limit excitation to a main chromophore group.

(2) Complicating effects due to different wavelengths can only be expected if radicals coming from two different absorbing species are able to interact. Such a case has not yet been reported in the literature on polymer degradation. Moreover, if only excitation of a main chromophore group is achieved, the complicating effect of wavelengths should not be expected. The relative spectral distribution of the incident light is important for kinetics but has no influence on the nature of observed monophotonic phenomena.

(3) The temperature of the films under irradiation must be strictly controlled. It is often observed that the activation energies of the overall photooxidation processes are rather high, especially in photocatalytic oxidations. Large variations in the oxidation rates with temperature are expected. The use of rather high temperature (50–80 °C) in photothermal oxidation may prove to be interesting as an accelerating factor; temperature control is therefore of major importance.

(4) The samples must be irradiated uniformly.

These requirements were met by the two following devices used in our experiments: (i) a SEPAP 40.07[13] (equipped with a 500-W high-pressure mercury source (or a 450-W high-pressure xenon source); working temperature could vary from 13 to 80 °C; filters removed polychromatic light at wavelengths below 300 nm) and (ii) a SEPAP 12.24 (equipped with four 400-W high-pressure mercury lamps in Pyrex envelopes (Mazda Type MA 400); the cutoff of the Pyrex is around 300 nm; working temperatures varied from 50 to 80 °C).

A SEPAP 254 setup equipped with a monochromatic low-pressure mercury arc ("resonance" lamp) was used for short-wavelength irradiation (254 nm). In that case, a cylindrical reflector with an elliptical base was built. The source was located along the first focal axis and the rotating support for the samples turned around the second focal axis. The temperature of the samples was controlled at 30 ± 1 °C.

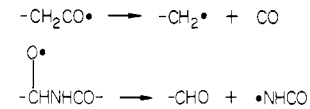
Analytical Method. IR and UV spectra were recorded on Perkin-Elmer Model 180 and 682 IR spectrophotometers and a Perkin-Elmer Model 554 UV spectrophotometer. The UV absorption was determined by using an integration sphere (which takes into account the scattering of transmitted light).

The titration of hydroperoxides is based on the oxidation at room temperature of Fe^{2+} and on the complexation of Fe^{3+} by SCN^- anions. This method, originally proposed by Scott et al.,[10] has been recently improved for polyethylene.[11] It has to be stressed that this method only gives correct results in good solvents of polyamides. Hexafluoro-2-propanol was used as the solvent in this study. Iodometric methods were unsuitable since they are carried out in a boiling CH_3COOH–2-propanol mixture and as shown previously, polyundecanamide hydroperoxides are decomposed at 60 °C.

References and Notes

(1) McKellar, J. F.; Allen, N. S. *Macromol. Rev.* **1978**, *13*, 241.
(2) McKellar, J. F.; Allen, N. S. "Photochemistry of Man Made Polymers"; Applied Science Publishers: Barking, Essex, England, 1979; pp 126–136.
(3) Margolin, A. L.; Postnikov, L. M.; Shlyapintokh, V. Ya. *Vysokomol. Soedin., Ser. A* **1977**, *19*, 1954–1955.
(4) Lock, M. V.; Sagar, B. F. *J. Chem. Soc. B* **1966**, 690.
(5) Sagar, B. F. *J. Chem. Soc. B* **1967**, 1047.
(6) Sharkey, W. H.; Mochel, W. E. *J. Am. Chem. Soc.* **1959**, *81*, 3000.
(7) Ly Tang; Lemaire, J.; Sallet, D.; Mery, J. M. *Makromol. Chem.* **1981**, *182*, 3467.
(8) Wheeler, O. H.; Rosado, O. "The Chemistry of Amides"; Patai, S., Ed.; Wiley: New York, 1970; p 356.
(9) Ginhac, J. M.; Gardette, J. L.; Arnaud, R.; Lemaire, J. *Makromol. Chem.* **1981**, *182*, 1017.
(10) Jamin, M.; Scott, G.; Tillekeraine, L. M. *Eur. Polym. J.* **1975**, *11*, 85.
(11) Petruj, J.; Marchal, J. *Radiat. Phys. Chem.* **1980**, *16*, 27.

