

FUNDAMENTAL PROCESSES IN THE UV DEGRADATION AND STABILIZATION OF POLYMERS

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ABSTRACT

The phenomenon of 'weathering' of polymeric materials is usually caused by a complex series of chemical reactions initiated by the absorption of ultra-violet light which ultimately result in the deterioration of the physical properties of the polymer. One of the most likely initiating sites for ultra-violet absorption in polymers is the ketone carbonyl group which is often introduced into the polymer by oxidation during its processing or preparation.

Studies have been made of the photochemistry of polymers containing various types of ketone groups to determine the effects of polymer structure, external and internal viscosity, and temperature on the quantum yields of the chemical and physical processes which dissipate the energy of the absorbed light. The application of this information to the stabilization of polymers against ultra-violet degradation is discussed in this paper.

The term 'weathering' refers to a wide variety of chemical reactions and physical processes which occur when macromolecules, either natural or synthetic, are exposed for extended periods of time to outdoor conditions. Extensive research over the past thirty or forty years has shown that for the great majority of synthetic macromolecules, used as plastics and synthetic fibres, the most important degradative mechanisms are associated with the absorption of ultra-violet (u.v.) light. Natural polymers, on the other hand, although they also degrade by photochemical mechanisms usually are more rapidly degraded biologically, that is by the attack of micro-organisms. The protection of polymers against the effect of u.v. radiation, thus becomes of particular importance to the plastics and synthetic fibre industries.

The problem of stabilizing synthetic polymers against u.v. light is not a simple one because polymers break down by a variety of mechanisms. Furthermore the reactions frequently involve the presence of moisture, oxygen or pollutants such as sulphur dioxide, hydrochloric acid, ozone, etc. This makes it very difficult to predict the effective lifetime of plastics in

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various locations of the earth's surface because the concentration of these ingredients, with the exception of oxygen, varies considerably from place to place over the surface of the earth. Furthermore, both the intensity of u.v. radiation and the ambient temperature change markedly with geographic location and with the seasons of the year.

Although their chemical reactions differ widely from one polymer to another, synthetic polymers can be classified into two groups with respect to their changes under the influence of u.v. light. In the first category are polymers such as polyvinyl chloride and polyacrylonitrile which tend to retain their physical properties for extended periods of irradiation but discolour rapidly when exposed to u.v. light. In these polymers the main result of radiation is a change in the chemical structure of the polymer inducing chromophoric groups, but not causing a scission of the backbone of the polymer chain. In the second category are polymers such as polyethylene, polypropylene and polystyrene which tend to embrittle under the action of u.v. light. This effect can be caused by one or a combination of three effects: (1) scission of the main chain, (2) photoinduced crystallization, (3) crosslinking. Although the latter two processes can, initially, improve the properties of the polymer, if the action is allowed to go on for an extended period of time the ultimate result is usually deleterious.

Because of the complexity of the reactions which occur after the absorption of light by synthetic polymers, the simplest route to the stabilization of polymers would seem to be either to prevent the polymer from absorbing the u.v. radiation or, if this is not possible, to prevent the chemical reactions of the excited states induced in the polymer by the absorption of light. To do this it is necessary to obtain a fundamental understanding of organic photochemistry in macromolecular systems.

In the first place it is important to establish the nature of the light to which the polymer will be exposed. The sun has an approximate Boltzmann distribution of energy with a peak maximum at a wavelength of approximately 5000 Å. However, the shorter wavelengths are not available at the earth's surface because they are absorbed by the ozone layer in the upper atmosphere. As a general rule, only light having a wavelength exceeding 3000 Å reaches the earth's surface. This restricts the number of reactions which may occur, since the energy of a quantum of a particular wavelength λ is given by $E = hc/\lambda$ where c is the velocity of light, λ is the wavelength and h is Planck's constant. One Einstein, which is defined as one mole (6.02×10^{23}) of quanta will have an energy which is inversely proportional to the wavelength of light and may be expressed in kilocalories per mole (kcal/mole).

