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# Photodegradable polyolefins. Photo-oxidation mechanisms of innovative polyolefin copolymers containing double bonds.

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**Abstract**

Photodegradable polyolefins based on ketone carbonyl and carbon monoxide copolymers are discussed. The proposed photo-oxidation mechanisms for these copolymers show efficient chain scission processes photoinduced by Norrish I and II reaction in polymer matrix. Other polyolefins copolymers containing unsaturation have been suggested as new innovative and photodegradable materials. In the photo-oxidative conditions, the formation of $\alpha,\beta$-unsaturated ketone impart high yields of chains scissions leading to a rapid embrittlement and fragmentation of these copolymers.

## 1. INTRODUCTION

Degradable plastic materials can be divided into photodegradable and biodegradable; materials in which the degradation mechanism is based on a starch component are often considered separately. Different approaches to develop photodegradable polyolefins have been adopted, including both the copolymerization with ketone or carbon monoxide carbonyl groups and addition of photosensitizer metal complexes [1].

One of the simplest ways of modifying existing polymers to increase the degradability is to accelerate processes already taking place. Most polymers are subject to photo-oxidative degradation upon exposure to sunlight. Additives and impurities catalyze the breaking of the polymer chains by a series of UV-initiated free radical reactions [2]. Initial research in this field was aimed at minimizing such degradation to stabilize materials [3]. Nowadays some efforts on the addition of photosensitizer species, such as carbonyl groups or metal complexes, are being made to accelerate some degradation processes [4-5]. Photosensitization of reactive

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blending polymer materials is presently achieved by inserting suitable chemical groups into the chains and by controlling the morphology and mechanical properties by synthesis. Some innovative copolymers containing double bonds are now available in industrial scale thanks to the developments of Ziegler-Natta catalysts in polyolefin polymerization. The presence of double bonds causes an enhanced photodegradability by favouring a rapid photo-oxidation processes of these plastic materials [6].

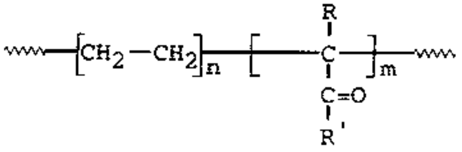
Areas of interest of these plastic materials based on polyolefins include agricultural mulch films and packaging products likely to end up as litter. Their use can avoid the costs of removal and disposal of these films each year [7]. These application require a well-defined degree of UV exposure as well as the adjustment of tailor made photoinitiating groups to control outdoor exposure lifetime.

Albertsson and co-worker elegantly demonstrated that the total environmental effects (photo-oxidation + biodegradation) work synergistically towards deterioration of polymer materials during the outdoor exposure [8]. The photo-oxidation increases the low molecular weight fractions by chain breaking and improves the surface area through embrittlement. In addition, the formation of carbonyl groups on polymer surfaces increases the hydrophylicity of polymers. Consequently, the possibility of further degradation induces a significant enhancement towards mineralization of plastic materials [9].

Finally, the progress in this field leads to the conclusion that the developments of biodegradation studies cannot be separately treated from the photo-oxidation improvement in plastic materials.

## 2. KETONE CARBONYL COPOLYMERS

In the past years, a commercial product as Ecolyte has provided a possible solution in the preparation of photodegradable polymers [4]. Ecolyte consists of a masterbatch or concentrate containing ketone groups copolymerized (see scheme I) with polyethylene, polypropylene or another industrial polymer, where R, R' are alkyl or aryl substituents.The rate of degradation of these copolymers can be modified both by changing the substituents or by blending with resins in different ratios from 1:20 up to 1:9, after extrusion with conventional methods [10]. The degradation mechanism of Ecolyte involves the absorption of light by carbonyl groups, which have a maximum at wavelengths from 280 to 330 n depending upon substituent. The sunlight causes a $n \rightarrow \pi^*$ transition localized on carbonyl groups including Norrish I (NYI) and Norrish II (NYII) type photochemical reactions [11] (see scheme II).

