

THE PHOTOCATALYZED OXIDATION OF POLYAMIDES AND POLYOLEFINS

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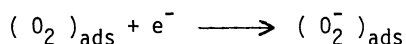
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Abstract - Photoactive pigments like TiO_2 , ZnO , CdS , which catalyze the photo-oxidation of polyolefins and polyamides afford a control on the primary and secondary initiation rates and on the accumulation of intermediate products. Furthermore, they avoid side effects due to the oxygen diffusion into the sample. The analytical and kinetic consequences of the introduction of ZnO and TiO_2 in polyundecanamide are described. In comparison with, a detailed analytical study of the photothermal oxidation of polyundecanamide at long and short wavelengths is at first summarized. In the polyundecanamide example, the role of the pigment on the formation and decomposition of hydroperoxides and the influence of the semi-crystalline morphology of the polymer on the photocatalyzed oxidation have been stressed. These conclusions are extended to the ZnO - and TiO_2 -photocatalyzed oxidation of an amorphous and semi-crystalline polyolefins (respectively atactic and isotactic polypropylene).

INTRODUCTION

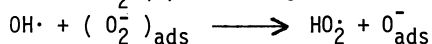
Introduction of a photoactive pigment in a non-absorbing polymer has been shown to be an excellent tool for understanding photochemical oxidation of polyolefins (see for example 1,2). Beyond any obvious practical interest, a photoactive pigment such as TiO_2 , ZnO or CdS presents the three following fundamental advantages;

i) In any quantitative approach to the kinetics of photooxidation of a polymer, the control of the initiation rate is of major importance. In polymers, in which the absorbing species are not identified, the absorption of the light is essentially dependent on the sample studied. For example, results obtained with polymers without any chromophore in the 300-400 nm range, depend on the absorbing impurities, at least for the initial steps. The addition of a photoactive pigment affords an efficient control of the absorption of the light and of the initiation rate, even at the initial stage of research. It is shown by means of opto-acoustic measurements or by the use of an integration sphere that TiO_2 , ZnO and CdS , for example, absorb up to wavelengths of 350, 380 and 500 nm respectively. Under uv irradiation, these pigments generate electron -positive hole pairs, each species being delocalized in the conduction band or in the valence band respectively. Electrons are then trapped by physisorbed molecular oxygen.



On the surface, annihilation of $(\text{O}_2^-)_{\text{ads}}$ by the positive hole leads to different excited forms of oxygen $\text{O}_2^* |^1\Delta_g|$ (3), $\text{O}_{\text{ads}}^{\cdot}$ and even O_{ads}^* (4,5). If water is present, neutralisation of the OH^- anion by the positive hole supplies OH^{\cdot} radicals. According to Völz *et al.* (6) and to Cundall (7), the O_2^- and OH^{\cdot} species may be formed through the excitation of a surface hydroxyl group (Ti^{4+} , OH^-) in the presence of water and oxygen. In the absence of oxygen,

such an excitation leads to the formation of a $\text{OH}\cdot$ radical and Ti^{3+} (through a reaction of OH^- with the positive hole and a reaction of Ti^{4+} with the delocalized electron). In the presence of oxygen, the delocalized electron is scavenged as O_2^- . The perhydroxyl radical $\text{HO}_2\cdot$ can be formed through protonation of O_2^- (6) or through annihilation of $\text{OH}\cdot$ with $(\text{O}_2^-)_{\text{ads}}$ (8):



Summarizing all the proposed mechanisms, the excitation of a photoactive pigment induces the formation of reactive species able to initiate a radical oxidation (i.e. $\text{O}_2^*|{}^1\Delta\text{g}|$, $\text{O}_{\text{ads}}\cdot$, O_{ads}^* , $\text{OH}\cdot$ and $\text{HO}_2\cdot$). In the chemisorbed phase, no definite data on the excess of energy localized on the different species have been reported. It has to be emphasized that even in the photocatalytic oxidation of the most simple molecular compounds, the predominant reactive species (if any) have not been definitively identified. However, most authors have proposed the $\text{OH}\cdot$ and $\text{HO}_2\cdot$ radicals as the predominant reactive species (6,7)

ii) In polymers without any chromophore absorbing in the range 300-400 nm, the photoproducts are generally disappearing in further photochemical steps. Then their photostationary or maximal concentrations are kept low. If an absorbing pigment is introduced into the polymer, it acts as an inner screen for the photoproducts. If these products are not photocatalytically oxidized, they accumulate in the matrix. Identification and study of the properties of the intermediate compounds then are easier.

iii) Since pigments act as highly absorbing additives, oxidative phenomena are limited to the surface of samples. Oxygen diffusion is not a controlling factor of the oxidation kinetics.

The analytical and kinetic consequences of the introduction of photoactive commercial pigments in polyundecanamide PA 11 are described in the following text. In comparison with, a detailed analytical study of the photothermal oxidation of PA 11, at long and short wavelengths must be at first summarized (for more details see 9). The role of the primary hydroperoxide groups is specially emphasized in PA 11. In a close analogy, the behaviour of hydroperoxides is cleared out in a ZnO-photocatalytic oxidation of atactic polypropylene. The photocatalyzed oxidation of a semi-crystalline polymer, as well as the photothermal oxidation, does not proceed uniformly in the crystalline and unpigmented zones and in the amorphous and pigmented zones of the polymer. The influence of the matrix structure is apparent on some features of the photocatalyzed oxidation of PA 11. But, this aspect is more emphasized when comparing the photocatalyzed oxidation of atactic and isotactic polypropylene.

I- ANALYTICAL STUDY OF THE PHOTOTHERMAL OXIDATION OF PA 11 AT LONG AND SHORT WAVELENGTHS

The photothermal oxidation of polyundecanamides of RILSAN R type (i.e. poly-imino-oxo-1-undecamethylene $(\text{NHCO}(\text{CH}_2)_{10})_n$) has been investigated on 40 μm films. These films were made by polycondensation of 1,1-amino undecanoic acid, either with an acidic catalyst (PA type B) or with a basic catalyst (type K). A preliminary study has shown that the two types behave similarly during photooxidation. The experiments reported in the text have been carried out with type B. No additive has been introduced into any of the samples. SEPAP* 40.07 and SEPAP 12.24 devices, described in previous papers (10,11) have been used for long wavelength irradiation ($\lambda > 300 \text{ nm}$) at $60 \pm 2^\circ\text{C}$.

A SEPAP 254 set-up, equipped with a monochromatic low pressure mercury arc (" resonance " lamp), was used for short wavelength irradiation (254 nm). In that case, a cylindrical

* SEPAP= Service d'Etude du Photovieillissement Accéléré des Polymères.

reflector with an elliptical base was built: the source was located along the first focal axis and the rotating support for samples turned around the second focal axis. The temperature of samples was controlled at $30 \pm 1^\circ\text{C}$.

