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International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

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To cite this Article Geuskens, G.(1992) 'Fundamental Aspects of the Photooxidation of Hydrocarbon Polymers', *International Journal of Polymeric Materials*, 16: 1, 31 – 36

To link to this Article: DOI: 10.1080/00914039208035406

URL: <http://dx.doi.org/10.1080/00914039208035406>

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Fundamental Aspects of the Photooxidation of Hydrocarbon Polymers

G. GEUSKENS

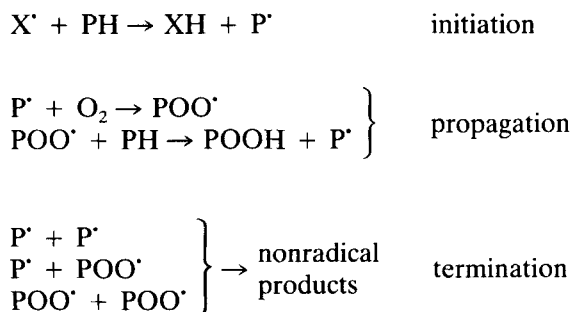
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Hydrocarbon polymers (polyolefins, polystyrene and many saturated and unsaturated rubbers) make up the largest group of synthetic polymers. They all degrade more or less rapidly on exposure to sunlight, though they should not absorb in the solar uv range (290–400 nm) if they are perfectly pure. This makes a clear understanding of their mechanism of degradation important not only from a practical but also from a fundamental point of view. We try to answer some fundamental questions such as the following. How is the photooxidation initiated? What is the exact mechanism of the reaction? How do chain scission and cross-linking proceed?

KEY WORDS photooxidation, hydrocarbon polymers

MECHANISM OF THE PHOTOOXIDATION OF HYDROCARBON POLYMERS

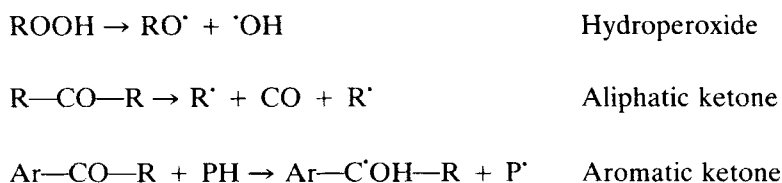
The basic mechanism of oxidation of hydrocarbon polymers, whether thermal or photochemical, is a chain reaction involving initiation, propagation and termination:



However, the nature and origin of X' , the kinetic chain length and the type of termination are specific features of each type of oxidation. Of course, the chemical nature of the polymer also has some influence.

a) Initiation

In natural aging conditions, on exposure to sunlight in the presence of air, the photooxidation of hydrocarbon polymers is initiated by anomalous structures absorbing above 300 nm that are usually thermal oxidation products. The relative efficiency of each type of chromophore depends on its absorption coefficient in the solar uv range and on the quantum yield of production of free radicals from its excited state. The following photochemical reactions of ketones and hydroperoxides are well known from low molecular weight model compounds¹:



Approximate values of absorption coefficients and quantum yields are collected in the following table, together with relative efficiencies that are the product of the two previous values.

Chromophore	Abs. coeff. at 310 nm ($1 \text{ mol}^{-1} \text{ cm}^{-1}$)	Quantum yield of radical production	Relative efficiency
Hydroperoxide	0.3	0.5	0.15
Aliphatic ketone	5	$2 \cdot 10^{-4}$	10^{-3}
Aromatic ketone	60	$3 \cdot 10^{-2}$	1.8

From the table above it can be predicted that in polyolefins, hydroperoxides are about 150 times more efficient than aliphatic ketones, at the same concentration, in initiating photooxidation, which is in agreement with experimental results.² In polystyrene, however, aromatic ketones of the acetophenone type are more efficient than hydroperoxides.^{3,4} Also it should not be overlooked that energy transfer from chromophores with a high absorption coefficient, such as ketones or phenyl groups, for instance, to hydroperoxides⁵⁻⁷ can result in a more efficient initiation of photooxidation.