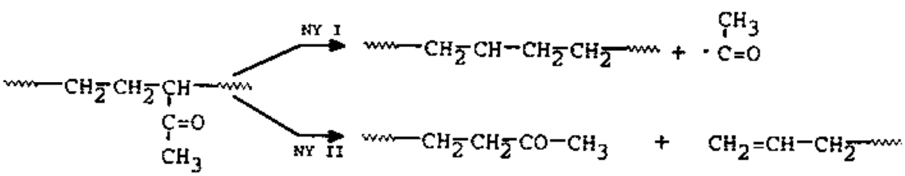


$$\sim\!\!\left[CH_2-CH_2\right]_n\left[\;-\underset{\underset{R'}{|}}{\underset{C=O}{|}}\overset{\overset{R}{|}}{C}-\right]_m\!\!\sim$$

Scheme I

In the case of ethylene-co-methylvinylketone copolymers and ethylene-co-methylisopropy-ketone copolymers, only a NYII reaction causes direct cleavage of the polymer backbone. The NYI is important in the formation of tertiary radicals initiating the chain hydroperoxidation [2]. These reactions generate a relatively rapid embrittlement and fragmentation of the polymeric product facilitating the final ingestion by microorganisms. The adjustment of R and R' substituents as well as of concentrations can tailor the degradation time to suit the amount of radiation in different areas and in different seasons.

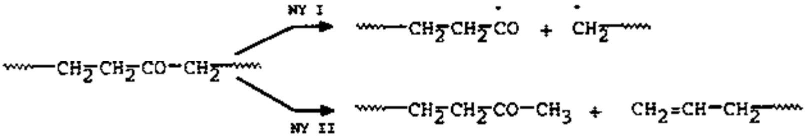
The main criticism levelled at these materials was that the presence of very mobile hydrogen atoms can develop degradation reactions also in absence of light, during the storage.



Scheme II

## 3. POLY(ETHYLENE-CO-CARBON MONOXIDE) COPOLYMERS

Another successful approach developed by Guillet and coworkers was the copolymerization of ethylene with carbon monoxide [4,12]. Some commercial products were used by Dow Chemical, DuPont and Union Carbide for beverages containers. The current catalytic system permits only the copolymerization with low density polyethylene (LDPE) at a level below 2% of CO in the chains. The degradation mechanism for these materials is similar to that of ketone carbonyl copolymers except that the carbonyl groups now are located along linear chains (see Scheme III). Their photochemical behaviour shows that



Scheme III

the quantum yield of the NYI reaction is quite low (~0.001). That of NYII processes was 0.02, independently of whether or not the polymer was photo-oxidized in solution or in the solid state above their glass transition [13]. The rate of photodegradation can be controlled by adjusting the percentage of CO in the chains. The chain scission processes can generate an efficient embrittlement and fragmentation followed by an eventual slow assimilation by micro-organisms.

As in case of ketone carbonyl photodegradable plastic materials, the photosensitive group is chemically bonded to the polymer backbone. This important condition can avoid the possible diffusion into food when this material is used for packaging applications.

A concentrated copolymer blended with homopolymer does not degrade as effectively as the pure one with the same CO amount [14].

## 4. ANTIOXIDANT-PHOTOSENSITIZER ADDITIVES FOR POLYOLEFINS

The third approach commonly followed by plastic industries is the use of a wide variety of inorganic or transition metal complexes which act as photosensitizer or photoinitiators. These additives have found applications particularly in the enhancement of the photodegradation of polyolefins [2], where several acetylacetonates, dithiocarbamates, stearates and oximes ligands were claimed as photoinitiators. The photosensitization activity of acetylacetonates depends mainly on the transition metal used increasing in the order: Ni < Zn < Fe < Co [15]. The nickel acetylacetonate works as a mild photostabilizer, while the corresponding cobalt one causes a rapid photo-oxidation and embrittlement even without exposure. Similarly, the dithiocarbamates showed an optimum concentration of about $4.10^{-5}$ mol/100 gr of polymer as limiting sensitizing activity [16]. On the other hand, this means that polyolefins containing a lower concentration than the limit value can be stabilized in the presence of this class of compounds.

The detrimental effects of some flame retardant additives under photo-oxidative conditions has been taken into consideration for photodegradation of polymers [17]. Some polychlorinated aromatic compounds can induce a prominent UV-initiated photo-oxidation for the hydrogen abstraction by chlorine radicals resulting in high hydroperoxidation yields.

The main difference between materials containing photosensitizer additives and the photodegradable ketone copolymers is that the activity of the former can be also present in absence of light [2]. From practical point view, these additives can be a source of toxic effects due to metal residues when they are used in packaging or in food preservation.

Rabek et al. recently contributed to this research field using Fenton reagents to obtain the photo-oxidative degradation of different polymers polyethyleneoxides, which are able to form complexes with the ferric salts [18]. The photolysis of $FeCl_3$ generating chlorine radicals has been indicated as the main responsible for the accelerated photodegradation of polyethyleneoxides.