(12) As suggested by a referee, the possible occurrence of the following decomposition also should be considered:



(13) The first number corresponds approximately to the ratio of the delivered incident intensity to a mean value of the intensity of solar light; this ratio is measured by an actinometer made with low-density polyethylene containing 8% TiO_2 RL90 + 0.12% carbon black of HAF type; the second number indicates the number of samples studied.

Photochemistry of Polyundecanamides. 2. TiO_2- and ZnO-Photocatalyzed Oxidation

Ly Tang,[†] Daniel Sallet,[‡] and Jacques Lemaire*[,†]

Laboratoire de Photochimie Moléculaire et Macromoléculaire (ERA CNRS No. 929), Université de Clermont II, Ensemble Universitaire des Cézeaux, 63170 Aubiere, France, and Centre d'Etudes, Recherche et Développement, Société Ato Chimie, 27470 Serquigny, France.

Received November 10, 1981

ABSTRACT: The photochemical oxidation of polyundecanamide catalyzed by the photoactive pigments TiO_2 and ZnO is described. A mechanism involving the pigment, the primary hydroperoxides, and the imide groups is proposed essentially on analytical grounds. Different pigments have been compared at different temperatures in a kinetic study of the photocatalyzed oxidation of PA11 under polychromatic light.

Introduction of a photoactive pigment in a nonabsorbing polymer has been shown to be an excellent tool for understanding photochemical oxidation of polyolefins.[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 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 reaction. It is shown by means of optoacoustic 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.

[†] Université de Clermont II, Ensemble Universitaire des Cézeaux.
[‡] Centre d'Etudes, Recherche et Développement, Société Ato Chimie.

0024-9297/82/2215-1437$01.25/0

Under UV irradiation, these pigments generate electron–positive hole pairs, each species being delocalized in the conduction or in the valence band, respectively. Electrons are then trapped by physisorbed molecular oxygen

$$(O_2)_{ads} + e^- \rightarrow (O_2^-)_{ads}$$

On the surface, annihilation of $(O_2^-)_{ads}$ by the positive hole leads to different excited forms of oxygen: $O_2^*[^1\Delta_g]$,[3] $O^{\bullet}_{ads}$, and even $O^{*\bullet}_{ads}$.[4,5] If water is present, neutralization of the OH^- anion by the positive hole supplies OH· radicals. According to Völz et al.[6] and to Cundall,[7] the O_2^- and OH· species may be formed through 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 OH· 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^-.[6] The perhydroxyl radical, HO_2·, can be formed through protonation of O_2^-[6] or through annihilation of OH· with $(O_2^-)_{ads}$.[8]

$$OH\cdot + (O_2^-)_{ads} \rightarrow HO_2\cdot + O^-_{ads}$$

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., $O_2^*[^1\Delta_g]$, $O^{\bullet}_{ads}$, $O^{*\bullet}_{ads}$, OH·, and HO_2·). 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 definitely identified. However, most authors have proposed OH· and HO_2· radicals as the predominant reactive species.[6,7]

(ii) In polymers without any chromophore absorbing in the range 300–400 nm, the photoproducts generally disappear 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.

In the present report, the analytical and kinetic consequences of the introduction of photoactive commercial pigments in polyundecanamide are described. Photocatalyzed oxidation of polyamides of the nylon 6 or 66 type has been briefly described.[9,10] In this previous work, attention was focused more on the photoactivity and emission properties of pigments than on the intermediate products of polyamide photooxidation.

Experimental Results

(i) Analytical Study of the TiO_2-Photocatalyzed Oxidation of Polyundecanamide. A sample of polyundecanamide containing 3% (by weight) TiO_2 RL65 (a rutile form of titanium dioxide that has received a surface treatment with alumina and silica) was exposed to long-wavelength irradiation (λ >300 nm) in a SEPAP 40.07 device. The temperature of the sample was kept constant at 60 ± 1 °C. In the IR absorption spectra of the sample recorded after different times of irradiation, a band appeared at 1735 cm^{-1}, and a shoulder of the main polyamide carbonyl band was observed at 1690 cm^{-1} (see Figure 1).

