

PHOTOSTABILIZATION OF MACROMOLECULES BY  
EXCITED STATE QUENCHING\*

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Abstract - One approach to imparting long-term outdoor stability to polymeric systems is to add to them small amounts of compounds which will quench the electronic excitation energy associated with specific chromophores as a result of photon absorption. Carbonyl groups, hydroperoxides and singlet molecular oxygen (or its precursors) are chromophores commonly believed to be involved in the photodegradative mechanisms for numerous hydrocarbon polymers. Nevertheless, carbonyl quenching additives are rarely effective stabilizers by themselves because carbonyl group photolysis is only infrequently the single most important degradative process. Hydroperoxide group formation and photolysis is frequently more significant but the first excited state is dissociative and cannot be quenched. Singlet oxygen can be quenched with certain additives but there is no evidence that it is a major contribution to the photo-oxidation of any polymer. Efficient photostabilization of hydrocarbon polymers really requires peroxide decomposition and radical scavenging.

INTRODUCTION

There is a great interest at present in the photodegradation of polymeric systems, and this is reflected in the large number of research papers and other scientific publications that appear each year in this subject area. A major reason for this interest is that macromolecular materials have increasingly wide commercial applications where outdoor durability is an important consideration. In this context, all commercial organic polymers will degrade in air when exposed to sunlight although there is a very wide range of photo-oxidative susceptibilities. It is usually the absorption of near ultraviolet (UV) wavelengths which leads to bond-breaking reactions and the concomitant loss of useful physical properties and/or discoloration. Nevertheless there are many factors, in addition to photochemistry, that ultimately determine the useful service life of plastics, fibers and rubbers exposed outdoors; such aspects as photophysics, polymer morphology, chain stiffness and the presence of additives are all significant.

It is obvious from review articles, and from compilations such as the recent one by Rånby and Rabek (1), that the photochemistry of many polymers has been studied extensively. It is equally obvious, however, that in no case is there a complete understanding of how photons interact with a polymer. This is not surprising in view of the complex physics and chemistry involved and because of the fact that polymers are not pure compounds. For example, they commonly contain additives (e.g., stabilizers, pigments, fillers, finishing agents, etc.) and impurities (e.g., oxidation products, catalyst residues, etc.) which may very well influence or even dominate the photochemistry of the polymeric system.

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It is not possible to properly control the outdoor lifetime of a polymer unless the mechanisms of photodegradation to which it is subjected are understood at the molecular level. Therefore, notwithstanding the complications referred to above, it is useful to identify the important chromophores, and to determine which among the dozens of reactions that may be occurring are the significant primary photoprocesses. This sequence begins with the interaction of particular chromophores with incident photons of specific energy to become electronically excited. Some of this absorbed energy is dissipated in one or more photophysical processes (Ref.2) but a fraction of it gives rise to chemical processes, including bond-breaking reactions. Further degradative reactions occur subsequently as a result of the radicals formed when bonds are broken.

The additives used to impart UV stability to commercially important polymers are selected to interrupt one or more of the steps in the sequence outlined above. Light shields, for example, operate basically by interfering with the first-stage in the photodegradative sequence of events, i.e., they stabilize by reducing the amount of energy absorbed by the chromophores in the macromolecular system. Pigment particles may be reflective or opaque; UV absorbers function by absorbing wavelengths which could otherwise initiate polymer photodegradation. To be effective, either type of light shield stabilizer must harmlessly dissipate the excitation energy that it has intercepted.

However effective such an additive may be, some incident radiation will be absorbed by chromophores and these will become electronically excited, normally to their first excited singlet state. Excited singlets have lifetimes in the range 1 to 10 ns whereas excited triplets have mean lifetimes of approximately 10 to 1000  $\mu$ s (Ref.3). Much of the known organic photochemistry involves the longer-lived triplet states (formed from the singlet state by intersystem crossing) and harmless deactivation of these is one of the ways of imparting photostability to polymeric systems. In this paper, a general discussion of the significant primary processes in polymer photodegradation will be used to identify those chromophores which are important in limiting the outdoor use period of the macromolecules. This will be followed by examples of practical UV stabilization by excited state quenching of these chromophores. Finally, attention will be drawn to areas in polymer stabilization for which either not enough is known about degradation mechanisms to apply quenching correctly or else excited state quenching is not applicable.