In any case, the absorbed water is completely eliminated under irradiation.

The consecutive oxidation reactions have been followed by chemical titration of hydroperoxide groups and ir- and uv-spectrophotometries.

11- Long-wavelengths photooxidation

The hydroperoxidic groups formed in the sample exposed to a long wavelength irradiation in a SEPAP 12.24 set-up at 60°C , have been titrated after different times of irradiation (see table 1). The method is based on an oxidation, at room temperature, of Fe^{2+} and on the complexation of Fe^{3+} by SCN^- anions (12,13). The titration is carried out in hexafluoroisopropanol, a fairly good solvent of PA 11 at room temperature.

TABLE 1. Variations in hydroperoxide concentration with irradiation time in photooxidation at long wavelengths.

Irradiation time (hours)	22	42	70	120	168	230
Hydroperoxide concentration ($10^{-2} \text{ mole.kg}^{-1}$)	0.50 ± 0.08	0.84 ± 0.08	1.22 ± 0.12	1.44 ± 0.14	1.58 ± 0.16	1.47 ± 0.15

These hydroperoxidic groups are unstable at temperatures higher than 60°C . At 60°C , a decrease from 1.5×10^{-2} to less than $0.1 \times 10^{-2} \text{ mole.kg}^{-1}$ is observed in 60 hours. At 110°C , the decomposition is complete in 10 min. A photochemical decomposition of the hydroperoxides can also be observed in the presence of oxygen, under an irradiation at 254 nm. In aliphatic polyamides, hydroperoxides absorb therefore more strongly below 300 nm, and although the polymer itself is more absorbing at 254 nm, their photolysis proceeds faster than their photochemical formation at lower concentration than above 300 nm.

The other products of the photothermal oxidation of PA 11 have been identified by means of ir- and uv-absorption measurements and of a thermal treatment of the irradiated samples (at 60, 90 and 140°C in the presence or in the absence of oxygen). The photooxidized samples have been too post-irradiated at short wavelength (254 nm). The following conclusions can be drawn.

The presence of imide groups is revealed in ir-absorption spectra (1735 and 1690 cm^{-1} absorptions) These groups are thermally unstable above 90°C . As shown in scheme I, the decomposition of the primary hydroperoxide leads to a mixture of imide and water. Imides are readily hydrolyzed into acids and amide terminaisons.

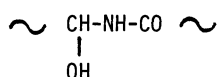
Imide groups which are not hydrolyzed in the matrix at 60°C are photochemically decomposed even at wavelengths longer than 300 nm.



Aldehydic and amide groups are formed through abstraction of hydrogen atoms from the chain. Aldehydic groups are immediately oxidized into acids. These consecutive reactions explain why the imide concentration passes through a maximum during irradiation and why acids are observed at temperatures lower than 90°C .

A photoproduct which absorbs around 3450 cm^{-1} (as a shoulder of the main amide band) and decomposes in thermal treatment around 90°C has been identified as a N-hydroxylated deriva-

tive

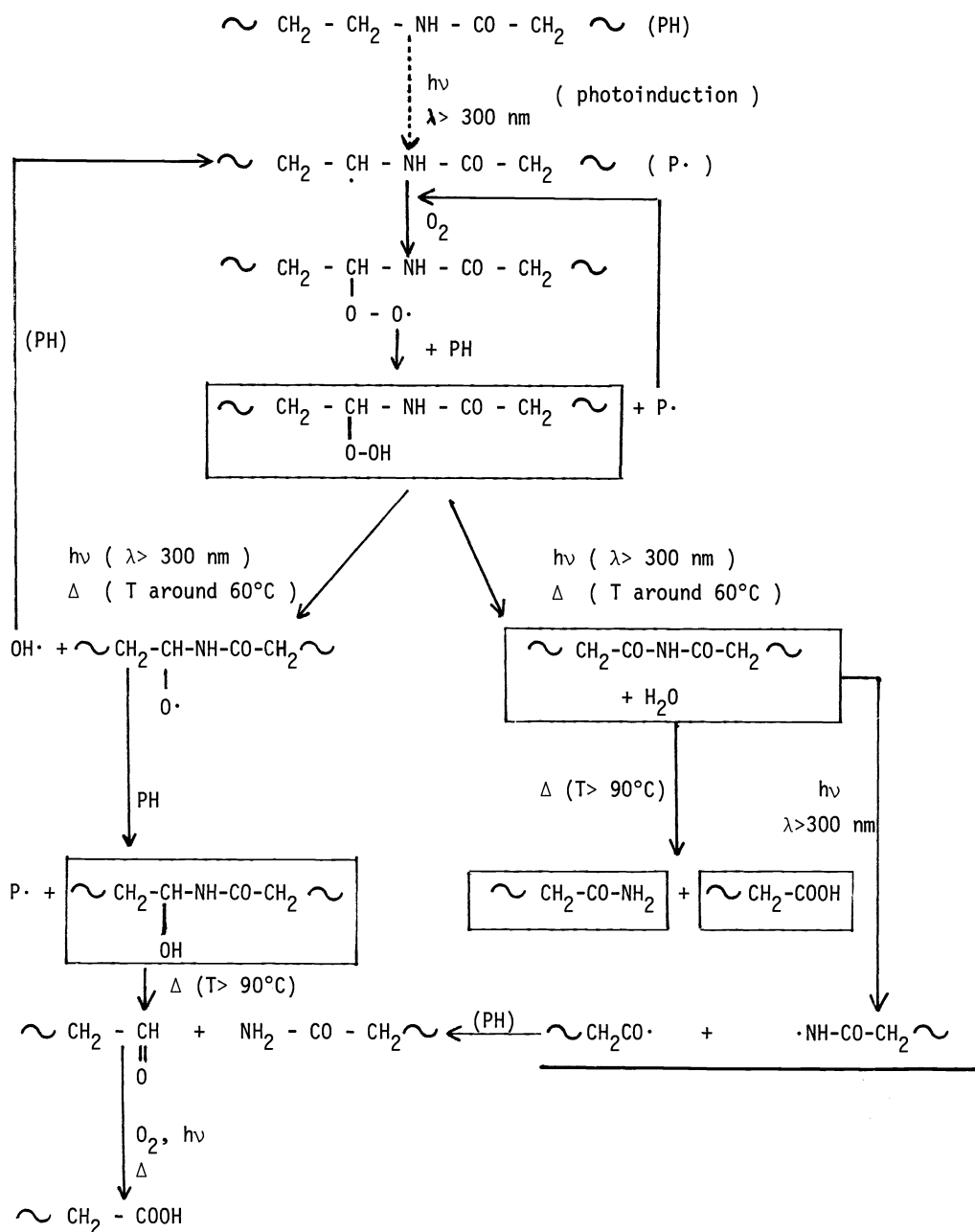


formed in the thermal or the photochemical decomposition of hydroperoxide groups. In the molecular field, N-(1 hydroxyalkyl) amides decompose around 100°C into amides and aldehydes (14,15).