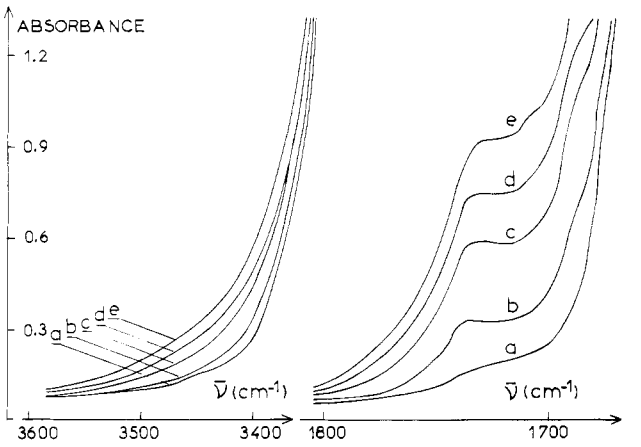


Figure 1. Infrared spectra of a polyundecanamide sample (40 μm) during TiO_2-photocatalyzed oxidation. Irradiation times: (a) 0 h; (b) 22 h; (c) 48 h; (d) 71 h; (e) 94 h. SEPAP 40.07 setup, polychromatic light λ >300 nm, sample temperature 60 °C.

These two bands develop until a photostationary value is reached; then a 1715-cm^{-1} band appears and increases continuously on prolonged irradiation. In the range of OH–NH stretching frequencies, a shoulder of the NH band of polyamide increased continuously. When a photooxidized sample was maintained at 90 °C under vacuum (or in the presence of oxygen), the IR absorption spectra showed a disappearance of the 1735- and 1690-cm^{-1} bands and a simultaneous appearance of the 1715-cm^{-1} band. The intensity of the shoulder observed around 3450 cm^{-1} decreased to a residual value that was unchanged on heating further at 140 °C.

The hydroperoxide groups, formed in the sample photocatalytically oxidized at 60 °C in a SEPAP 12.24 setup, were titrated after different times of irradiation. The titration carried out at room temperature in a hexafluoro-2-propanol solution, was based on the oxidation of Fe^{2+} and on the complexation of Fe^{3+} and the SCN^- anions. Our results are as follows (irradiation time (h), hydroperoxide concentration (10^{-2} mol·kg^{-1})): 24, 1.0 ± 0.10; 48, 1.7 ± 0.17; 72, 2.1 ± 0.21; 120, 2.5 ± 0.25; 190, 2.4 ± 0.24.

The photostationary concentration of hydroperoxides, at about 2.5×10^{-2} mol·kg^{-1}, would depend on the relative rates of the formation process and of the photochemical and thermal disappearance processes. In the previous paper, the hydroperoxide groups were shown to be thermally unstable at 60 °C. Therefore, we have carried out titrations of hydroperoxides in a sample photochemically oxidized at 25 °C. The results are as follows (irradiation time (h), hydroperoxide concentration (10^{-2} mol·kg^{-1})): 49, 0.37 ± 0.10; 96, 0.46 ± 0.10; 170, 0.83 ± 0.08; 222, 0.91 ± 0.09; 455, 2.1 ± 0.21; 640, 2.35 ± 0.24.

If the initial rate of formation of hydroperoxides is higher at 60 °C than at 25 °C, as shown in the preceding two paragraphs and in Figure 2, the photostationary concentration is temperature independent and essentially controlled by photocatalysis until 60 °C.

In photocatalytic oxidations, 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 TiO_2; 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% TiO_2 RL65 and exposed to 254-nm irradiation (in a SEPAP 254 setup). The results are as follows (irradiation time (h), hydroperoxide concentration (10^{-2} mol·kg^{-1})): 22, 0.5; 46, 0.84; 64, 0.92; 69, 1.10; 90, 1.17;

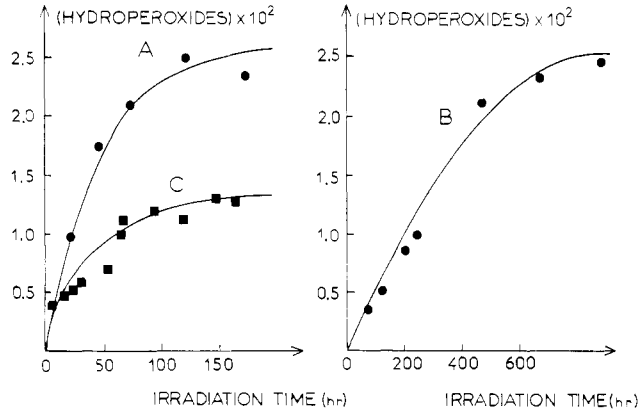


Figure 2. Variations in hydroperoxide concentration in a TiO_2 RL65 photocatalyzed oxidation of a polyundecanamide sample (pigment concentration is 3% by weight): curve A SEPAP 40.07 setup, polychromatic light $\lambda > 300$ nm, sample temperature 60 °C; curve B, SEPAP 40.07 setup, polychromatic light $\lambda > 300$ nm, sample temperature 25 °C; curve C, SEPAP 254 setup, monochromatic light (254 nm), sample temperature 30 °C.