#### PHOTODEGRADATION MECHANISMS

##### Carbonyl groups

Since literally dozens of reactions can be occurring in a solid polymer during exposure to UV light, it is logical to identify the absorbing chromophore(s), to identify the products (gaseous or polymeric) which are formed, and to relate these two aspects on the basis of known photochemical processes. It is well known, for example, that the ester carbonyl group is the significant chromophore in the photodegradation of poly(ethylene terephthalate) (PET) although only about 1 absorbed photon in a thousand leads to the formation of new products following the rupture of a polymer backbone bond (Ref.4). Similarly, there are other polymers, including many which absorb strongly at wavelengths above 290 nm, for which primary photodegradation processes follow directly from the absorption of photons by carbonyl groups. Examples are the aramids (Ref.5, 6) poly(phenylene oxide), polycarbonates, etc. Furthermore, the work of Guillet et al (Ref.7, 8) clearly shows that the photochemistry of ethylene/carbon monoxide copolymers is the direct result of electronic excitation of the ketone carbonyl groups. The well-known Norrish photochemical reactions (e.g. type I is the more important for the aramids and type II for the ethylene/CO copolymers; both are important in the case of PET) follow on from carbonyl excitation. Clearly, the use of carbonyl quenching additives could reduce the rate of actinic deterioration.

Polymers which do not absorb wavelengths >290 nm should be extremely resistant to sunlight and yet polyethylene (PE) polypropylene (PP) and polyvinyl chloride (PVC) are very sensitive to UV degradation. Since none of these has chromophores in the repeat unit, they must contain UV absorbing impurities or substituents, introduced during synthesis, processing or storage. Carbonyl groups are among those which are formed as a result of

thermal oxidation during processing, e.g., extrusion. Polystyrene (PSty) has an intermediate absorption (> polyolefins, < PET) and this can be attributed in part to O<sub>2</sub> copolymerization with the monomer (Ref.9) as well as to the presence of acetophenone units formed by thermal oxidation (Ref.9,10). However, while it seems certain that carbonyl groups will play a part in the photochemistry of these "non-absorbing" polymers, the importance of these groups (as compared to other chromophoric impurities) is not as clear-cut as in those cases where carbonyl groups are part of the repeat unit in the polymer chains. This uncertainty also applies to the usefulness of carbonyl quenching additives in imparting UV stability to "non-absorbing" polymers.

#### Hydroperoxide groups

There is no question that hydroperoxide group photolysis is a key element in the photodegradation processes of numerous hydrocarbon polymers. The sequence



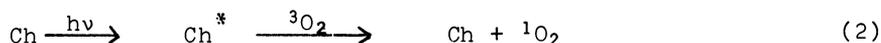
illustrates the wide potential for the formation of these groups. Indeed, together with peroxides, they appear to be formed during the processing of PE, PP and PVC in which case they are likely to act as photoinitiators as well as playing a highly significant role throughout the ongoing photo-oxidation. In addition Geuskens and David (Ref.11) have described the involvement of hydroperoxide groups in the photo-oxidation of PSty, and the mechanism whereby such groups are formed and photolyzed during the UV exposure of PET has been suggested by Day and Wiles (Ref.4).

Upon irradiation with near UV light, peroxides and hydroperoxides photolyze readily (cleavage of the O-O bond) to produce free radicals. It is logical to consider minimizing this effect to improve polymer stability but the first excited state of these groups is dissociative, and deactivation by quenching is not a viable approach.

#### Oxygen and impurities

Singlet molecular oxygen (<sup>1</sup>O<sub>2</sub>, <sup>1</sup>Δ<sub>g</sub>) is known to react with C-C unsaturation, and the importance of this in the degradation of plastics and rubbers has been reviewed recently by Carlsson and Wiles (Ref.12) and by Ranby and Rabek (Ref.13). There is no doubt that singlet oxygen can accelerate the photo-oxidation of numerous commercially important thermoplastics by reacting with the inevitable C-C unsaturation that they contain to produce unstable hydroperoxide groups. The important question, however, from the point of view of photostabilization is to what extent does this really happen under actual exposure conditions.