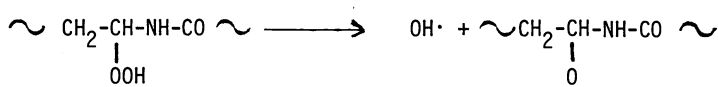
A photoproduct which absorbs too around 3450 cm^{-1} and is thermally stable at 140°C has been identified to an amine group. The evidence of such a process is specially clear under a 254 nm irradiation but a direct excitation of the amide group is still occurring at wavelengths longer than 300 nm.

On scheme I, the consecutive steps occurring during photooxidation of PA 11 are represented.

SCHEME I - Photothermal oxidation of polyundecanamide at $\lambda > 300$ nm



The mechanism of formation of imide groups from hydroperoxides is of a special interest. The homolytic cleavage of the peroxidic bond leads to hydroxyl radical and corresponding macro-radical.



In a cage reaction in the polymer matrix, the hydroxyl radical can abstract the very labile hydrogen atom of the macroradical. Imide groups are formed in the cage. In a previous work, it was shown that the secondary hydroperoxides formed in the chain of low density polyethylene were unable to initiate secondary oxidative process. This experimental observation was explained by a similar reaction of initial scavenging of the radicals formed (16).

12- Short-wavelength photooxidation (254 nm)

Results of chemical titrations of the hydroperoxidic groups formed in the sample exposed to the 254 nm radiation at $30 \pm 2^\circ\text{C}$ are shown in table 2.

TABLE 2. Variations in hydroperoxide concentration with irradiation time during the 254 nm photooxidation

Irradiation time (hours)	6	40	45	68	113	138	160
Hydroperoxide concentration (10^{-2} mole.kg $^{-1}$)	0.12 ± 0.10	0.32 ± 0.10	0.16 ± 0.10	0.28 ± 0.10	0.18 ± 0.10	0.16 ± 0.10	0.28 ± 0.10

The reproducibility is low since the measured concentrations are closer to the detection limit of the chemical titration. However, it is apparent that the concentration of hydroperoxides is being kept low under such irradiation conditions.

Through the same analytical techniques as under long wavelengths irradiation, the following conclusions have been drawn and represented on scheme II.

A primary photodissociation is induced by the 254 nm radiation which is directly absorbed by the amide chromophore. A C-N scission occurs and the two macroradicals formed, through abstraction of a hydrogen atom of the polymer chain, are transformed into aldehyde and amine groups with production of a secondary macroradicals.

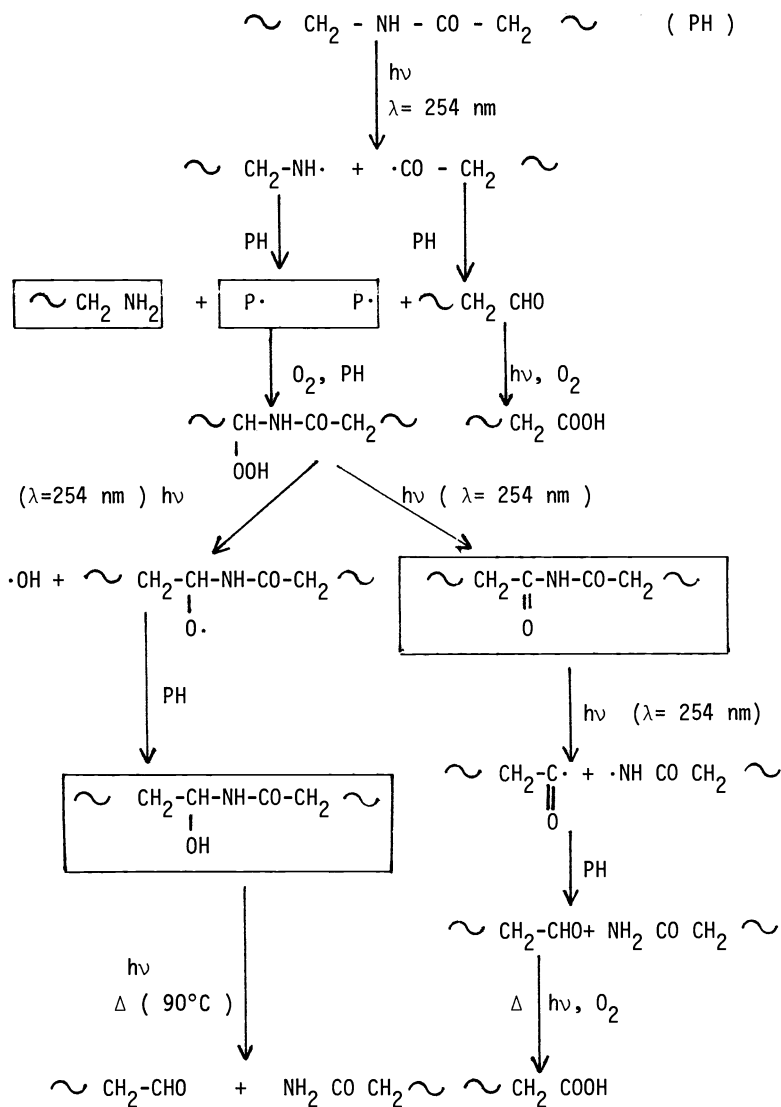
The aldehyde groups are easily observed in the uv spectra of a photo-oxidized sample ($\lambda_{\text{max}} = 290 \text{ nm}$). Their concentration is close to $10^{-1} \text{ M.kg}^{-1}$ and reaches a photostationary value which depends on the competitive absorption by the polymer itself and the photoproducts. At 254 nm, most of the photons are absorbed by the polymer and the aldehyde groups which are photochemically protected, can accumulate at 30°C . If the sample photooxidized at 254 nm is then exposed to a long wavelength irradiation, the photons are mostly absorbed by the aldehyde groups. Therefore, the photostationary concentration falls below the limit of uv detection and acidic compounds are formed from the photooxidation of aldehydes.

The amide groups formed in the first step are thermally stable at 140°C and are observed in the ir spectra around $3400\text{-}3500 \text{ cm}^{-1}$. Indeed, the NH absorption band of the primary amine hydrogen bonded with the polymer chain, must appear between 3470 cm^{-1} and 3410 cm^{-1} . It can be easily checked through ir spectrophotometry that such amine compounds are not formed in thermooxidation of PA 11.

As shown by chemical titration, the photostationary concentration of hydroperoxide is far

lower under an excitation at 254 nm than under long wavelength irradiation. Both hydroperoxides and the polymer can absorb the 254 nm radiation and the hydroperoxides photolyze into imides and N-1-hydroxypolyamides. The hydroxylated derivatives are observed in the ir spectra around 3450 cm^{-1} and are characterized by their thermal instability above 90°C . The formation of imide groups is not apparent in the carbonyl stretching range (1735 and 1690 cm^{-1}) in the ir spectra. In fact, the imide groups formed during long wavelengths photo-oxidation are readily destroyed by subsequent short wavelength excitation. Therefore, under 254 nm, their concentration is kept too low to be detected by means of ir.