Figure 1 shows a plot of the distribution of energy from the sun in terms of the intensity at the earth's surface as a function of the wavelength or energy per Einstein. Both scales are shown together with the bond strengths of a number of typical covalent bonds. Since the major reaction in the degradation of physical properties is usually the breaking of chemical bonds in the backbone of the polymer, we are interested in what proportion of the total radiation of the sun is sufficiently energetic to break a chemical bond. It is apparent from this figure that, although a large portion of the sun's radiation is sufficiently energetic to break weak bonds such as the O—O bond in a peroxide or an N—N bond, very little of the total radiation is sufficiently

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energetic to break strong bonds such as the carbon-carbon bond and none is available to break bonds such as $C=O$ or $C=C$, which have energies greater than 100 kcal/mole. The chemical bonds involved in the formation of the backbone of most stable polymers usually have strengths comparable to those of the carbon-carbon bond and since biphotonic processes are rather rare in organic photochemistry, we can, therefore, expect from the data shown in this figure that radiation with wavelengths longer than about 4000 Å will be ineffective in bond-breaking processes. Since the radiation having wavelengths shorter than 3000 Å is filtered out by the earth's atmosphere, for many practical purposes we can restrict our photochemistry to the wavelength range of 3000 to 4000 Å.

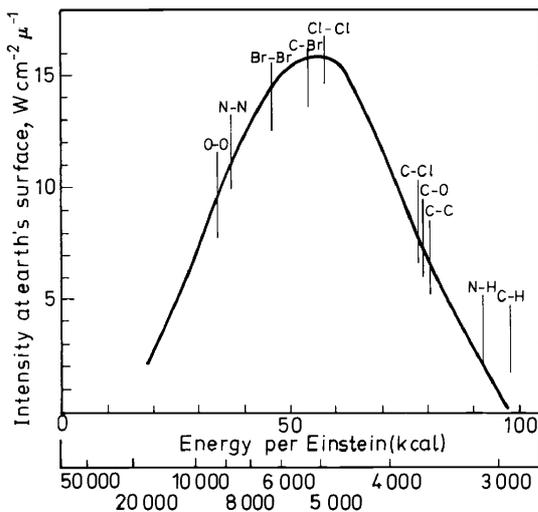


Figure 1. Distribution of solar energy

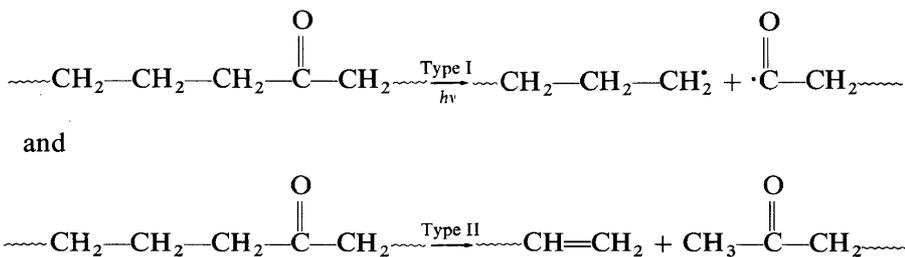
Polymers are known to undergo nearly all of the typical photochemical reactions exhibited by small molecules having the same chromophoric groups; however, the quantum yields are modified and usually reduced by the fact that these reactions must now take place in the solid state. For example, butadiene polymers have been shown by Golub¹ to undergo *cis-trans* isomerization under the action of u.v. light. Polymers containing cinnamic acid groups crosslink by a mechanism similar to the dimerization of cinnamic acid under u.v. radiation, and polycarbonates and polyesters containing phenyl groups undergo reactions analogous to the photo-Fries reaction. Although the occurrence of such reactions does affect the physical properties of the polymer to a certain extent, they do not lead to the ultimate breakdown of the polymer into smaller and smaller fragments.