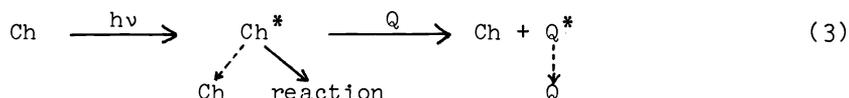
Several ways in which <sup>1</sup>O<sub>2</sub> could be generated in solid polymer systems have been listed (Ref.14) and these include both thermal and photochemical mechanisms. A general version of the formation of singlet oxygen within a UV irradiated polymer is indicated as



where Ch is a chromophore such as dyes, pigments, antioxidant products, carbonyl groups, a variety of impurities or pollutants such as polynuclear aromatic compounds. In principle, therefore, polymer stability could be improved, for those polymers in which <sup>1</sup>O<sub>2</sub> is contributing to photo-instability, by the use of singlet oxygen quenchers. Moreover, quenchers for Ch\* - whatever that may be - could be useful provided that such quenchers can compete successfully with ground state oxygen in the type of excitation-energy transfer illustrated in equation 2. To be of any practical significance, the use of such quenchers against singlet oxygen or its precursor(s) is called for only on the basis of detailed knowledge of the photo-oxidative mechanisms which apply to specific polymer systems.

#### EXCITED STATE QUENCHING

The excited state of a chromophore (Ch) may revert to the ground state by some photophysical process(es) or it may react but it can also be made to transfer its excess electronic energy to a quenching entity (Q):



If energy transfer to the quencher can compete with reaction, decomposition etc. by  $\text{Ch}^*$ , and if  $\text{Q}^*$  can dissipate the excess energy harmlessly, then the system is stabilized. Energy transfer can occur efficiently only if the energy level of the quencher is below that of the chromophore (Ref.15).

Quenching of electronically excited states (singlets or triplets) is frequently described in terms of two distinct phenomena: (i) Long-range energy transfer, e.g., a dipole/dipole interaction as described by Forster is considered to operate between the chromophore and quencher even at distances  $>50\text{\AA}$  if there is significant overlap between the emission spectrum of  $\text{Ch}^*$  and the absorption spectrum of  $\text{Q}$  (Ref.15). It has been suggested (Ref.3) that this process is normally observed in the quenching of excited singlet states. (ii) Contact (collisional) energy transfer of various kinds is said (Ref.16, 17) to require that  $\text{Ch}^*$  and  $\text{Q}$  be within 10 to 15  $\text{\AA}$ . In practice, the quenching of excited triplets is usually ascribed to collisional transfer.

A number of questionable assumptions are made about the stabilization of polymers by additive quencher during outdoor exposure. For example, it is a mistake to assume that polymer stability will invariably be enhanced by quenching a particular chromophore unless there is unambiguous mechanistic evidence about the importance of that chromophore in key photoprocesses. Furthermore, it is frequently assumed that additives in macromolecular systems will be evenly distributed, and this would seem to be very unlikely. Further research is required to elucidate this point as well as to determine the ultimate chemical fate of stabilizing additives.

In order to illustrate the photostabilization of polymers by means of excited state quenching, examples will now be presented of both carbonyl and singlet oxygen de-excitation.

#### Carbonyl groups

Much of the recent work on the quenching of excited carbonyl chromophores by energy transfer to UV stabilizers has been summarized (Ref.18), and it seems that there is a very limited amount of experimental evidence in support of long-range transfer. For example, although Briggs and McKellar (Ref.19) have shown that some nickel chelates quench anthracene triplets in the liquid phase, this appears not to relate to the UV stabilization of PP through ketone carbonyl quenching by these chelates. Subsequently, it has been concluded (Ref.14) that the photolysis of carbonyl groups (Norrish types I and II) is not especially important in the photo-oxidation of PP and that such stabilization as can be obtained with carbonyl quenchers occurs by collisional energy transfer rather than by the long-range process.