SCHEME II - Photooxidation of polyundecanamide at 254 nm



II- PHOTOCATALYTIC OXIDATION OF PA 11

21- Analytical study

Film samples of PA 11 ($40\ \mu\text{m}$) containing 3% (by weight) of different commercial TiO_2 - and ZnO -pigments were exposed to a long wavelength irradiation ($\lambda > 300\text{ nm}$) in a SEPAP 40.07 set-up. The hydroperoxidic groups formed in a TiO_2 RL 65 - PA 11 blend, photooxidized at 60°C in a SEPAP 40.07 set-up, were titrated for several durations of light exposure. Our

results are reported in table III. The mean concentrations which appear, are not corrected for the heterogeneity of the light absorption (such a correction is rather uncertain for exposure under polychromatic light).

TABLE 3. Variations in hydroperoxide concentration with time of irradiation in a photocatalytic oxidation (60°C)

Irradiation time (hours)	24	48	72	120	190
Hydroperoxide concentration (10^{-2} mole.kg $^{-1}$)	1.0 ±0.10	1.7 ±0.17	2.1 ±0.21	2.5 ±0.25	2.4 ±0.24

The photostationary concentration of hydroperoxides, at about 2.5×10^{-2} mole.kg $^{-1}$ would depend on the relative rates of the formation process and of the photochemical and thermal disappearance processes. The hydroperoxidic groups have been shown to be thermally unstable at 60°C. Therefore, we have carried out titrations of hydroperoxides in a sample photocatalytically oxidized at 25°C (see table 4).

TABLE 4. Variations in hydroperoxide concentration with time of irradiation in a photocatalytic oxidation (25°C)

Irradiation time (hours)	49	96	170	222	455	640
Hydroperoxide concentration (10^{-2} mole.kg $^{-1}$)	0.37 ±0.10	0.46 ±0.10	0.83 ±0.08	0.91 ±0.09	2.1 ±0.21	2.36 ±0.24

If the initial rate of formation of hydroperoxides is higher at 60°C than at 25°C, as shown in tables 3 and 4, the photostationary concentration is temperature independent and essentially controlled by photocatalysis until 60°C.

In photocatalytic oxidation, the primary formation of reactive species is wavelength independent, as long as the energy of the radiation is higher than the width of the forbidden band of the photoactive pigment (3.5 eV in TiO₂ - 3.2 eV in ZnO). Excitation in the range 300-400 nm or at 254 nm must therefore induce the same phenomena. Titration of hydroperoxide has been carried out in a sample containing 3% of TiO₂ RL 65 and exposed to 254 nm irradiation (in a SEPAP 254 set-up). The results are appearing in table 5.

TABLE 5. Variations in hydroperoxide concentration with time of irradiation in a 254 nm photocatalytic oxidation

Irradiation time (hours)	22	46	64	69	90	144	160
Hydroperoxide concentration (10^{-2} mole.kg $^{-1}$)	0.5	0.84	0.92	1.10	1.17	1.25	1.20

These results prompt the following comments.

The photostationary concentration of hydroperoxide groups in a non-pigmented polyundecanamide sample oxidized under the same experimental conditions has been shown to be about $0.2 \cdot 10^{-2} \text{ mole.kg}^{-1}$. The inner filter effect of the pigment is clearly shown in the present data.

Although the photocatalytic oxidation must be wavelength independent, the mean photostationary concentration of hydroperoxide is lower under an excitation at 254 nm than under long wavelength irradiation ($1.20 \cdot 10^{-2}$ vs $2.5 \cdot 10^{-2} \text{ mole.kg}^{-1}$ respectively). This means, in polyundecanamide as well as in other semi-crystalline polymers, that wavelength-dependent photochemistry occurring in unpigmented zones is superposed on the photocatalytic oxidation of amorphous and pigmented zones. In the pigmented zones, the formation and decomposition of hydroperoxides are induced by the reactive radical species appearing on the excited pigment which form stationary concentrations of hydroperoxide. At short wavelengths, the direct photolysis of the primary hydroperoxides proceeds faster than at longer wavelengths. At short wavelengths, the direct photolysis of the unpigmented zones is an additional route of disappearance of the hydroperoxides and lower stationary concentrations are observed.

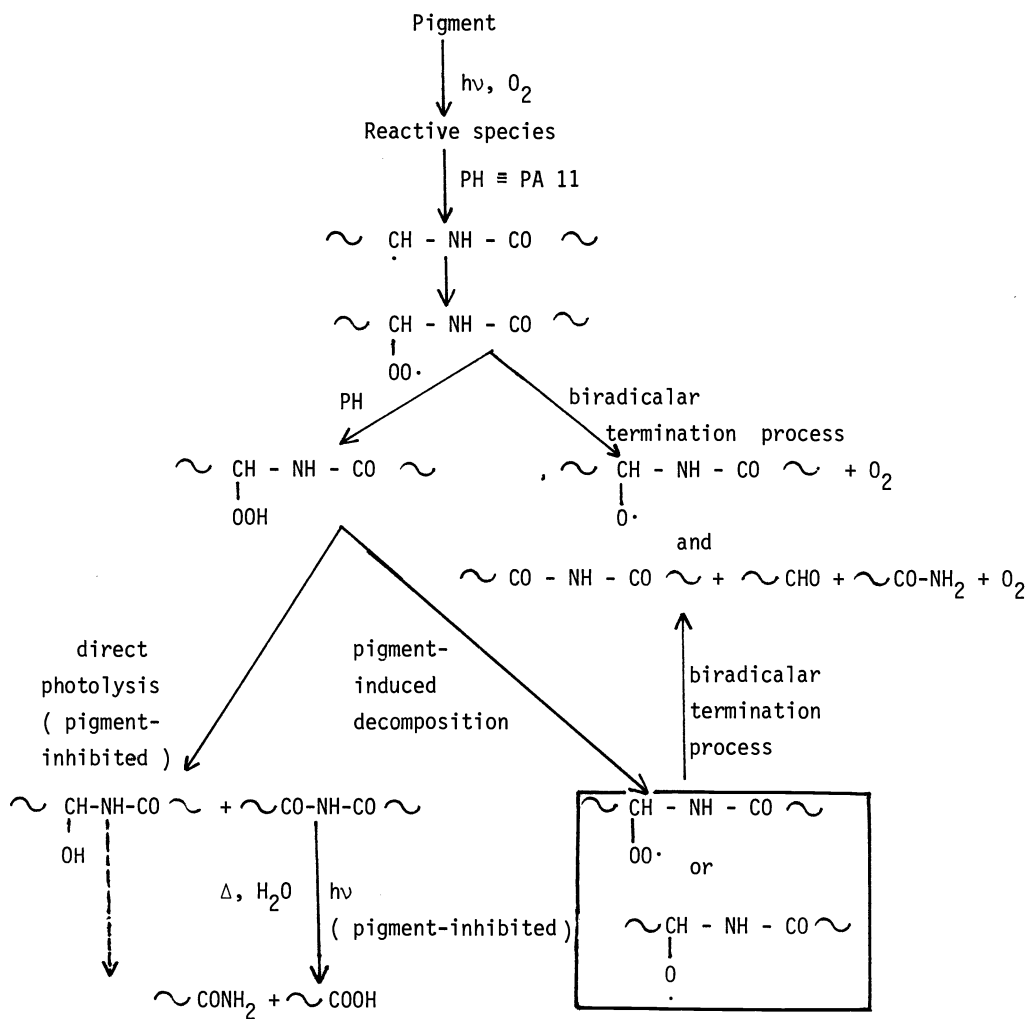
As shown by ir spectrophotometry, the stoichiometries of the TiO_2 -photocatalyzed oxidation and of the long wavelength photothermal oxidation are very similar. Imide and hydroxylated compounds result from the homogeneous or heterogeneous photochemical decomposition of hydroperoxidic groups. No apparent accumulation of imide groups due to the inner filter effect of pigment is observed. Acid compounds are formed through an hydrolysis which proceeds even in "dry" atmosphere.