Many authors refer to any reaction which alters the properties of a polymer as a photodegradation but in our opinion only those reactions which lead to an ultimate destruction of the polymer's most important physical

properties can be considered to fall under the latter classification. Extensive studies have been made on the weathering of a very wide variety of synthetic polymers and in almost every case the reactions involved in the true photodegradative processes have been shown to involve photooxidation. For example, in the photodegradation of polyethylene Tambllyn and co-workers² showed that there was an excellent correlation between the decrease in the physical properties of the polyethylene and the increase in the oxygen content caused by photodegradation. They also showed that the rate of oxidation was closely correlated with the intensity of the u.v. light absorbed and suggested that polyethylene can be used as an actinometer to monitor the amount of near u.v. radiation absorbed by a specimen.

Oxidation processes are notoriously complex and, although in principle it is possible to retard such processes by the addition of additives which interfere with the oxidation chain, a more promising approach to the stabilization of polymers would be to inhibit the photoreactions leading to initiation of the reaction. Consequently, in our work at the University of Toronto, we have concentrated on the fundamental photochemistry of reactions which might be involved in the initiation of photodegradative processes.

One of the most likely chromophores absorbing in the near u.v. is the ketone carbonyl group which is formed in the thermal oxidation of polyolefins and other polymers such as polystyrene containing hydrocarbon backbones. This has been shown to be the group responsible for major damage in the weathering of polyethylene and possibly also in polypropylene. If the carbonyl is located in the main chain or on the adjacent carbon in the sidechain, degradation may occur by one of two processes:



If the carbonyl is in the main chain, both of these processes contribute to the scission of the main chain of the polymer, and hence the degradation of molecular weight and subsequent deterioration of the physical properties of the polymer. If the ketone group is in the sidechain but adjacent to the main chain, only the type II reaction results in scission and degradation of the molecular weight. In both cases the radicals formed by the type I process may initiate further oxidation to produce more chromophoric groups. Additional scission usually occurs as a result of this photooxidation, which can also be initiated by additives which give radical intermediates under the action of u.v. light.

STABILIZATION

The stabilization of polymers against weathering damage involves the retardation or elimination of primary photochemical processes similar to those we have discussed above. There are, in principle, three general ways in which this can be done: (1) by preventing the light from reaching the polymer by use of a coating or an u.v. screen; (2) by preferential absorption of the light by some compound which can dissipate the energy harmlessly (such compounds are known as u.v. absorbers); and (3) by addition of a compound which can remove the excited state energy from the polymer before harmful reaction can occur. This process is designated as quenching.

(1) Ultra-violet screens

These compounds function by rendering the polymer opaque to both visible and u.v. light and thereby prevent the penetration of u.v. radiation beyond the surface thus restricting the total amount of degradation to a thin surface layer. The most important of these substances is carbon black which is the most effective stabilizer for most polymers. The effectiveness of carbon black is dependent on first the type, second, the size of the particles, and third, the degree of dispersion of the particles within the polymer. Channel black, about 250 Å in diameter and highly dispersed throughout a polymer in a concentration of from one to two per cent is probably the best weathering stabilizer known. The stabilization of polyethylene increases with concentration of carbon black up to some practical limit but concentrations greater than five per cent may result in the loss of mechanical properties such as elongation and impact strength. Carbon black is considerably more efficient as a weathering stabilizer than would be predicted on the basis of just its ability to screen the polymer from u.v. light. The increased efficiency of carbon black is usually ascribed to its ability to trap radicals produced during the photooxidative processes which lead to chain degradation. However, Heskins and Guillet³ have suggested that carbon black may also stabilize polymers by its ability to quench the excited states induced in the polymer by the absorption of u.v. radiation.

