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Wiles, D. M.; Carlsson, D. J.

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# PHOTOSTABILISATION MECHANISMS IN POLYMERS: A REVIEW\*†

### D. M. WILES & D. J. CARLSSON

Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R9

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### ABSTRACT

Key degradative processes for various polymers are itemised, together with photostabilisation mechanisms which can minimise these processes. Polymers can be conveniently classified as inherent absorbers, which absorb large amounts of solar uv, and as `non-absorbers', that is polymers transparent in the near uv. The former group which includes aramids, polycarbonates and polyesters is predominantly photodegraded by primary processes causing direct bond scission and stabilisation is best effected by the use of uv absorbing additives or opaque pigments. The `non-absorbers' include polyolefins and poly(vinylchloride) which are degraded as the result of oxidative chain processes initiated by chromophoric impurities. For polypropylene the dominant photooxidation product is hydroperoxide which photocleaves to initiate further oxidation. Various uv, stabilisers for polyolefins appear to owe their effectiveness to their ability to decompose hydroperoxide groups and/or to their ability to scavenge free radical intermediates in the oxidative process.

### INTRODUCTION

Sunlight interacts with virtually all organic polymers to cause irreversible chemical changes. The useful lifetimes of polymeric materials are normally measured in terms of their retention of mechanical properties and, for practical purposes, the photooxidative degradation of polymers usually manifests itself in the form of embrittlement, followed by loss of tensile properties on greater exposure. Objectionable discoloration and increased electrical conductivity accompany the photodegradation of some polymers.

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Polymer Degradation and Stability 0141-3910/80/0003-0061/\$02.25 © Applied Science Publishers Ltd, England, 1980 Printed in Great Britain It is obvious that the number and nature of the light-absorbing groups in a polymer system are important considerations but other factors such as photophysics, chemical chain reactions, polymer morphology, chain stiffness, crystallinity, etc. are also involved. The photochemistry of many macromolecular systems has been studied extensively<sup>1-7</sup> and yet no system is fully understood. This is not surprising in view of the complex physics and chemistry involved, and because the mechanics of entangled, high molecular weight molecules is unusually susceptible to chemical changes.

# **KEY PROCESSES**

Since it is polymer backbone scission that leads to embrittlement during photodegradation, it is important to understand what primary photoreactions cause main chain bond rupture as a result of photon absorption. The photooxidative degradation of all polymers can be described in terms of a combination of the following processes:

- (i) absorption of photons by chromophores resulting in electronic excitation of the latter;
- (ii) the breaking of some bonds by a fraction of the excitation energy to produce free radicals (the rest of the electronic energy is dissipated in one or more photophysical processes);
- (iii) subsequent reaction(s) of the radicals, frequently with atmospheric oxygen, in chain processes.

A large number of secondary reactions may occur but the essence of the key initial steps is summarised in Fig. 1. In so far as deterioration of mechanical properties is concerned, the most important primary or secondary reactions are those involving scission of the polymer backbone. Possible scission reactions are indicated in Fig. 1. The range of quantum yields for bond-breaking reactions in polymers spans more than six orders of magnitude.



Fig. 1. The photochemistry of hydrocarbon polymers, (a) indicates processes which can cause backbone scission.

Two extremely important chromophores for polymer degradation are the carbonyl and the hydroperoxide groups. It has been shown,<sup>8</sup> for example, that electronic excitation of the carbonyl chromophores in polyethylene terephthalate (PET) leads to approximately equivalent amounts of Norrish types I and II reactions, both of which cause molecular weight reduction and lead directly to embrittlement of this semi-crystalline polymer, and to some discoloration (reaction (1)). Poly(*m*-phenylene isophthalamide) absorbs strongly in the near uv because of the aromatic carbonyl groups in the repeat unit and the molecular weight decreases during irradiation because of homolytic cleavage (Norrish type I) of the amide bond.<sup>9</sup> Although both of these polymers strongly absorb near-uv radiation, the quantum yields for permanent bond breakage are low ( $\sim 10^{-4}$  mol/einst<sup>8</sup> for the polyester,  $5 \times 10^{-5}$  mol/einst<sup>9</sup> for the aramid in the presence of O<sub>2</sub>). The low values may result from the rigidity of these polymers, which is caused by the relative stiffness of ring-containing backbones. In fact, the presence of O<sub>2</sub> enhances bond scission for both polymers, presumably by reacting with radicals, and preventing back bone 'healing' by radical-radical reactions (for example the reverse of reaction (1a)).