Amine compounds formed by the direct photo-scission of C-N bonds are observed as final products that are thermally stable at 140°C and absorb around 3450 cm^{-1} in the ir spectra. This experimental result again shows the coexistence of phenomena which are occurring in pigmented zones and of phenomena which result from the direct excitation of PA 11 and photoproducts in unpigmented zones. The mechanism of photocatalyzed oxidation of PA 11 which is occurring only in the pigmented zones is represented in scheme III.

22- Kinetic study

As previously pointed out in the introduction, a kinetic study of the photooxidation of a non-absorbing polymer is significant only if the absorption of the light is controlled. Introducing 3% of TiO_2 RL 65 in PA 11 films ensures the absorption of more than 99% of the photons in the range 300-400 nm, by the pigment dispersed in the $40 \mu\text{m}$ film. In this uv range, the photocatalytic oxidation is essentially superficial and limited to a layer of a few microns. Under polychromatic light, the photocatalytic influence of titanium dioxide and zinc oxide can be observed at wavelengths longer than 400 nm and at larger distances (up to $160 \mu\text{m}$). For example, the irradiation of four $40 \mu\text{m}$ films pressed together shows that the film farthest from the source is still oxidized. The 300-400 nm photons are indeed totally absorbed by the first sample, but photons of longer wavelengths can be scattered and reach the last film. The concentrations of carbonyl compounds measured in the first sample is however 11 times higher than in the last one. The photocatalysis due to visible light can be therefore neglected compared to the uv photocatalysis. This is a fortunate situation since it is very difficult to treat the oxidation induced by the visible light on quantitative grounds. Since above 400 nm, a competition between absorption and scattering occurs in the different elementary layers, the determination of the number of absorbed photons cannot easily be ascertained, either experimentally or through computations (17).

SCHEME III - Photocatalyzed oxidation of polyundecanamide



Though, relative kinetic determinations have been carried out under polychromatic light of known spectral distribution, the useful irradiation range may be considered as limited between 300 and 400 nm. Preliminary measurements have shown that the initial rate of appearance of the imide groups in the irradiated sample at wavelengths longer than 300 nm, is independent on the content of the TiO_2 RL 65 pigment above 1% (11). The same first experiments have shown too that the introduction of a TiO_2 RL 65 pigment enhanced the rate of photooxidation of a transparent PA 11 sample. This influence is still more pronounced when the incident light only consists of wavelengths longer than 360 nm. This result is important for practical applications, but it must be emphasized again that the rate of photooxidation of a non-absorbing polymer is essentially controlled by defects and impurities of the sample. (In samples contaminated by inductive impurities, an inhibiting effect of titanium dioxide might be observed). A comparison of pigmented samples exposed to the same polychromatic light is far more acceptable.

In figure 1 are shown the curves representing the variations of the absorbance at 1735 cm^{-1} (imide groups) with irradiation time of a PA 11 sample containing 3% by weight of pigment and exposed to irradiation in a SEPAP 40.07 set-up. Three pigments have been used at a concentration of 3% by weight:

a titanium dioxide of the rutile type, TiO_2 RL 65 which had received a surface treatment with alumina and silica,

a titanium dioxide of the same type TiO_2 RL 90 with a surface treated with alumina, silica and hydrophobic products,

a zinc oxide, characterized by a small BET surface of 2 to $4\text{ m}^2\cdot\text{g}^{-1}$ and produced from metallic zinc by the " French process " .

Although the two titanium pigments have received a " passivating " surface treatment, they are somewhat more photoactive than ZnO . It should be noted that the differences between the photoactivities of titanium dioxides (anatase or rutile , treated or untreated) and zinc oxide are not as marked with macromolecules as with small molecules.

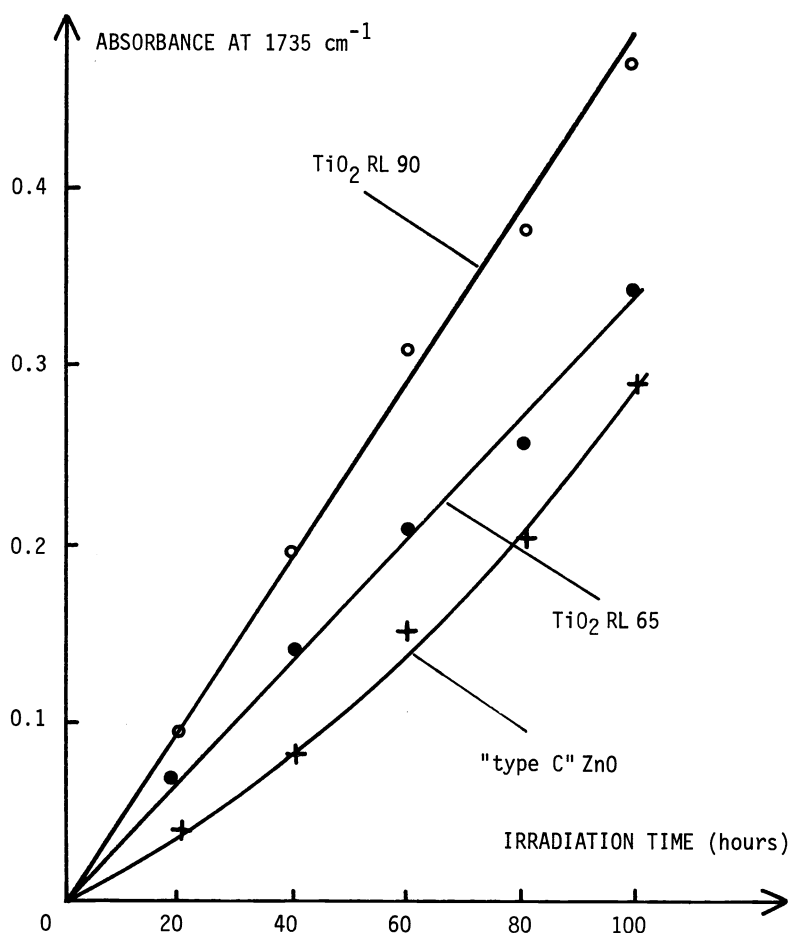


Fig. 1 - Variation of absorbance at 1735 cm^{-1} during a photocatalyzed oxidation of polyundecanamide (SEPAP 40.07 set-up, polychromatic light $\lambda > 300\text{ nm}$, temperature of samples: 60°C , content of photoactive pigment: 3%).