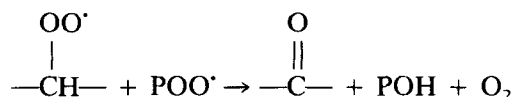
b) Propagation

In the photooxidation of polymers at room temperature, the mobility of free radicals produced close together is rather limited. Therefore, the probability of recombination is quite high. This makes the kinetic chain length very short as compared to thermal oxidation at higher temperatures. It has been shown that propagation involves no more than one² to four⁴ steps. As a consequence, termination products are practically as important as hydroperoxides formed in the propagation and their nature is a key parameter in the mechanism of degradation. Indeed, the nature of

termination products accounts for different behaviors of saturated and unsaturated hydrocarbon polymers⁸ (see below) and the efficiency of some photostabilizers can result more from a change in the nature of termination products than from inhibition of the propagation.⁹

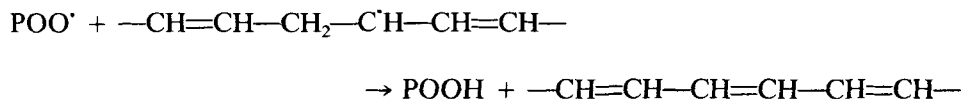
c) Termination

Alkyl radicals formed in polyolefins react very quickly with oxygen and in natural or even accelerated aging conditions in the presence of air, there is no evidence of cross-linking by recombination of alkyl radicals. The most likely termination involves two peroxy radicals and, if at least one of them is secondary, a ketone is produced that is responsible for further chain scission in the polymer:



The same situation prevails in polystyrene, although recombination of benzyl-type radicals resulting from abstraction of tertiary hydrogen atoms also occurs to some extent.⁴

In unsaturated hydrocarbon polymers of the polybutadiene type, more stable allyl radicals are formed and also labile allylic hydrogen atoms are available. This makes the following termination much more likely:



In this case, no ketone is formed initially and infrared spectra in the carbonyl region reveal an apparent induction period.^{8,9}

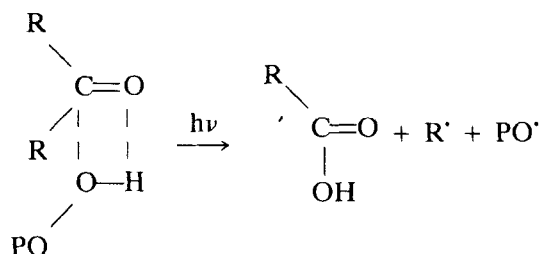
CHANGE OF MECHANICAL PROPERTIES DURING PHOTOOXIDATION

From a practical point of view, what really matters in the photooxidation of polymers is a change of their mechanical properties. This is usually the consequence of either chain scission or cross-linking. Now, this occurs neither in propagation nor in termination of the photooxidation of hydrocarbon polymers. It is thus obvious that sooner or later a change in the above-mentioned mechanism should happen.

a) Change of mechanism

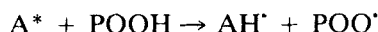
One specific feature of the photooxidation of hydrocarbon polymers is that polar oxidation products (hydroperoxides or (and) ketones) are formed in a nonpolar matrix in conditions such that they cannot diffuse apart. Thus, they form clusters in which they are usually hydrogen bonded. In polyolefins, hydroperoxides and

ketones are produced from the very beginning of the photooxidation and, if their local concentration is high enough, they form ground state complexes the absorption of which is shifted to longer wavelengths with respect to the components.¹⁰ The absorption coefficient of such complexes in the solar uv range thus is also larger than those of ketones and hydroperoxides. Moreover, the quantum yield of radical production is probably close to that of hydroperoxides because efficient energy transfer occurs from ketones to hydroperoxides.^{11,12} At a certain level of oxidation, a new mechanism thus becomes operative, resulting in chain scission and simultaneous production of carboxylic acids.^{10,13}