144, 1.25; 160, 1.20. These results prompt the following comments.

The photostationary concentration of hydroperoxide groups in a nonpigmented polyundecanamide sample photooxidized under the same experimental conditions has been shown to be about 0.2×10^{-2} mol·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 photostationary concentration of hydroperoxide is lower under an excitation at 254 nm under long-wavelength irradiation (1.20×10^{-2} vs. 2.5×10^{-2} mol·kg^{-1}, respectively). This means that in polyundecanamide as well as in other semicrystalline polymers, 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 (as shown in the previous paper). At short wavelengths, the direct photolysis in the unpigmented zones is an additional route of disappearance of the hydroperoxides and lower stationary concentrations are observed.

The superposition of the photocatalyzed oxidation of pigmented zones and of a secondary photochemistry occurring in unpigmented regions has been reported in mixtures of isotactic and even atactic polypropylene and titanium dioxide.[11] Up till now, the only reported example of a purely photocatalytic phenomenon in a polymer oxidation was observed in ZnO–atactic polypropylene mixtures.[11]

(ii) Kinetic Study of the TiO_2-Photocatalyzed Oxidation of Polyundecanamide. As previously pointed out in the introduction, a kinetic study of the photooxidation of a nonabsorbing polymer is significant only if the absorption of the light is controlled. The UV absorption spectrum of PA11 films containing different amounts of TiO_2 RL65 appears in Figure 3. Introducing 3% TiO_2 ensures the absorption of more than 99% of the photons in the range 300–400 nm by the pigment dispersed in the 40-μm film. In this UV range, the photocatalytic oxidation is essentially superficial and limited to a layer of a few microns. Under polychromatic light, the photo-

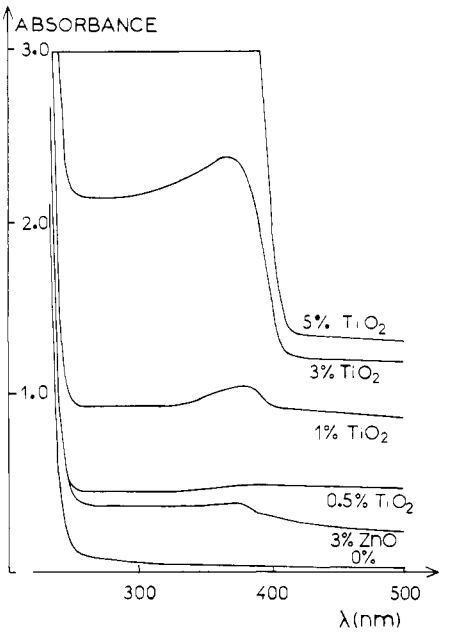


Figure 3. UV absorption spectra of a pigmented polyundecanamide sample (40 μm).

catalytic influence of titanium dioxide and zinc oxide can be observed at wavelengths longer than 400 nm and at larger distances (up to 160 μm). For example, the irradiation of four 40-μm 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 film, but photons of longer wavelengths can be scattered and reach the last film. The concentration of carbonyl compounds measured in the first film is, however, 11 times higher than in the last one; the photocatalysis due to the visible light can be therefore neglected compared to the UV photocatalysis. This is a fortunate situation since it is very difficult to treat 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.[12]

Though in the present work relative kinetic determinations have been carried out under polychromatic light of known spectral distribution, the useful irradiation range may be considered as limited to the range 300–400 nm. The aim of the study was to investigate the influence of the main parameters of the photocatalyzed oxidation, i.e., (a) the nature of pigment (for practical reasons, the study is limited to some typical commercial pigments actually used in polyamides) and, (b) the temperature of the sample.