An overall activation energy can be measured, when existing, from the variations in the " initial " rate of photocatalytic oxidation with the temperature. The logarithm of the initial rates, measured as the initial rate of appearance of imide groups (the initial rate of appearance of imide groups appears to be constant during the first 80 hours in our SEPAP 40.07 apparatus, even at 70°C) is found to vary linearly with the reciprocal of absolute temperature until at least 333 K. The activation energies measured with each pigment are shown on table 6.

TABLE 6. Activation energy of the photocatalyzed oxidation of PA 11

Nature and percent of pigment	1% TiO ₂ RL 65	3% TiO ₂ RL 65	5% TiO ₂ RL 65	3% TiO ₂ RL 90	3% ZnO type C
Activation energy (kcal.mole ⁻¹)	10.9	11.5	10.3	11.2	10.2

The activation energy of the photocatalyzed formation of imide groups in PA 11 is essentially independent of the nature and of the concentration of pigments.

III- PHOTOCATALYTIC OXIDATION OF ATACTIC POLYPROPYLENE

In PA 11-photocatalyzed oxidation, two points have been stressed:

- i) the reactive species formed on the pigment induce the formation and the simultaneous decomposition of hydroperoxides,
- ii) a superposition of photocatalytic processes in the pigmented zones and of photo-thermal oxidative processes in the unpigmented zones has been observed in this semi-crystalline polymer.

These conclusions have prompted us to study the behaviour of the hydroperoxidic groups in the ZnO-photocatalyzed oxidation of atactic polypropylene, a completely amorphous matrix , and of isotactic polypropylene.

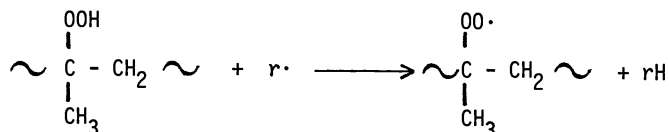
A 200 μm film of atactic polypropylene (86% atactic + 14% polyethylene) containing for example 3% by weight of type A-ZnO (9.44 m²/g) were photooxidized in a SEPAP 12.24 set-up at 60°C. Titration of hydroperoxides afforded the results reported in table 7.

TABLE 7. Variations in the hydroperoxide concentration in the presence and in the absence of ZnO

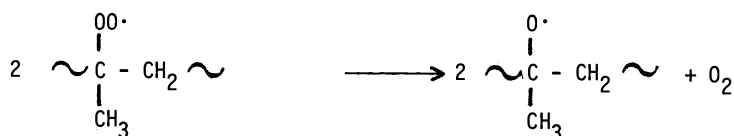
irradiation time (hours)	50	93	160	202	273	326	350
Hydroperoxide concentration in atactic PP (mole.kg ⁻¹)	0.010 ±0.010	0.010 ±0.010	0.052 ±0.010	0.075 ±0.010	0.096 ±0.010	0.120 ±0.012	0.140 ±0.010
Hydroperoxide concentration* in atactic PP + 3% ZnO (mole.kg ⁻¹)	0.037 ±0.010	0.063 ±0.010	0.100 ±0.010	0.147 ±0.014	-	0.193 ±0.019	0.220 ±0.022

*mean concentration uncorrected for light absorption heterogeneity

In pigmented samples, the initial rate of appearance of hydroperoxide groups is higher than in transparent samples (even if mean concentrations are compared). But as the photocatalyzed oxidation proceeds, the difference between hydroperoxide concentration in pigmented and non-pigmented samples decreases. The direct photolysis of hydroperoxides is completely inhibited by the pigment absorption as the direct photolysis of ketone compounds (see below). Therefore, a photocatalyzed decomposition of hydroperoxides is observed which accounts for the photostationary state. The inner filter effect of the pigment is antagonized by its photoinductive influence. The reactive species $r\cdot$ formed on the pigment are able to induce the decomposition of hydroperoxides.



An increase in the concentration of peroxy macroradicals favours the rupture processes like (18).



Tertiary alcohols and ketones are formed, which are shown in ir spectra. The carbonyl stretching range is specially interesting. As shown in figure 2, in the presence of type A - ZnO or " active " ZnO (44.5 m²/g), only two absorption bands peaking at 1720 and 1780 cm⁻¹ are observed. These bands are attributed to ketonic and lactonic groups which accumulate until photostationary concentrations. No acid groups (1710 cm⁻¹), no esters (1745 cm⁻¹) and no vinyl groups (1640 cm⁻¹) are formed through the usual Norrish type I and type II processes occurring from the excited ketonic groups. These processes are easily observed in the photothermal oxidation of atactic polypropylene (see figure 2 (I)) and are completely inhibited by the two pigments used. A superposition of photocatalyzed and photothermal oxidation of atactic polypropylene is observed in the presence of 3% of less-absorbing ZnO pigments (type C - 3.1 m²/g) or type D ZnO (2.4 m²/g) (see figure 3).

Up to now, the atactic polypropylene - ZnO mixtures are the only macromolecular systems in which a pure photocatalyzed oxidation proceeds. A specific build up of carbonyl and lactonic compounds is observed through a catalyzed formation and decomposition of hydroperoxides.

The photocatalyzed oxidation of small molecules like n-heptane, n-octane, n-dodecane and 2,4 dimethylpentane are presently studied as a modelisation of the polymer oxidation. Type A - ZnO and TiO₂ RL 90 are currently used. GPC analysis can be added to ir spectrophotometry and to chemical titration. In the n-heptane case, three main ketones i.e. 2-, 3- and 4-heptanone can be detected by GPC. The ir spectra of the oxidized sample is very similar to that of oxidized atactic PP in the range of carbonyl stretching. Lactones appear too as in the polymer substrat . However, the alcoholic compounds are formed in a much smaller extent with the model than in the polymer.