## 5. POLYOLEFIN COPOLYMERS CONTAINING UNSATURATIONS

A new generation of Ziegler-Natta catalysts has been recently developed for the

## a) Photo-oxidation of poly(propylene-co-hexadiene) copolymers

The photodegradability of this copolymer as a functions of hexadiene content in the polymer chains has been carried out with a photoaccelerating equipment (Sepap 12.24) simulating the outdoor exposure [27]. The method commonly proposed to detect the changes during accelerated photo-oxidation is based on a kinetic approach by analysing the different oxidation products using some spectroscopic techniques such as UV-visible, FTIR and ESR [28].

In the case of PPH copolymers the main changes in FTIR spectra have been detected in the CH out-of-plane deformation of double bonds, which decreases smoothly during the photo-oxidation (Fig.2).

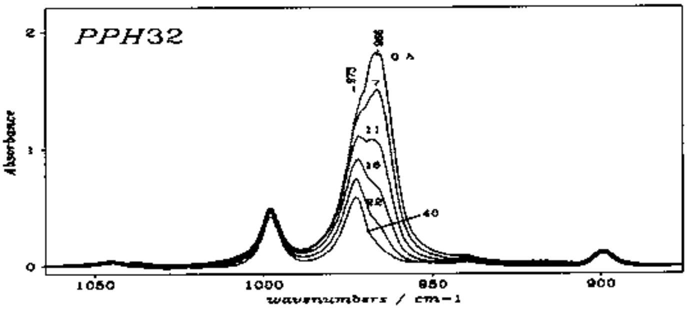


**Fig.2.** Disappearance of the CH out-of-plane deformations of double bonds at 966 cm$^{-1}$ during the photo-oxidation. of PPH copolymer.

A typical spectroscopic pattern for polyolefins has been observed between 1800 and 1500 cm$^{-1}$ and attributed to the formation of aliphatic acids (1710 cm$^{-1}$), carbonyl (1720 cm$^{-1}$), esters (1735 cm$^{-1}$) and $\gamma$-lactones (1765 cm$^{-1}$) groups [29-30]. Similarly, an increase of a broad band centred at 3420 cm$^{-1}$ in the OH stretching region is assigned in these plastic materials to the formation of hydrogen bonded hydroperoxides in the early stage of photo-oxidation [31].

It is well-known that the presence of butadienic unsaturations units in the chains involves an efficient hydroperoxidation of allylic positions, which are very reactive in the photo-oxidation conditions of polymer matrices [32]. The further photoinduced chain breaking reactions of allylic hydroperoxides can give origin to macroalkoxy radicals forming, by $\beta$-scission mechanisms, the above-mentioned carbonyl groups [29-32]. Some results of Carlsson and Wiles [33] indicate that macroalkoxy radicals in polypropylene undergo $\beta$-scission to give roughly equal quantities of backbone ketone and terminal methyl ketone (see Scheme II). The photochemical behaviour of carbonyl groups in polymer matrices is similar to that of ketone copolymers which are known undergo by NYI and NYII type reactions.

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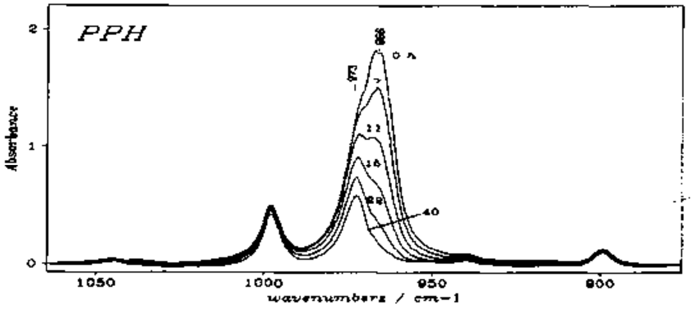

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### b) Photo-oxidation of poly(ethylene-co-hexadiene)

The polyethylene based copolymers bearing trans hexadiene units (PEH) show the same behaviour as that of the corresponding polypropylene ones under photo-oxidative degradation conditions. Isolated hydroperoxides groups have been detected at 3550 $cm^{-1}$ in FTIR spectra. The rate of formation can be related to the total amount of hexadiene unsaturations in the chains. As in case of the PPH copolymers, hydroperoxidation occurs at the allylic positions without modifying the wavenumbers of double bonds deformation vibrations in the FTIR spectra [31,33]. It is widely accepted that the formation of hydroperoxides in these plastic materials occurs at the allylic positions by hydrogen abstraction processes. In facts, the hydrogen abstraction are most probable in mobile hydrogen atoms, which can be readily abstracted by radical chain mechanisms. A typical reactivity of hydrogen atom bonded to carbon one reflects the following order in the photo-oxidative conditions: benzylic > allylic > tertiary > secondary > primary carbons [34].