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 of the content of the TiO_2 RL65 pigment above 1%.[15] The same first experiments have shown that the introduction of a TiO_2 RL65 pigment enhanced the rate of photooxidation of a transparent PA11 sample. This influence is still more pronounced when the incident light 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 nonabsorbing polymer is essentially controlled by defects and impurities of the sample. (In samples contaminated by adventitious impurities, an inhibiting effect of titanium dioxide might be observed.) A comparison of pigmented

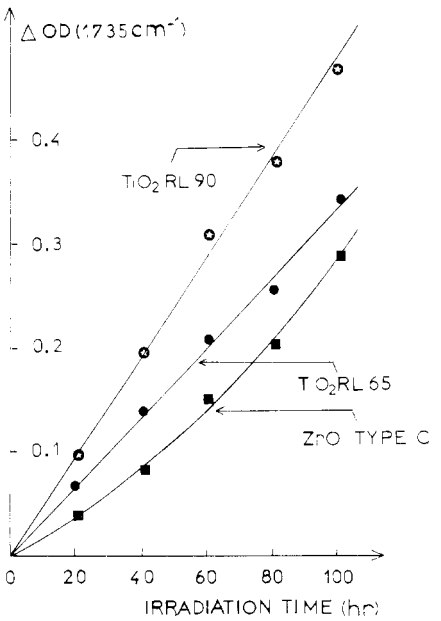


Figure 4. Variation of absorbance at 1735 cm^{-1} during a photocatalyzed oxidation of polyundecanamide. SEPAP 40.07 setup, polychromatic light $\lambda > 300$ nm, sample temperature 60 °C, content of photoactive pigment 3%.

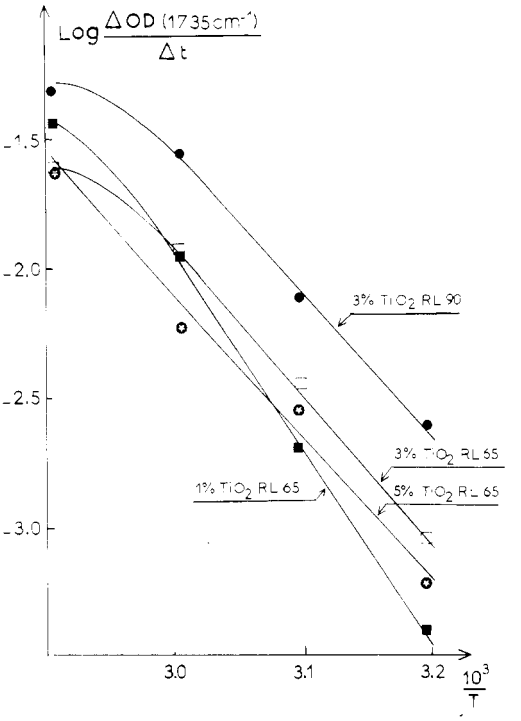


Figure 5. Determination of the activation energy of the TiO_2-photocatalyzed oxidation of polyundecanamide. $\Delta OD(1735\ cm^{-1})$ is the variation in absorbance at 1735 cm^{-1}, t is the irradiation time, and T is the absolute temperature.

samples exposed to the same polychromatic light is far more acceptable.

(a) Influence of the Nature of Pigment. In Figure 4 are shown curves representing the variations of the absorbance at 1735 cm^{-1} with irradiation time of a PA11 sample containing 3% by weight of pigment and exposed to irradiation in a SEPAP 40.07 setup. (As discussed in the previous paper, the 1735-cm^{-1} absorption is attributed to the imide groups formed on the polymer chain.) Three pigments have been used at a concentration of 3% by weight: a titanium dioxide of the rutile type, TiO_2 RL65, which had received a surface treatment with alumina and silica; a titanium dioxide of the same type, TiO_2 RL90, surface treated with alumina, silica, and hydrophobic products; a zinc oxide, characterized by a small BET surface of 2–4 $m^2 \cdot g^{-1}$ 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.[12]