When the ZnO-photocatalyzed oxidation of isotactic PP is compared to that of atactic polypropylene, it should be pointed out that the photothermal oxidation of unpigmented crystalline zones must be superposed to the photocatalyzed oxidation of the amorphous zones. The formation of the usual products of the photocatalysis (hydroperoxides, ketones and lactones) is not exclusive. Zinc carboxylates, esters and unsaturations are observed simultaneously.

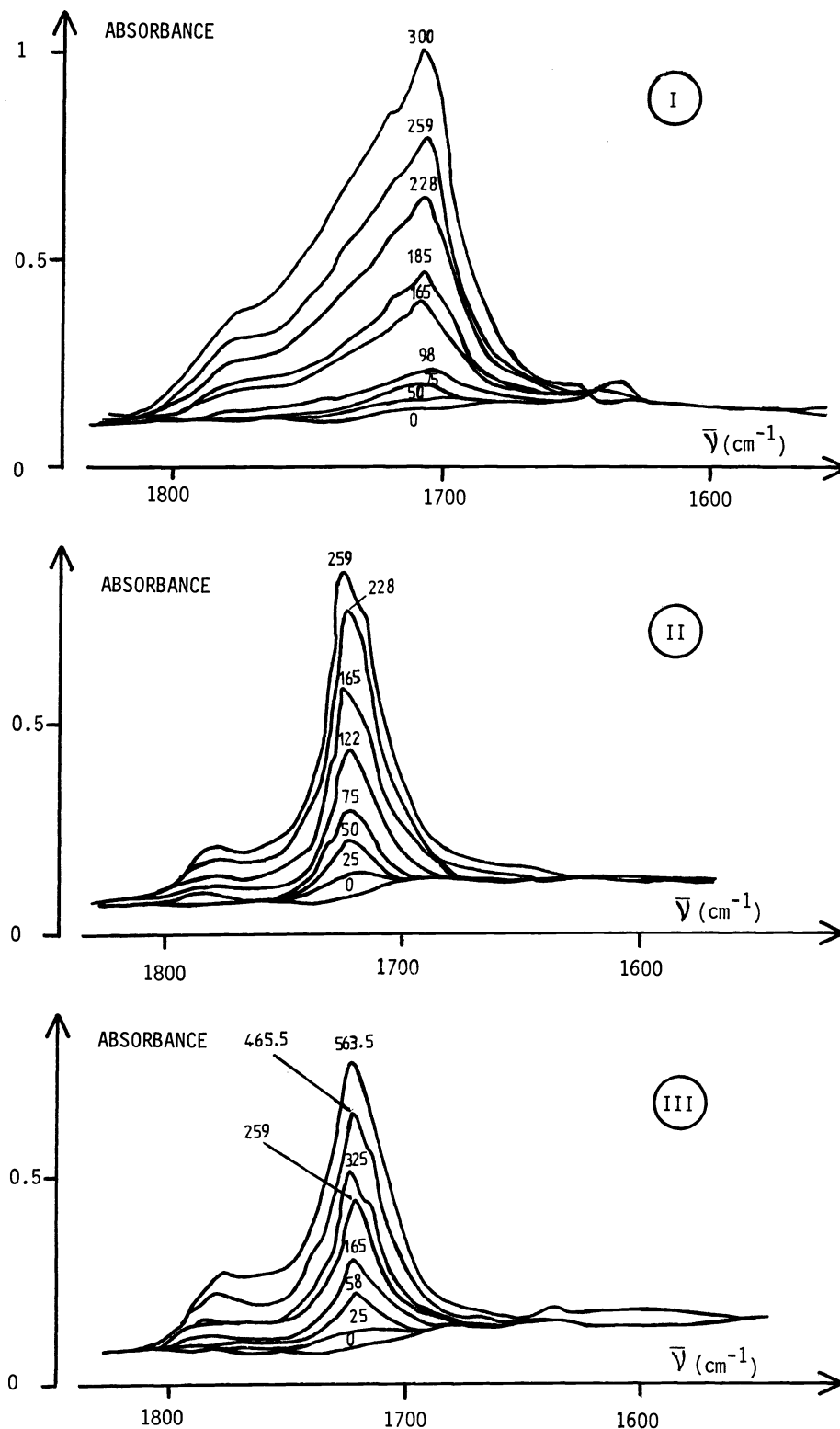


Fig.2 - Infra-red spectra in the range 1850-1550 cm⁻¹ of a 200 μ m sample of atactic polypropylene containing no (I), 3% type A-ZnO (II) and 3% active ZnO (III) and exposed to a polychromatic irradiation ($\lambda > 300$ nm, 60°C, SEPAP 12.24 set-up) On each spectrum the subscript number is the exposure duration (hours).