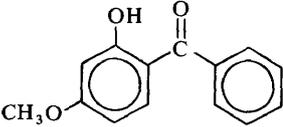
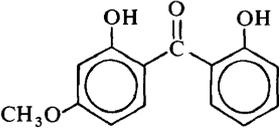
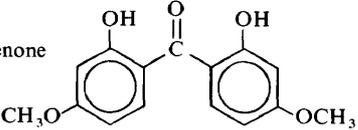
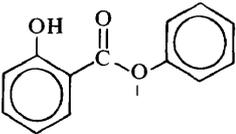
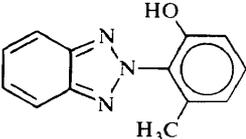
(2) Ultra-violet absorbers

Let us consider some of the factors which must be taken into account in choosing an u.v. absorber to stabilize a polymer system. The first of these is high absorptivity in the region of wavelengths most harmful to the polymer. Since this region of maximum sensitivity varies from one polymer system to another, a universal stabilizer should absorb throughout the entire solar u.v. region. The most widely used stabilizers consist of derivatives of salicylic esters, benzotriazoles and orthohydroxybenzophenones. The structures of typical compounds are shown in *Table 1*. They may be listed in order of increasing absorptivity in the 3000 to 4000 Å range as follows: phenyl salicylate < 2-hydroxy-4-methoxybenzophenone < substituted benzotriazole < 2,2'-dihydroxy-4-methoxybenzophenone. A typical absorption spectrum for 2-hydroxy-4-dodecyloxybenzophenone is shown in *Figure 2* along with the absorption of a ketone group in a typical hydrocarbon polymer. On a molar basis the absorptivity of the stabilizer is about 1000

times that of the polymer. so that relatively small concentrations will absorb most of the incident light. The substance should also impart no colour to the medium, especially when clear films or coating are required. Ideally, then, a stabilizer should absorb strongly in the u.v. region of the solar spectrum incident on the earth's surface, but should have a sharp cutoff at the visible region.

Ultra-violet absorbers, to be effective stabilizers, must also be stable to u.v. radiation or the stabilizer will eventually be used up if it undergoes an irreversible reaction. Compounds which do not chemically react on exposure may still be unsuitable as stabilizers. Fluorescent compounds, unless they re-emit their absorbed energy at sufficiently low energies and sufficiently high rates relative to collisional processes may sensitize degradation by the process of reabsorption by the polymer. Compounds with long-lived excited

Table I. Typical structures of u.v. absorbers

Name	Structure	Wavelength of maximum absorbance, Å	Specific absorptivity
2-hydroxy-4-methoxy benzophenone		3260	42.4
2,2'-dihydroxy-4-methoxy benzophenone		3270	41.2
2,2'-dihydroxy-4,4'-dimethoxy benzophenone		3430	50.2
phenyl salicylate		3100	23.6
2-(2'-hydroxy-5'-methyl phenyl)-benzotriazole		3400	73.0

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states may also transfer energy through collision to the polymer. Therefore it is essential that the electronic energy of excitation of a stabilizer must be dissipated quickly and in a harmless manner.

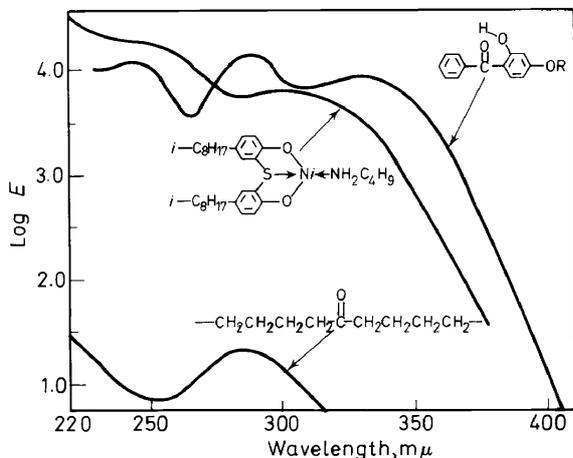


Figure 2. Absorption spectra of polymer and stabilizers in hydrocarbon solution

The orthohydroxybenzophenones represent an important class of light stabilizers. Their effectiveness appears to depend on the reversible formation of a six-membered hydrogen-bonded ring.