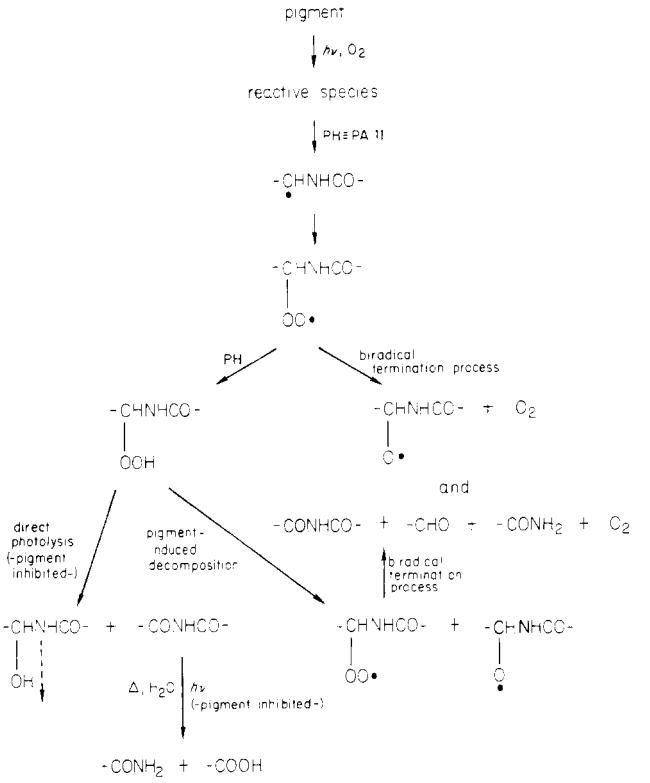
(b) Influence of Temperature. An overall activation energy which is measured from variations in the "initial" rate of photocatalytic oxidation rates (measured as the initial rate of appearance of imide groups[16]) is found to vary linearly with the reciprocal of absolute temperature up to at least 333 K (see Figure 5). The activation energies ($kcal \cdot mol^{-1}$) measured for each pigment are as follows: 1% TiO_2 RL65, 10.9; 3% TiO_2 RL65, 11.5; 5% TiO_2 RL65, 10.3; 3% TiO_2 RL90, 11.2; 3% ZnO (type C), 10.2.

The activation energy of the photocatalyzed formation of imide groups in PA11 is essentially independent of the nature and concentration of the pigments.

Discussion

The mechanism of TiO_2-photocatalyzed oxidation of polyundecanamides is presented in Scheme I. As pointed out in the introduction, an excitation of the photoactive pigment leads to the formation of reactive species such as

Scheme I
Photocatalyzed Oxidation of Polyundecanamide



$OH\cdot$, $HO_2\cdot$, and eventually $O_2{}^*[^1\Delta_g]$, $O\cdot_{ads}$, and $O^*\cdot_{ads}$. A conventional radical mechanism accounts for hydroperoxidation α to the nitrogen. An attack on the other CH_2 groups cannot be completely ruled out. However, no experimental results favor this possibility.

Photostationary concentrations of hydroperoxidic groups are observed under most experimental conditions even at room temperature. These intermediate products decompose into imide and hydroxylated compounds as is ob-

served in the photothermal oxidation of PA11. Such a decomposition results either from photocatalytic action in the pigmented zones or from direct excitation of hydroperoxides in the unpigmented zones of PA11. In the pigmented zones, the radical reactive species abstract labile hydrogen atom from hydroperoxides[17] and, in higher stationary concentration, the peroxy radicals disappear through termination processes:

(i) Under long-wavelength irradiation, the observed photostationary concentrations of hydroperoxide are temperature independent below 60 °C and controlled only by the superposition of the photocatalyzed formation and decomposition of hydroperoxides.

(ii) At 254 nm and approximately 30 °C, the hydroperoxides reach a photostationary concentration far higher in the presence of pigment than in its absence. However, the measured concentration is still lower than it is under a long-wavelength irradiation. This effect must be explained by the direct photolysis of hydroperoxides in unpigmented zones. This process is superposed on the pigment-induced decomposition.

As shown by IR spectrophotometry, the stoichiometries of the TiO_2-photocatalyzed oxidation and 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 a hydrolysis which proceeds even in a "dry" atmosphere. In water this reaction is favored and imides cannot be observed.

Amine groups formed by direct photoscission of the C–N bond 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 which result from the direct excitation of PA11 and photoproducts in unpigmented zones.

The kinetic study of the TiO_2- and ZnO-photocatalyzed oxidation of PA11 leads to the following conclusions:

(i) The rate of photocatalyzed oxidation of PA11, measured as the rate of formation of imides, is essentially independent of the concentration of pigments since the incident light is totally absorbed in the 300–400-nm range. Differences in photoactivity of the different pigments used in this work are not as marked as in oxidative photocatalysis of small molecules.