The decomposition of allylic hydroperoxides must be considered to explain the high radical contents generating extensive oxidation under photo-oxidative conditions. The high concentration of macroalkoxy and macroperoxy radicals are the main responsible of the saturation reactions involving double bonds observed in FTIR spectra.

The corresponding ethylene-based copolymers bearing cis-hexadiene units can isomerize forming trans-hexadiene units during the overall chain radical reaction in photo-oxidative degradation. The presence of trans-hexadiene unit formation can be detected at 966 $cm^{-1}$ simultaneously with the disappearance of cis double bonds at 690 $cm^{-1}$ as reported in Fig. 3.

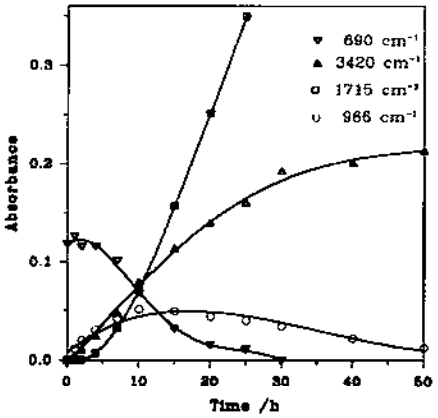

**Fig. 3.** The overall oxidation products formed in a PEH copolymer containing 7% of cis-hexadiene unsaturations in the chains.

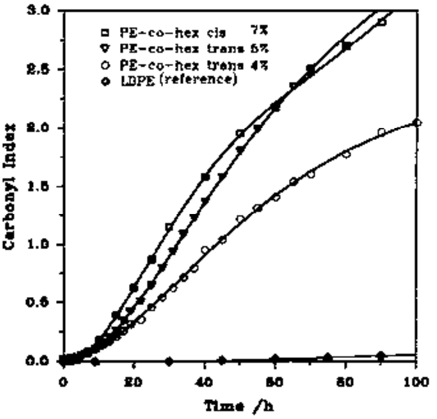

**Fig. 4.** Carbonyl index of some polyethylene based copolymers containing different amounts of hexadiene in the chains.

The other oxidation products corresponding to alcohols (3420 $cm^{-1}$) and carbonyls (1715 $cm^{-1}$) are also related to the disappearance of double bonds at 690 $cm^{-1}$. Figure 3 shows that carbonyl groups are formed after appreciable accumulation of hydroperoxides in the polymer matrix. The rate of hydroperoxides formation can influence the duration of the induction time of carbonyl generation which is dependent on the efficiency of hydrogen abstraction reactions to form hydroperoxides on the allylic positions for these copolymers. The amount of unsaturations is of great importance to accelerate the carbonyl formation rate in polymer matrix as reported in Fig. 4. The degree of photo-oxidation is usually expressed as carbonyl index derived from the following expression: $CI=[A_{1715\ cm^{-1}} / \text{thickness in } \mu]\cdot 100$ [2].

### c) Photo-oxidation of poly(propylene-co-butadiene) copolymers

The photo-oxidized copolymers have a percentage reaching at maximum 9.4% of butadienic unsaturations. The butadiene unsaturations are present both as 1,2 vinyl and 1,4 trans units in the chains. The detailed estimation of the content of these two types of unsaturation can be simply carried out with $^{13}C$ NMR spectra [35].

Our results show the effect of butadiene type unsaturations during the accelerated photo-oxidation following the different photoreactivity between vinyl and 1,4 trans butadiene unsaturation by FTIR spectroscopy in polymer films. In FTIR spectra these copolymers show a rapid decrease of the absorption at 966 and 908 $cm^{-1}$, which have been attributed to 1,4 trans and vinyl butadienic unsaturations in the copolymer chains, respectively. The kinetic behaviour of the overall photo-oxidation products during the photo-oxidation detected in polymer matrix