The two tautomeric forms in equilibrium apparently provide a facile pathway for deactivation of the excited state induced by absorption of a quantum of light, by a mechanism which does not cause reaction in the polymer and leaves the stabilizer molecule unchanged. The stabilizing efficiency of these compounds increases with the strength of the intramolecular hydrogen bond as measured by the chemical shift in the proton magnetic resonance.

A further requirement of any stabilizer is compatibility. Since protection over long periods of exposure is expected from a stabilizer it must remain soluble in the polymer for an appreciable time.

For similar reasons it is imperative that good light stabilizers have low volatility.

In addition to all of the above requirements, u.v. absorbers should also be heat-stable since the stabilizers may be subjected to heating when they are incorporated into the polymer or during subsequent processing or fabrication.

(3) Quenchers

Recently it has been demonstrated that compounds which do not absorb light can also stabilize polymers by abstraction of the excited state energy from the polymer molecule. This process is known as energy transfer.

There are two basic mechanisms by which such transfer may occur. These are known as resonance energy transfer, which is caused by dipole-dipole interactions over relatively long distances, from 50–100 Å and requires a large overlap of donor emission and acceptor absorption spectrum. The second is exchange energy transfer which requires actual overlap charge clouds of the donor and acceptor molecule and total electronic spin conservation. The latter process usually occurs at diffusion-controlled rates.

Table 2. Quantum yield of chain breaking in ethylene-CO copolymers

Concentration of COD, mol/l.	ϕ , mol/Einstein	Concentration of COD, mol/l.	ϕ , mol/Einstein
0.000	0.0505	0.122	0.0326
0.038	0.0430	0.207	0.0281
0.079	0.0355	0.387	0.0283
0.092	0.0350	0.410	0.0270

Exchange energy transfer was shown by Heskins and Guillet³ to stabilize the photodegradation of ethylene-carbon monoxide copolymers when relatively large amounts of 1,3-cyclooctadiene (COD) were added to the polymer. These results are shown in Table 2. The data are plotted as in Figure 3 in the form of a Stern-Volmer plot, which shows that not all of the degradation can be quenched by the addition of COD. The reason for this is that COD quenches only that part of the reaction which comes out of the triplet state and in aliphatic ketones only about 65 per cent of the reaction results from a triplet excitation state, the remainder coming from an excited singlet.

In the case of aromatic ketones such as in poly(phenyl vinyl ketone) nearly all of the scission reaction results from the triplet excited state and in this case COD can quench nearly all of the degradation reaction.

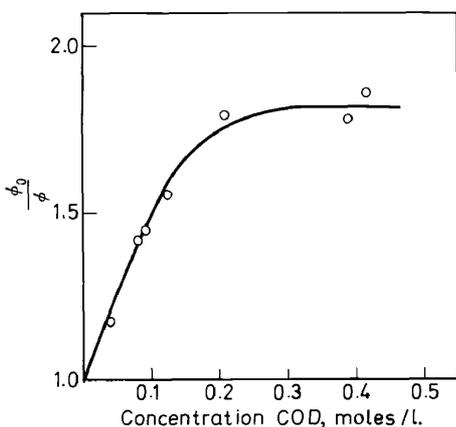


Figure 3. Stern-Volmer plot for quenching by COD

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Experimental results on the photodegradation of poly(phenyl vinyl ketone) and the copolymer of phenyl vinyl ketone and styrene are shown in *Tables 3* and *4*. In this case it is interesting to note that the slopes of the two curves are not the same and this is attributed to the fact that there are two types of

Table 3. Photolysis of poly(phenyl vinyl ketone) (PPVK) in the presence of cyclo-octadiene (COD)