(ii) The activation energies of photocatalyzed oxidation are rather high.

(iii) Under irradiation, the pigments–polymer interactions are largely dependent upon the polymer. For example, introducing titanium dioxide in the rutile form (RL90) into low-density polyethylene[14] or into polyundecanamides enhances the rate of photooxidation. In isotactic and atactic polypropylene, pigments are moderate stabilizing agents.[11] But, since pigments are not affording sufficient photostabilization, their action must be reinforced by additives such as quenchers, antioxidants, and hydroperoxide reducers.

In conclusion, it might be stressed that the photocatalyzed oxidation of pigmented amorphous zones in semicrystalline polymers is superposed on the photolytic or photooxidative processes occuring in the unpigmented zones. This fact has prompted us to investigate photocatalytic oxidation in completely amorphous polymers. This work is now in progress in our laboratory.

Experimental Section

Our experimental apparatus and the analytical methods have already been described in the previous paper. Therefore only a description of the sample preparation procedure follows.

The photoactive pigments, including a titanium dioxide of the rutile type TiO_2 RL65 (from Titafrance Thann et Mulhouse S.A., France), a titanium dioxide of the rutile type TiO_2 RL90 (from Titafrance, Thann et Mulhouse S.A., France), and a zinc oxide type C (from Société des Mines et Fonderies de la Vieille Montagne, Belgique), were introduced during the polycondensation without any other additives. The Rilsan samples were extruded as 40-μm films from a Audouart 40.20 D apparatus and then water cooled. A type B polyundecanamide (acidic catalyst) was used throughout this experimental study.

References and Notes

(1) Arnaud, R.; Lemaire, J. "Developments in Polymer Degradation"; Grassie, N., Ed.; Applied Science Publishers: London, 1979; Vol. 2, p 159.
(2) Arnaud, R.; Lemaire, J. "Developments in Polymer Photochemistry; Allen, N., Ed.; Applied Science Publishers: London, 1981; Vol. 2, p 135.
(3) Pappas, S. P.; Fisher, R. M. *J. Paint Technol.* **1974**, *46*, 65.
(4) Djeghri, N.; Formenti, M.; Juillet, F.; Teichner, S. J. *Faraday Discuss. Chem. Soc.* **1974**, *58*, 185.
(5) Herrmann, J. M.; Disdier, J.; Pichat, P. *J. Catal.* **1979**, *60*, 369.
(6) Völz, H. G.; Kaempf, G.; Fitzky, H. G.; Klaeren, A. *ACS Symp. Ser.* **1981**, *No. 151*, 163.
(7) Cundall, R. B.; Hulme, B.; Rudham, R.; Salim, M. S. *J. Oil Colour Chem. Assoc.* **1978**, *61*, 351.
(8) Bickley, R. I.; Jayanti, R. K. *Faraday Discuss Chem. Soc.* **1974**, *58*, 194.
(9) Allen, N. S.; McKellar, J. F.; Phillips, G. O.; Chapman, C. B. *J Polym. Sci., Polym. Lett. Ed.* **1974**, *12*, 723.
(10) Allen, N. S.; McKellar, J. F. *Macromol. Rev.* **1978**, *13*, 241.
(11) Ginhac, J.-M.; Arnaud, R.; Lemaire, J. *Makromol. Chem.* **1981**, *182*, 1229.
(12) Wicks, Z. W.; Kuhhirt, W. *J. Paint Technol.* **1975**, *47*, 49.
(13) Irick, G., Jr.; Newland, G. C.; Wang, R. H. S. *ACS Symp. Ser.* **1981**, *No. 151*, 147.
(14) Laurenson, P.; Quemner, J.; Roche, G.; Lemaire, J. *Eur. Polym. J.* **1978**, *14*, 129.
(15) Ly Tang; Lemaire, J.; Sallet, D.; Mery, J. M. *Makromol. Chem.* **1981**, *182*, 3467.
(16) The initial rate of appearance of imide groups appears to be constant during the first 80 h in our SEPAP 40.07 apparatus, even at 70 °C.
(17) As suggested by a referee, the reactive species may also convert the hydroperoxide groups into alkoxy radicals.