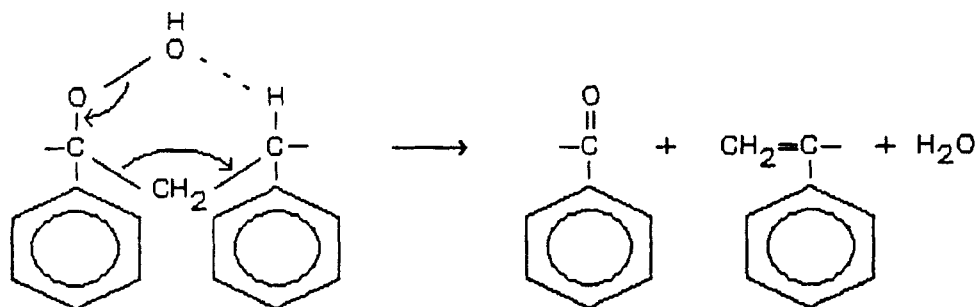


As a consequence, the rate of oxygen absorption increases very quickly because free radicals are produced with a higher quantum yield and the polymer soon becomes unserviceable. Also the carbonyl absorption increases dramatically but this is mainly due to conversion of ketones into carboxylic acids the absorption coefficient of which is twice higher.

In polystyrene, as the local concentration of aromatic ketones of the acetophenone type and of hydroperoxides is high enough, exciplexes are formed involving the excited state of the ketone. These result partly in hydrogen abstraction⁵:

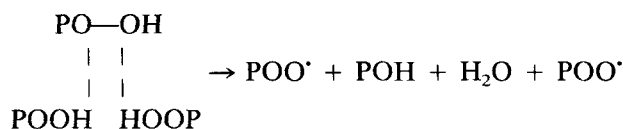


and partly in chain scission through decomposition of the hydroperoxide moiety^{4,13} without production of carboxylic acid groups:



In unsaturated hydrocarbon polymers, hydroperoxides are the only type of oxidation product formed initially in both propagation and termination steps. They

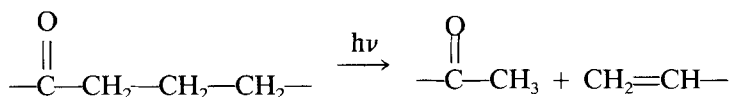
progressively form clusters responsible for a change of mechanism because, on absorption of light, they now decompose by a concerted mechanism and generate two geminate peroxy radicals^{8,9}:



Most peroxy radicals quickly react in a cage and produce ketones (see above) but some abstract hydrogen atoms and generate neighboring allyl radicals. As these now recombine, cross-linking occurs when no change of the molecular weight could be detected earlier.

b) Change of molecular weight

In polyolefins, chain scission occurs from the very beginning with a quantum yield of the order of 0.01 as a consequence of the Norrish Type II reaction of ketones:



But later, as a change in the mechanism occurs resulting in the production of carboxylic acids (see above) the quantum yield is expected to increase close to that of decomposition of hydroperoxides (thus at least by a factor 10). Cross-linking is only a minor process.

In polystyrene, chain scission proceeds by the same mechanism (see above) throughout the photooxidation range with a quantum yield of about 0.003 while cross-linking is one order of magnitude less efficient.⁴

In unsaturated hydrocarbon polymers of the polybutadiene type, no molecular weight change occurs initially. Cross-linking is the consequence of a change of mechanism induced by clustering of hydroperoxides (see above).

CONCLUSION

The photooxidation of hydrocarbon polymers is usually initiated by hydroperoxides or (and) ketones present as impurities. These are responsible for the production of free radicals that initiate a very short chain reaction. Therefore, products formed in the termination step are as important as hydroperoxides formed in the propagation. At an early stage of photooxidation, they are most often ketones and alcohols, sometimes hydroperoxides and unsaturations and seldom recombination products. Only in this last case does photooxidation directly result in a change of the molecular weight from the very beginning.

Chain scission, responsible for a change of the mechanical properties in poly-

olefins and in polystyrene, is the consequence of the photolysis of ketones, hydroperoxides or complexes and exciplexes of these two species.

In the photooxidation of hydrocarbon polymers, clustering of polar oxidation products in a nonpolar matrix sooner or later results in a change of the reaction mechanism. This usually has a strong influence on the mechanical properties of the polymer since it provides new ways to chain scission or cross-linking.

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