In contrast to polymers with a high inherent absorption of the solar spectrum (cf. spectra shown in Fig. 2), polymers of very low absorption (frequently immeasurably low) from sunlight are usually photodegraded as a result of the absorption of uv wavelengths by impurities. Polyolefins have no inherent absorption at wavelengths as high as 290 nm (cf. Fig. 2 for polypropylene) and should be transparent to terrestrial sunlight. Chromophoric impurities are introduced during synthesis, processing or storage and include hydroperoxide, peroxide and carbonyl groups, catalyst residues, conjugated unsaturation, etc.<sup>7</sup> Polystyrene with an intermediate absorption contains, in addition to oxidation products, some copolymerised oxygen which contributes to its absorption of near uv-radiation. This information is summarised in Table 1.

It should be noted that, regardless of the nature of the photoinitiating chromophores, for polymers containing oxidisable C—H links (polyolefins, PVC,



Fig. 2. Sunlight emission and polymer absorption. Absorbances calculated from  $10 \mu m$  films of polypropylene (PP), polystyrene (PS), poly(ethylene terephthalate) (PET), and poly(*m*-phenylene isophthalamide) (PmPiPA). Reprinted from ref. 6 with permission.

TABLE 1 ABSORBERS IN 'NON-ABSORBING' POLYMERS

(Hydro)peroxides (PP, PE, PVC, PS)	
Carbonyls (PP, PE, PVC, PS)	
$C = C (PP, PE, PVC, PS \dots)$	
Catalyst residues (PP, HDPE, PVC)	
O <sub>2</sub> -hydrocarbon charge transfer complexes (PP, PE, PS)	

etc. and even PET), the following sequence of reactions may occur during photooxidative degradation

$$\mathbf{R} + \mathbf{O}_2 \xrightarrow{k_2} \mathbf{R}\mathbf{O}_2$$
 (2)

$$RO_2 + R'H \xrightarrow{k_3} ROOH + R'$$
 (3)

whenever a covalent bond is cleaved homolytically. Since polymeric hydroperoxides (ROOH) absorb in the near uv and cleave with a quantum yield close to 1.0 (reaction (4)),<sup>7</sup> this group will usually be a significant chromophore. Whichever light-absorbing impurities may be important at the early stages of exposure, it is to be expected that the formation and photolysis

$$ROOH \xrightarrow{hv} RO + OH$$
(4)

of hydroperoxide groups will become a key photolytic sequence during subsequent irradiation (reactions (3) and (4)). The reactions will perpetuate themselves during sunlight irradiation ( $\lambda > 290$  nm) in air, following homolytic bond scission in a

hydrocarbon polymer. This sequence is considered to dominate the photochemistry of polypropylene<sup>7</sup> and probably polyethylene<sup>10</sup> but, it should occur also in the photodegradation of poly(vinylchloride) and perhaps of polystyrene as well. This means that an important bond-breaking process in all of these polymers is the  $\beta$ scission (reaction (5)) of the alkoxy radical (RO·) formed in reaction (4) and also in peroxy self-reactions. An analogous secondary reaction plays an important role in the photochemistry of PET.<sup>8</sup>



Although hydroperoxide photocleavage (reaction (4)) is an efficient process, it must be emphasised that in semi-rigid polymer systems, the efficiency of formation of propagating peroxy radicals by reactions (2) and (3) is very low  $(\sim 1\%^{11})$ presumably because of efficient radical combination reactions before O<sub>2</sub> interception of a macroalkyl. Of the peroxy radicals which result from this cage process, a high percentage can be expected to terminate after only a few propagation cycles (reactions (2) and (3)) by interaction with a peroxy resulting from the same initiation event (secondary cage combination<sup>12</sup>). However a small percentage of the initiation events ( $\sim 0.05\%$ ) yields peroxy radicals which escape secondary combination, and propagate with huge kinetic chain lengths.<sup>12</sup> These truly free freeradicals cause the bulk of the oxidation (and —OOH chromophore production) in polypropylene, and probably also in polystyrene.

