilization technology towards multicomponent systems of antioxidants and UV stabilizers which reinforce one another by complementary mechanisms [14]. It has been suggested that a UV absorber may protect an antioxidant from photolysis, but it also appears that the metal complex may protect the UV absorber from photo-oxidation by preferentially destroying the hydroperoxide responsible for this process.

4. Time-controlled stabilization

The ideal requirement for “disposable” packaging or agricultural film is for a photodegradant which has no effect on the polymer until

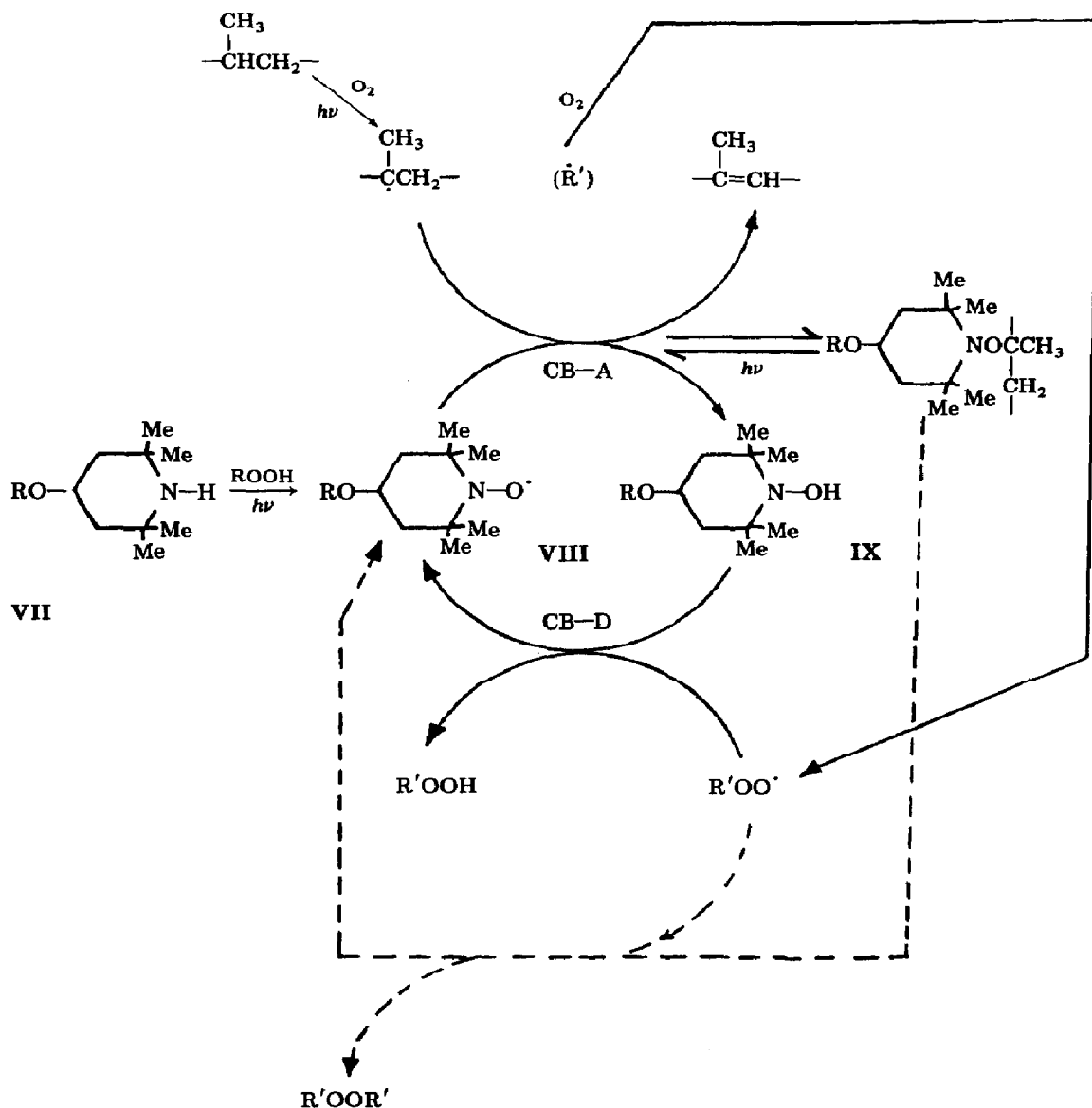


Fig. 2. Mechanisms involved in the photoantioxidant activity of a hindered piperidine.

it is triggered by the effect of UV light. This must occur sharply and controllably [15]. Iron(III) dithiocarbamates fill this requirement almost ideally. At very low concentrations, they are much less photostable than the nickel or cobalt analogues, but at higher concentrations they undergo a role reversal and become short-term stabilizers, changing to photo-pro-oxidants at the end of the induction period. The higher the concentration of iron, the higher is the rate of photo-oxidation at the end of the induction period, because of the photo-pro-oxidant effect of the liberated ionic iron.

In commercial practice a two-component combination of a nickel and an iron dithiocarbamate is used; the former controls the length of the induction period and the latter the rate of the post-induction period oxidation [15]. This allows accurate control of induction times with associated sharp embrittlement.

5. Conclusion

The chemistry of polymer photodegradation has undergone considerable revision during the past decade. Photoexcited carbonyl groups and derived singlet oxygen have been shown to be much less important as initiators for photo-oxidation than was originally thought, and photoantioxidants which were originally believed to function by quenching photoexcited states have been shown to act by interfering with photo-oxidation of polymers by conventional antioxidant mechanisms.

Acknowledgments

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