Concentration COD, mole/litre	Concentration PPVK g/litre	ϕ_{rs} (avg)	Number of determinations	ϕ_0/ϕ (avg)	$k_q\tau$ (avg)
0.000	7	0.245	8	1	—
0.079	7	0.053	2	4.6	45.6
0.185	7	0.030	3	8.2	38.9
0.250	15	0.0194	2	12.6	46.4
0.314	7	0.0175	3	14.2	42.0

ketone groups in the copolymer, namely an isolated ketone group in which a monomer unit of PVK is surrounded by two styrene groups, and PVK groups in sequence containing two or more PVK monomer units. It appears from this that the isolated ketone groups are quenched more rapidly than ketone groups in sequence. In this case the photodegradation is quenched entirely by a compound which does not absorb light of the wavelength used in the experiment (in this case 3130 Å). Unfortunately, compounds such as COD are not particularly effective as stabilizers because of the relatively short lifetime of the excited states of these ketone groups. From the Stern-

Table 4. Photolysis of copolymer styrene-PVK (14 mole % PVK) in the presence of COD

Concentration COD, moles/litre	ϕ_{rs}	ϕ_0/ϕ	$k_q\tau$
0.000	0.176	1.0	—
0.021	0.051	3.4	114
0.040	0.031	5.6	115
0.067	0.021	8.4	110
0.067	0.022	8.0	104
0.145	0.0143	12.3	78
0.285	0.0089	19.8	66
0.285	0.0098	18.0	60

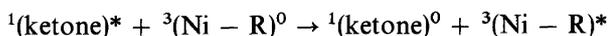
Table 5. Comparison of copolymer and homopolymer

Type	ϕ_0	$k_q\tau$	$\tau_1 \text{ sec} \times 10^8$
Homopolymer	0.245	43	1.7
Copolymer	0.176	120 (initial slope)	4.8

Volmer equation the slope of the quenching curve is proportional to the lifetime of the excited state and thus, to have complete quenching with a small amount of additive it is necessary that the excited state have a long half-life. Alternatively, one must use larger quantities of the stabilizing additive. The lifetimes estimated for various types of ketone groups are summarized in the tables. Ketone groups located in glassy or crystalline regions of the polymer might be expected to have longer excited state lifetimes than those listed in Table 5. One can estimate, however, that the lifetimes would have to be several orders of magnitude longer (i.e. of the order of 10^{-5} sec) in order to have 95 per cent quenching of excited states with an additive concentration less than one per cent by this mechanism. Such long lifetimes may well occur in ketone groups contained in certain aromatic polymers particularly in the glassy state.

Recently Chien and Connor⁴ have reported that certain organometallic complexes may stabilize polypropylene by a resonance energy transfer mechanism as well as by light absorption. The compounds studied were the nickel chelates of 2,2'-thio-bis[4-(1,1,3,3-tetramethyl-butyl)phenol] which quenches the phosphorescence of diethyl ketone in a low temperature glass and also the photooxidation of cumene in solution. In this case the stabilizing molecule also absorbs at wavelengths of 3130 Å and so it is necessary to separate the two effects. However, their evidence appears to be quite strong in this case and these compounds are known to be exceptionally good stabilizers against the photooxidation of polypropylene. These authors suggested that the most probable process for resonance exchange in this case involves quenching of the excited singlet of the ketone group by the nickel chelate which is postulated to have a triplet ground state.

This can be written schematically in the following way;



By quenching of excited carbonyl singlets in this way, it is postulated that the photooxidation process is drastically reduced. The chromium chelate is also effective and both the nickel and chromium compounds are characterized by high absorptivity and excellent stability to u.v. light.

Ershov and his collaborators⁵ have also postulated that hydroxybenzophenones stabilize the photooxidation of polymers by a resonance energy transfer mechanism but in this case the evidence is much less strong. However, it is quite clear that the use of stabilizers which are capable of quenching photoexcited states in polymers could well lead to great advances in the stabilization of polymers. In order to be used effectively, however, it will be necessary to develop very much more fundamental information about the nature of the excited states involved in the photodegradation of polymers and the general photochemistry of polymeric materials.

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