There is no doubt, however, about the efficient cleavage of the backbone of ethylene/methyl vinyl ketone copolymers owing to the Norrish type II photoreaction of the pendant ketone groups (Ref.20). In addition, Guillet and coworkers (Ref.17, 21) have shown that cis, cis-1,3-cyclooctadiene will quench both backbone (in ethylene/carbon monoxide copolymers) and pendant [in poly(methyl vinyl ketone)] carbonyl groups in solid polymers. These authors ascribe the requirement for relatively high concentrations of diene quencher to the proximity necessary for the collisional quenching process. Notwithstanding the known participation of carbonyl groups in the photochemistry of high density PE, Scott et al (Ref.22) have shown that the formation of hydroperoxide groups during processing has a dominant effect on the UV stability of this polymer.

Beavan and Phillips (Ref.23) have suggested the importance of  $\alpha,\beta$ -unsaturated carbonyl groups in the photo-oxidation of polybutadiene. They have further concluded (Ref.16) that, unlike the situation with polyolefins, quenching of the unsaturated carbonyls by suitable additives (e.g. benzotriazoles) may be the reason why these compounds are effective UV stabilizers for polybutadienes. Unequivocal evidence that this is the case at room temperature for a variety of triplet quenchers has yet to be published.

### Oxygen and impurities

Since a great many commercial polymers contain carbon-carbon unsaturation, there is a potential contribution to the photo-instability of them from singlet oxygen ( $^1O_2$ ,  $^1\Delta_g$ ) which reacts very rapidly with this unsaturation. Moreover, since ground state oxygen, does not absorb near UV radiation, the formation of  $^1O_2$  by photochemical means in a polymer system will involve an electronically excited triplet precursor (cf. equation 2). Thus, in principle, UV stabilization could be imparted to many polymers by the use of additives which can quench  $^1O_2$  and/or its precursors. Recent discussions of this subject (e.g., Ref. 12, 13) lead one to believe, however, that there is a paucity of evidence for the commercial relevance of this approach to polymer stabilization. The example of PP will serve to illustrate the complexities involved.

Infrared measurements indicate residual unsaturation at a level of  $\sim 0.05M$  in PP and prolonged exposure of a solid film to a stream of  $^1O_2$  results in a hydroperoxide concentration of  $\sim 5 \times 10^{-4}M$  in the polymer (Ref.24). In subsequent UV irradiation, the rate of photodegradation of the  $^1O_2$  treated film is much greater than that of an untreated film. Polynuclear aromatics (PNA), which are present in the atmosphere, are known to concentrate in polyolefins (Ref.25, 26, 27); naphthalene, phenanthrene and anthracene have been detected in commercial PP films from their characteristic fluorescence emission spectra (Ref.24). Finally, PP films which are doped with anthracene before UV exposure photodegrade at a much higher rate than do films from which the PNA have been removed by solvent extraction. This acceleration is more than compensated for, however, if the anthracene-containing film also contains a singlet oxygen quencher, e.g., nickel dibutyldithiocarbamate.

It seems quite clear that singlet oxygen is likely to be formed in PP films exposed outdoors and yet the use of  $^1O_2$  - quenchers as stabilizing additives by themselves will not provide adequate UV stability. There are at least three reasons for this: (i) as soon as hydroperoxide groups are formed - from  $^1O_2$  reactions or from thermal oxidation, for example - these groups will progressively dominate the photochemistry of PP and probably of other hydrocarbon polymers as well; (ii) it can be seen in Fig. 1 that there are