An important aspect of -OOH initiated degradation is the suggestion that excited carbonyl species can transfer their energy to -OOH groups (reaction (6)).<sup>13,14</sup> This mechanism will markedly increase the amount of absorbed uv energy (absorbed by the C=O groups) which is available for -OOH cleavage, -OOH groups being very weak absorbers in the near uv. Reaction (6) only occurs by a collisional process and so is efficient only at relatively high concentrations. However, Geuskens and David<sup>13</sup> have pointed out that polyolefin photooxidation produces highly oxidised domains in which the local concentration of oxidation products ( $\supset C=O$  and -OOH) will be high enough for efficient transfer of energy. In addition several other uv absorbing species which are known impurities in polyolefins (such as polynuclear aromatics) can also energy transfer to -OOH by a reaction (6) in solid macromolecular systems is required to allow a meaningful appraisal of its contribution to polymer photooxidation.



### POLYMER PHOTOSTABILISATION

The use outdoors of plastics, fibres and elastomers which have a significant susceptibility to sunlight (e.g. PP, PVC, polycarbonate, etc.) is practical only by means of uv stabilisers; which can be added to the material at an economical level (0.1-1.0 wt %). These additives must interrupt or retard the primary photochemical processes and/or secondary reactions shown in Fig. 1 which lead to the deterioration in mechanical properties by directly or indirectly causing bond scission. From Fig. 1, uv stabilisers may be categorised according to their ability to act as:

- (i) absorbers to reduce the number of photons absorbed by chromophores (Ch),
- (ii) compounds which can deactivate excited species such as  $Ch^*$ ,  $C=O^*$  and  ${}^1O_2$ , normally in some collisional process,
- (iii) compounds which can catalyse the decomposition of hydroperoxides before these groups absorb photons,
- (iv) compounds which can react with free radicals and thus interrupt degradative chain processes.

Obviously it is desirable to use a uv stabiliser which protects by more than one of these mechanisms. In addition, there are situations in which synergistic protection will result from the use of a second additive which 'preserves' the effectiveness of a uv stabiliser.

It is ironic that those polymers with the highest inherent uv absorption, because of chromophores in the repeat unit (cf. Fig. 2), are the hardest to photoprotect. Fortunately they do not deteriorate physically as rapidly as one might expect on the basis of the energy they absorb, quantum yields for backbone scission being only  $10^{-4}$  to  $10^{-6}$  mol einst<sup>-1</sup>. These strongly absorbing polymers are degraded primarily by reactions shown in the left hand section of Fig. 1, whereas impurity initiated polymers are largely degraded as a result of the cyclical reactions. Bearing in mind these differences, it can be seen from Fig. 1 that uv stabilisation can be approached in the same general way for all polymers. Comments on specific stabilisation processes are outlined below.

# uv Absorption

It is obvious from Fig. 1 that polymer additives which reduce the amount of light reaching the chromophores should reduce the rate of polymer degradation and there are opaque or reflective pigment particles that are stabilisers for this reason. Additives which can protect solely by absorbing radiation in the 290–380 nm region are only of limited effectiveness at normal additive concentrations because of the surface photochemistry that dominates strongly absorbing systems (e.g. PET, Nomex) and impurity sensitised systems (e.g. polyolefins). It is worth emphasising that efficient stabilisers, which are commonly referred to as uv absorbers (e.g. the 2-hydroxybenzophenones), probably protect polyolefins by at least one other mechanism.<sup>15–17</sup> Nevertheless uv absorption would seem to be the only clearly proven route by which the intensely absorbing polymers (those destroyed by reactions shown in the left hand section of Fig. 1, such as PET, the aramids, polycarbonates, etc.) can be protected to any degree. Suggestions of energy transfer deactivation of aramids by triazoles<sup>18</sup> need further confirmation to preclude photoprotection solely by the triazole's intense near-uv absorption.