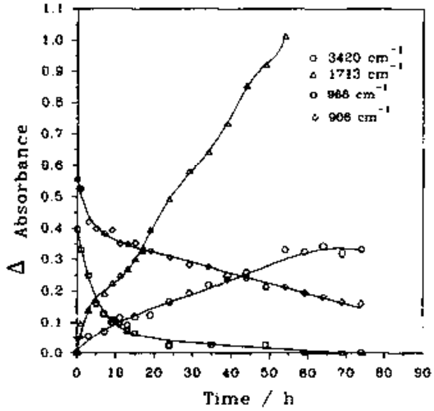

**Fig.5.** The overall oxidation products formed in PPH copolymers containing 9.4% (w/w) of butadiene in the chains.

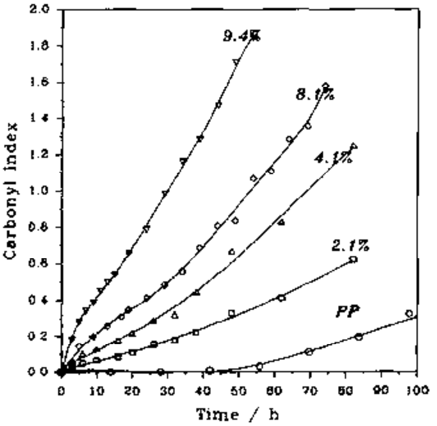

**Fig. 6.** Carbonyl index of some PPH copolymers containing different amounts of butadiene in chains.

by FTIR spectroscopy is reported in Fig. 5. The figure indicates the complete disappearance of the band at 966 $cm^{-1}$ after 15h of photo-oxidation. In the early stage (< 15h) the disappearance rate of vinyl unsaturations at 908 $cm^{-1}$ is as fast as that at 966 $cm^{-1}$ in the early stage of photo-oxidation. For long irradiation times, the absence of the 1,4-trans-butadienic units at 966 $cm^{-1}$ influences significantly the decreasing rate of the absorption changes of vinyl unsaturations at 908 $cm^{-1}$ .

The formation of typical photo-oxidation products, such as carbonyl (1713 $cm^{-1}$) and bonded alcohols (3420 $cm^{-1}$) can be also correlated on the disappearance of butadienic unsaturations. In addition, the growing band at 1713 $cm^{-1}$ attributed to carbonyl groups can be also detected at the early stages of photo-oxidation when the disappearance of butadienic double bonds shows a rapid saturations reactions [36-37].

**Table 1.** Degree of crystallinity during photo-oxidation in function of butadiene contents in polypropylene-based copolymers

| | Percentage of the total butadiene content in copolymers | | | |
|---|---|---|---|---|
| Time /h | 2% | 4% | 8.1% | 9.4% |
| 0 | 51 | 44.9 | 40.1 | 38.7 |
| 5 | 51 | 47.8 | 45.4 | 43.7 |
| 10 | 54.3 | 51.2 | 48.7 | 45.4 |
| 25 | 54.9 | 53.7 | 50.2 | 47.5 |
| 45 | 57.2 | 55.4 | 52.9 | 48.1 |
| 65 | 60.5 | 57.8 | 54.7 | 50.6 |

See ref. [38].

These copolymers show high reactivity towards hydroperoxidation reactions as function of butadienic content in polymer matrix . The formation of carbonyl groups is so rapid that no induction time can be observed (see fig. 6).

In agreement with PPH and PEH copolymers behaviour, the morphological changes investigated by X-rays spectra indicate for these copolymers an increase of degree of crystallinity of polymer matrix during the photo-oxidation as reported in Table I. This effect has been usually found in semicrystalline polymer demonstrating the consumption of amorphous phase during the photo-oxidative conditions [39]. In polyolefins, the consumption of amorphous fraction produces high degree of crystallinity up to 60% generating a very brittle films at long photo-oxidation times [40]. The embrittlement and further fragmentation are very important conditions to facilitate a rapid assimilation for micro-organism ingestion.

### d)Photo-oxidation mechanism of polyolefin copolymers containing unsaturations in the chains

The rapid formation of hydroperoxides on the allylic position on the double moieties is not enough to explain the high photodegradability of these copolymers. The high degree of carbonyl index suggests a detailed investigation on the photo-oxidation mechanism to clarify the role of some intermediate species which can catalyze the photodegradation processes. For these reasons, a mild oxidation conditions have been applied using both a cut-off filter with transmittance λ> 400 n and an oven ageing apparatus at 70°C in absence of UV light. In those conditions, some photolabile intermediates have been identified in polymer matrices and readily detected both the conventional FTIR and UV spectroscopies [34].