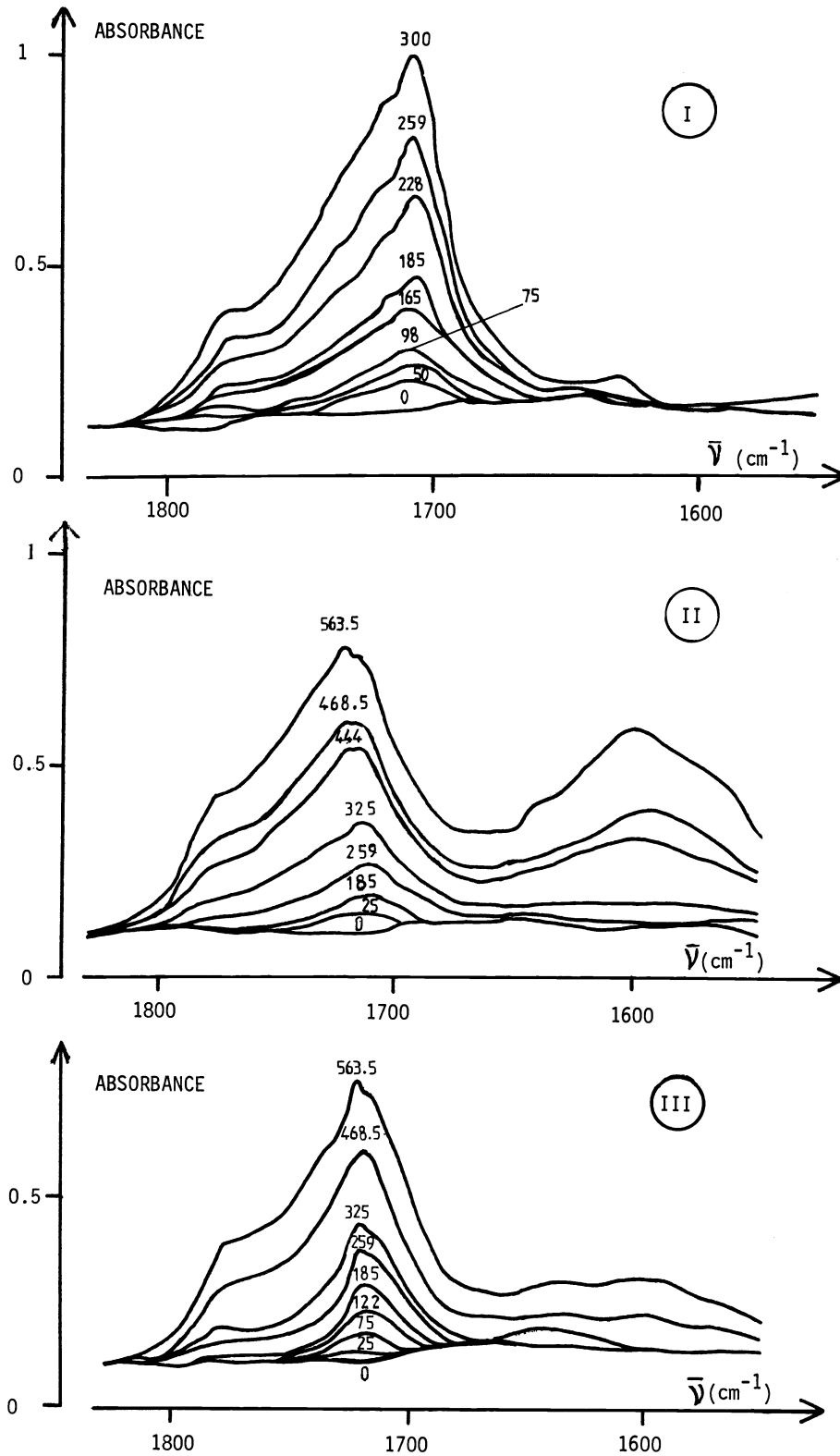


Fig.3 - Infra-red spectra, in the range $1850-1550\text{ cm}^{-1}$ of a $200\text{ }\mu\text{m}$ sample of atactic polypropylene containing no (I), 3% type D-ZnO (II) and 3% type C-ZnO (III) and exposed to a polychromatic irradiation ($\lambda > 300\text{ nm}$, 60°C , SEPAP 12.24 set-up)

On each spectrum, the subscript number is the exposure duration expressed in hours.

Therefore, kinetics of the total oxidative phenomena can only be observed. It presents the following features:

* as shown on figure 4, difference in photoactivity of the pigments studied is at most within a factor of 5.

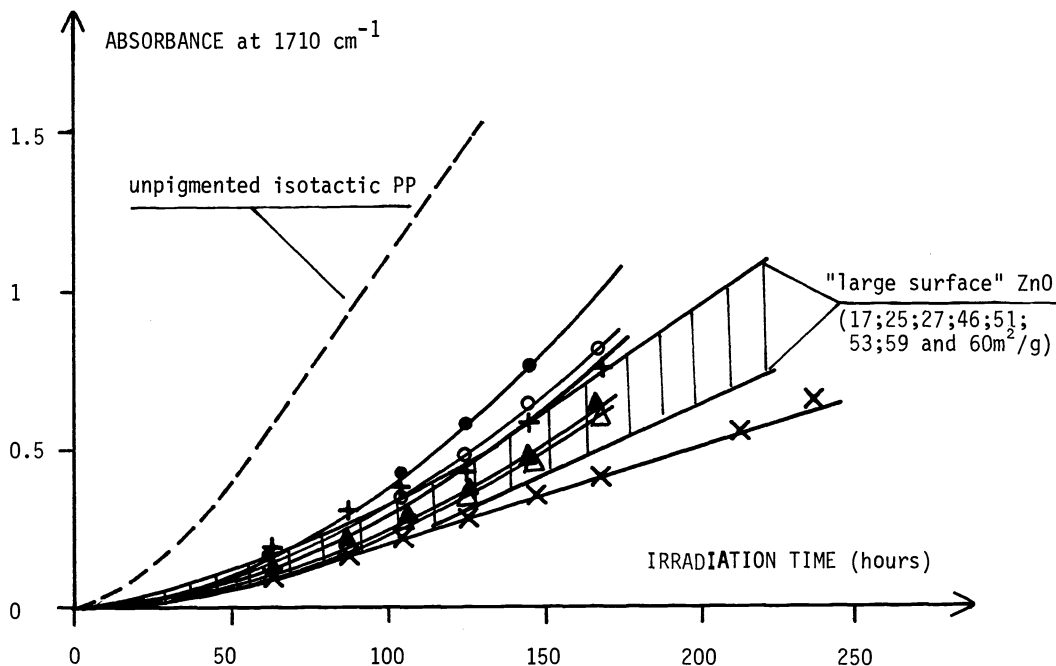


Fig.4 - Variations of absorbance at 1710 cm^{-1} during a photocatalyzed oxidation of isotactic polypropylene. (SEPAP 12.24 set-up - polychromatic light $\lambda > 300\text{ nm}$ - temperature of samples: 60°C - content of photoactive pigment: 3%).

- | | |
|--|---|
| ● "type direct" ZnO ($2.44\text{ m}^2/\text{g}$) | ▲ "emissive" ZnO ($4.53\text{ m}^2/\text{g}$) |
| + "type A" ZnO C ($9.44\text{ m}^2/\text{g}$) | × "active" ZnO ($4.45\text{ m}^2/\text{g}$) |
| ○ "acidular" ZnO ($2.36\text{ m}^2/\text{g}$) | △ "type C" ZnO ($3.10\text{ m}^2/\text{g}$) |

* the oxidation rate appears to be independent on the pigment concentration as soon as the total absorption of the light intensity is insured (concentrations higher than 1% and 3% by weight for titanium dioxide and zinc oxide respectively),

* overall initial activation energies determined when the absorbance of carbonyl groups is 0.5 for a $200\text{ }\mu\text{m}$ sample, are rather high

$$E(\text{ZnO}) = 13 - 14.6\text{ kcal/mole}$$

$$E(\text{TiO}_2) = 11 - 13.8\text{ kcal/mole}$$

* under monochromatic light, initial quantum yields of the appearance of carbonyl compounds are low

$$\phi_o(\text{type C-ZnO}) = 0.0055 (50^\circ\text{C}, \lambda > 300\text{ nm})$$

$$\phi_o(\text{type RL 90 - TiO}_2) = 0.0008 (38^\circ\text{C}, \lambda > 300\text{ nm})$$

* it is interesting to stress that for large area - type ZnO, made at low temperature (32°C), large variations of the specific area (from 17 to $60\text{ m}^2\cdot\text{g}^{-1}$) do not modify the pigment photoreactivity with the polymer matrix. If a molecular reducing agent is included

in the polymer, an induction period appears (through reduction of hydroperoxides and annihilation of the ramified oxidation). The induction period decreases as the specific area of the pigment increases.

This experimental fact stresses again the difference between small molecules and polymers reacting with photoactive pigments. Large variations in photoreactivity are observed with small molecules, very moderate variations are observed with polymers.

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