# Excited state quenching

Considerable attention has been paid to the photostabilisation of polymers by means of additives which accept electronic excitation energy by a transfer (or quenching) mechanism before bond scission can occur.<sup>19</sup> The sequence



illustrates the principle, and examination of Fig. 1 shows that energy transfer to additive molecules from initiating chromophores, from carbonyl groups and from singlet oxygen could in principle be photoprotective. In a few specific instances,<sup>19</sup> there is evidence that it does occur.

One of the more common chromophores in macromolecular systems is the carbonyl group (cf. Fig. 1). Not only is it present in the repeat units of many systems (polyesters, polyamides, polyalkyl or aryl vinyl ketones, ethylene/carbon monoxide copolymers, etc.) it is also present as a low-level impurity in many 'non-absorbing' polymers (cf. Table 1), frequently as a consequence of thermal oxidation. In principle, a carbonyl quenching additive should prevent bond breaking Norrish type I and II processes, and should impart photostability to a wide variety of polymer types. In fact there is direct evidence for such protection in only a few instances. In addition it has been concluded recently that the direct photolysis of carbonyl groups is not especially important in the photooxidation of, for example, polypropylene<sup>7</sup> and of high density polyethylene.<sup>20</sup> The Norrish processes are very important, however, in the photodegradation of ethylene/methyl vinyl ketone.<sup>21,23</sup> Moreover, *cis,cis*-1,3-cyclo-octadiene can quench the carbonyl groups in these solid polymers but only by a collisional process, requiring high concentrations.

Beavan and Phillips<sup>24</sup> suggested that  $\alpha,\beta$ -unsaturated carbonyl groups are important chromophores in the photooxidation of polybutadiene. These same authors have also concluded<sup>25</sup> that stabilising additives such as benzotriazoles owe their effectiveness to quenching of the unsaturated carbonyls. Subsequently Allen and McKellar have suggested that  $\alpha,\beta$ -unsaturated carbonyl groups are important chromophores in a host of polymers (e.g. ref. 26 for polyamides) and that quenchers for these groups are effective stabilisers. However there is so far no unequivocal evidence that this is generally the case at room temperature for a variety of triplet quenchers. Many polymers exhibit characteristic luminescence properties<sup>27</sup> but the relevance of this to polymer photodegradation and photostabilisation is not established in most cases.

In principle, during the actinic deterioration of polymeric materials, singlet molecular oxygen can be formed by the interaction of atmospheric oxygen with electronically excited chromophores (cf. Fig. 1). If this occurs, the singlet oxygen  $({}^{1}\Delta_{x})$  will interact with the carbon–carbon unsaturation present in many polymers to form hydroperoxide groups by the 'ene' mechanism. Summaries of such reactions<sup>28,29</sup> clearly indicate that singlet oxygen can contribute to the oxidative degradation of polymers but there appears to be no unambiguous evidence that it is a really significant factor.<sup>30</sup> The basic reason for this is simply that once hydroperoxide groups are formed, the photolysis and subsequent formation of them in a chain process will swamp any  ${}^{1}O_{2}$  effects. Moreover, some of the effective polymer stabilisers (e.g. Ni chelates, and to a lesser extent the hindered amines) will, among other things, quench singlet oxygen anyway.

The reports of excited carbonyl groups being able to efficiently energy transfer to -OOH groups in polyolefins (reaction (6)) has re-opened the question of uv stabilisation by the deactivation of excited carbonyl species. Obviously C=Odeactivation will play an important role in stabilisation if C=O sensitisation of -OOH groups is important in photooxidation. Additive quenching of the excited -OOH groups themselves would be of obvious advantage in polyolefin photostabilisation, but has not yet been reported. The dissociative nature of the first excited -OOH state limits the possibilities of its quenching.