PEH copolymer containing 5% w/w of trans-hexadiene in the chains shows in the carbonyl region of FTIR spectra two additional bands at 1680 and 1625 cm-1 both during photo-oxidation at long irradiation wavelengths (λ> 400) and with thermo-oxidative conditions in absence of light. These two additional bands have been assigned to α,β-unsaturated carbonyl groups and their corresponding conjugated double bonds, respectively (see Fig. 7) [32]. The derivatization reaction with 2,4-dinitro-phenylhydrazine confirms these two vibrational assignments[41]. The role of α,β-unsaturated carbonyl groups is very important in the acceleration of the carbonyl index degree because of their high photoreactivity is due to the n→π* transition occurring at about 325 n in presence of UV light[42]. This fact explains why in the drastic oxidation conditions (irradiation with λ>300 n at 60°C), these photolabile intermediates cannot be detected and accumulated in polymer matrix. Accordingly to polybutadiene polymer and styrene-co-butadiene copolymers, in which α,β-unsaturated carbonyl groups have been detected, a proposal of photo-oxidation mechanism for these polyolefins containing butadienic and hexadienic unsaturations in the chains is reported in Scheme IV.

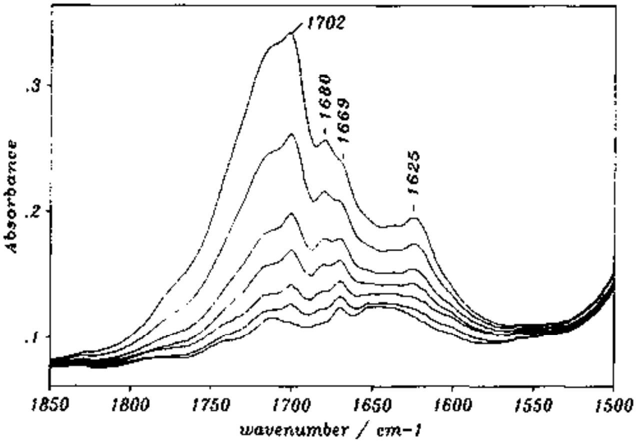

**Fig.7.** The carbonyl products after photo-oxidation at λ>400nm in PEH copolymers containing 5% w/w of trans-hexadiene (1669cm$^{-1}$) in the chains.

The suggested mechanism is based on the intrinsic reactivity of double bonds units in the chains, which is very high for the unsaturations localized along the linear chains. As in case of Ecolyte, the different reactivity towards oxidation of allylic position is better in 1,4-trans-butadiene than the corresponding vinyl ones showing a slow hydroperoxidation. The results for butadiene-type unsaturations show that vinyl can preferably undergo chain radical addition reactions instead of hydrogen abstraction ones in the allylic positions.

The presence of unsaturations, such as cis and trans hexadiene, in side chains induce a minor photosensitization effects both in carbonyl formation and chain scission processes during the photo-oxidation. Similarly to poly(ethylene-co-monoxide) copolymers, the presence along the linear chains of photoreactive groups is very important if high yields of carbonyl index must be achieved.

Finally, the intrinsic reactivity towards photo-oxidation processes should be conveniently combined with the morphological and stereochemical properties of polyolefinic copolymer to obtain reliable photodegradable copolymer.

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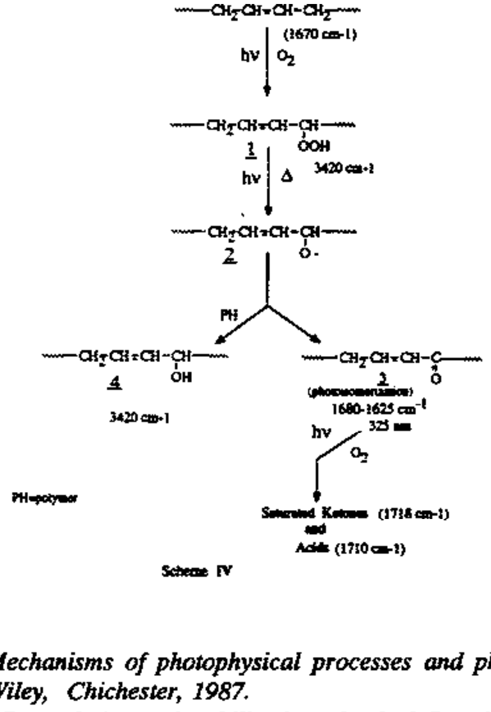

Scheme IV

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