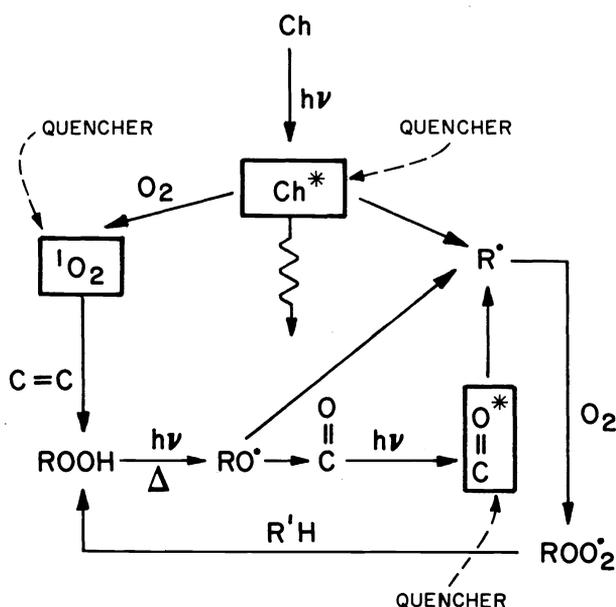


Fig. 1. Schematic illustration of the types of reactions which occur in the photodegradation of hydrocarbon polymers. The potential applicability of quenching stabilizers is also indicated.

numerous routes to bond-breaking reactions that do not involve singlet molecular oxygen; (iii) in many cases those additives which can quench  $^1\text{O}_2$ , and which have been used to show the importance of it in polymer photodegradation, can provide UV stability by one or more other mechanisms (e.g., screening, radical scavenging, OOH decomposition). Notwithstanding the large number of publications on the subject,  $^1\text{O}_2$  has not yet been shown to be the single most important factor in the photo-oxidation of any polymer. Since it can contribute in the early stages of UV exposure, however, it makes sense to use a stabilizing additive which can quench  $^1\text{O}_2$  or its precursors as well as to protect by other mechanisms.

#### CONCLUSIONS

1. Since radiation of near UV wavelengths can be absorbed by solid polymers only in the presence of specific chromophores, bond-breaking (degradative) reactions will normally derive only from the electronically excited state(s) of those chromophores, in the first instance.
2. A detailed knowledge at the molecular level is required of the photolytic and photo-oxidative mechanisms involved in the photochemistry of the polymer under investigation. Only with this information can efficient UV stabilization be achieved.
3. The common features of the photochemistry of hydrocarbon polymers are shown in Fig. 1. It is indicated that stabilization by quenching three types of reactive species is possible, i.e., the original chromophores, carbonyl groups and singlet oxygen.
4. The identity of the chromophores prior to UV exposure is well known in the case of those macromolecules where the repeat unit contains an absorbing group; this is frequently a carbonyl group. After the onset of irradiation, other chromophores may become important.
5. The concentrations of chromophores in "non-absorbing" polymers are commonly below the detection limit prior to irradiation. The identity of them will depend on the conditions of synthesis, processing and storage, as well as on the formulation system involved. Once exposure to UV radiation has begun, hydroperoxide groups are frequently involved in (and may dominate) the subsequent photochemistry.
6. Additives which can quench electronically excited carbonyl groups may be used whether these groups are chromophores present initially or whether they are formed subsequently as part of a free radical chain process. The efficiency of stabilization obtained with such additives depends on several factors, among them the actual contribution to bond-breaking reactions of excited carbonyls.
7. Hydroperoxide groups are important chromophores in the photochemistry of numerous polymers; they are present initially in some polymers (e.g., PE, PP, PVC) and they are formed (and photolyzed) during the photodegradation of these and other (e.g., PET, PSty) polymers. Because the first excited state of hydroperoxides is dissociative, there can be no additives which will quench these groups.
8. Singlet oxygen can, in principle, be formed in a variety of polymers by triplet energy exchange with an excited chromophore. Although singlet oxygen so produced could then contribute to the oxidative degradation of the polymer, the use of additives which only quench  $^1\text{O}_2$  is unlikely to contribute substantially to the outdoor stability of that polymer. This is because of the greater significance of the other degradative routes (especially the cycle involving  $\text{R}^\cdot$ ,  $\text{RO}_2^\cdot$ ,  $\text{ROOH}$ ,  $\text{RO}^\cdot$ ) shown in Fig. 1, at least for those polymers for which the photochemical mechanisms have been established.
9. While the judicious use of quenching stabilizers is justifiable in some macromolecular systems, it appears that two other types of stabilizing additives are of greater importance for protecting hydrocarbon polymers in general. These two are peroxide decomposers and radical scavengers.

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