#### PEROXIDES

There is good evidence that hydroperoxides, formed in polymers as a result of inadvertent thermal oxidation during processing, etc., are significant chromophores in the photodegradation of polyolefins,<sup>6,7</sup> poly(vinylchloride),<sup>6</sup> polystyrene<sup>31</sup> and possibly polyamides.<sup>26</sup> Furthermore, the formation and photolysis of hydroperoxides is believed to be important in the photodegradation of at least one strongly absorbing polymer, poly(ethylene terephthalate).<sup>8</sup> It is obvious from Fig. 1 that hydroperoxides will photocleave very readily to start chain oxidations,

reforming —OOH at each propagation step. Although a high proportion of the radical pairs resulting from —OOH photocleavage will self-terminate, and contribute little to photooxidation, any further reduction in the efficiency of radical production from —OOH will enhance photostability. In fact, there are additives which can catalyse the decomposition of hydroperoxides and thus can reduce the rate of photoinitiation, at least in the case of 'non-absorbing' polymers. In the case of polypropylene, for example, hydroperoxide-decomposing additives, such as transition metal dialkyl-dithiocarbamates and dialkyl-dithiophosphates (and/or their active products), can migrate through the solid polymer and destroy —OOH in the relatively long interval (a few days) between —OOH formation and photocleavage during outdoor exposure.<sup>15</sup> Scott has concluded<sup>10</sup> that this phenomenon applies in general to the uv stabilisation of polyolefins. The peroxide-decomposing additives and their active products must of course have adequate light stability, and be nonsensitising.

## RADICAL SCAVENGING

A common feature of the processes by which the useful properties of polymers are lost during outdoor exposure is the homolytic cleavage of covalent bonds. Thus, regardless of the photoinitiators, or of the precise nature of the subsequent photoprocesses, the degrading system will contain radicals such as alkyl (and/or aryl), alkoxy, peroxy, hydroxy, and one or more of these reactive species will be involved in the perpetuation of photodegradation. Stabilisation of some polymers (particularly the polyolefins), therefore, can be obtained by reducing the number and the activity of radicals.<sup>16,32</sup>

Chaudet and Tamblyn<sup>33</sup> some years ago emphasised that free radical scavenging is important in the uv stabilisation of polymers. This observation appears not to have been systematically exploited until relatively recently because of the early observation that hindered phenols do not uv stabilise. However this failure results from the rapid loss or destruction of these compounds during uv irradiation and formation of sensitising products. In fact, if additive loss by volatilisation is physically prevented, hindered phenols do provide some photostabilisation of polypropylene, and the effectiveness of radical scavenging uv stabilisers such as the hindered amines is enhanced.<sup>32</sup> Further evidence that radical scavenging can lower the rate of photooxidation has been obtained by irradiating hydroperoxidised polypropylene film into which scavenging additives had been diffused from solution.<sup>15</sup>

Of the recently commercialised light stabilisers, the hindered amine class has undoubtedly excited the most interest. Efforts have been made to identify the mechanism(s) by which hindered amines derived from 2,2,6,6-tetramethylpiperidine provide such effective uv stabilisation, certainly for polypropylene and probably for other polymers as well.<sup>34</sup> It is generally agreed  $^{16,35-38}$  that the starting structure of the additive is altered during uv exposure to form the nitroxide (reaction (7)).

$$NH \xrightarrow{\text{radicals}} NO$$
 (7)

Nitroxides are known to rapidly scavenge alkyl radicals to give a substituted hydroxylamine by reaction (8), which parallels the oxidative step (reaction (2)). In

$$NO^{\cdot} + R^{\cdot} \xrightarrow{k_s} NOR$$
(8)

addition, further radical scavenging by the substituted hydroxylamine has been suggested to explain the ability of nitroxides to scavenge many times their stoichiometric equivalent of radicals. Although not unequivocally confirmed, reaction (9) is suggested for peroxy radical scavenging with regeneration of the  $\ge NO \cdot .^{38}$  Reaction (9) is in direct competition with the propagation reaction (reaction (3)).

$$RO_2 + NOR' \xrightarrow{k_0} NO' + ROOR'$$
 (9)

Based on the values for  $k_9/k_3$  and  $k_8/k_2$  derived from liquid phase model systems, and the expected concentrations of  $NO \cdot$ , NOPP and  $O_2$  in a photooxidising polypropylene sample, the rate ratios of reaction (3)/reaction (9) and reaction (2)/reaction (8) are ~23 and  $\geq 160$  respectively.<sup>38</sup> Thus  $NO \cdot$  and the substituted hydroxylamine are very weak scavengers in photooxidising PPH. However, several factors appear to allow photostabilisation by  $NO \cdot / NOPP$ . Most important is the suggestion of extremely long kinetic chain lengths (KCL) for PPO<sub>2</sub> · which dominate the oxidation of the polymer.<sup>38,39</sup> With KCL values of  $10^3-10^4$ , only weak scavenging is required to cause a dramatic drop in KCL. In addition, few of the radicals produced by PPOOH photolysis (only 1 in 5 ×  $10^3$ )<sup>39</sup> escape to propagate freely with high KCL, so that a large fraction of PPOOH photolyses actually destroy these chromophores, to give less light-sensitive products.

Two other peculiarities of piperidine chemistry can potentially aid their uv stabilisation effectiveness. First  $NO \cdot$  associates with -OOH groups, with  $\sim 96\%$  of all  $NO \cdot$  groups being associated in model liquid systems.<sup>37</sup> Thus  $NO \cdot$  concentrations adjacent to -OOH groups may be very high, greatly enhancing their radical scavenging propensity. Secondly the substituted hydroxylamines are thermally unstable, slowly decomposing even at room temperature both in the case of NOPP and its low molecular weight models.<sup>40</sup> Decomposition is quite complex

in the liquid phase, and is summarised in reaction (10). Reaction (10a) occurs at only 1/50 of the rate of reaction (10b) in the presence of air. However, in the solid polymer reaction (10a) (a true radical termination process) may be favoured over the peroxy regeneration step. In addition, hydroxylamine (from reaction (10a)) is a highly efficient  $RO_2$  scavenger and hydroperoxide decomposer.

$$NO - \stackrel{i}{C} - \stackrel{i}{C} - \stackrel{i}{C} - \stackrel{i}{C} + \stackrel{i}{C} = C$$

$$NO + \stackrel{i}{C} - \stackrel{i}{C} - \stackrel{i}{C} + \stackrel{i}{C} +$$

In summary, it is reasonable to assume that piperidine derivatives are efficient uv stabilisers because a chain sequence involving the nitroxide radical is selfperpetuating. Thus, it appears possible to photoprotect an inherently susceptible polymer like polypropylene largely (if not entirely) with a radical-scavenging additive.

### CONCLUSIONS

It is worth emphasising some of the key factors essential for effective uv stabilisation. These factors apply to the active species from a stabiliser, that is either the additive itself or its intermediates. Above all adequate light stability of the key constituent is essential, as is persistence in the polymer (resistance to processing conditions, blooming, volatilisation, and extraction). The additive and all of its products must be non-sensitising. Only if these above-mentioned parameters are optimised does the actual protective role bear consideration. From Fig. 1, for inherently absorbing polymers, protection by uv screening is the sole mechanism of any proven importance, albeit an inefficient mechanism in thin articles and moderate additive concentrations. For impurity initiated polymers, where relatively rare initiation events are followed by an oxidative chain producing —OOH chromophores, radical scavenging appears to be the sole essential uv stabilisation mechanism. However photoprotection will be enhanced if the additive or its products can decompose —OOH, and possibly also act as quenchers of some excited states ( $\subset C=O$  and  ${}^{1}O_{2}$ ) in the early stages of photodegradation.

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