a helical wormlike chain model[21] would be more appropriate.

Acknowledgment. We thank Dr. E. Helfand and Dr. A. E. Tonelli for useful discussions.

References and Notes

(1) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience: New York, 1969; Chapters I, IV, VIII, and IX.
(2) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971; Chapter 2.
(3) Buckingham, A. D. *J. Chem. Phys.* **1956**, *25*, 428.
(4) Kielich, S. In "Dielectric and Related Molecular Processes; Davies, M., Ed.; Chemical Society: London, 1972; Vol. 1, p 192.
(5) Parry Jones, G. In "Dielectric and Related Molecular Processes"; Davies, M., Ed.; Chemical Society: London, 1975, Vol. II, p 198.
(6) Khanarian, G. *J. Chem. Phys.* **1982**, *76*, 3186.
(7) Khanarian, G.; Tonelli, A. E. *Macromolecules* **1982**, *15*, 145.
(8) Khanarian, G.; Schilling, F. C.; Cais, R. E.; Tonelli, A. E. *Macromolecules*, in press.
(9) Khanarian, G.; Cais, R. E.; Kometani, J. M.; Tonelli, A. E. *Macromolecules* **1982**, *15*, 866.
(10) Mark, J. E.; Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1415.
(11) Mark, J. E.; Flory, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 3702.
(12) Abe, A.; Mark, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6468.
(13) Williams, A. D.; Flory, P. J. *J. Am. Chem. Soc.* **1969**, *91*, 3118.
(14) Pickles, C. J.; Flory, P. J. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 632.
(15) Yoon, D. Y.; Sundararajan, P. R.; Flory, P. J. *Macromolecules* **1975**, *8*, 776.
(16) Krupkowski, T. Parry Jones, G.; Davies, M. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1348.
(17) Fujiwara, Y.; Flory, P. J. *Macromolecules* **1970**, *3*, 280.
(18) Cais, R. E., private communication.
(19) Pyzuk, W. *Macromolecules* **1980**, *13*, 153.
(20) Brown, B. L.; Parry Jones, G. *J. Polym. Sci.* **1975**, *13*, 599.
(21) Yamakawa, H.; Shimada, J.; Nagasaka, K. *J. Chem. Phys.* **1979**, *71*, 3573.

Photochemistry of Polyundecanamides. 1. Mechanisms of Photooxidation at Short and Long Wavelengths

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ABSTRACT: An experimental and analytical study of the photooxidation of polyundecanamide films carried out at long wavelengths ($\lambda > 300$ nm) and 60 °C or at short wavelengths (254 nm) and 30 °C is reported. Mechanisms are proposed that account for the behavior of the different intermediate photoproducts observed in each case. The hydroperoxides formed are shown to be thermally unstable above 60 °C and when photolyzed at short wavelength. At long wavelengths, they can accumulate until a fairly high photostationary concentration (1.5×10^{-2} mol·kg^{-1}) is reached. Photochemical decomposition of hydroperoxides into imide groups and *N*-1-hydroxypolyundecanamide is observed. The imide groups are either hydrolyzed or photolyzed into acidic and amide groups. At short wavelengths, products of a direct photoscission of the C–N bond (i.e., aldehydes and amides) are also observed. At long wavelengths, only amines can be detected.

The behavior of aliphatic polyamides, especially nylon-type polymers, on exposure to UV irradiation has attracted much attention (see, for example, ref 1 and 2). Most of the reported research in this field concerns either vacuum photolysis and photooxidation of the polymer at wavelengths shorter than 290 nm or autoxidation and photooxidation of model compounds.

It has been shown by means of ESR spectrometry that a primary process of photodissociation leading to the formation of two macroradicals is occurring when light is absorbed by the NHCO chromophore.

$$\text{-CONH-} \xrightarrow[\lambda < 290\ \text{nm}]{h\nu} \text{-CO}\cdot + \cdot\text{NH-} \qquad \text{(I)}$$

In secondary steps, these macroradicals abstract a hydrogen atom from the polymer matrix:

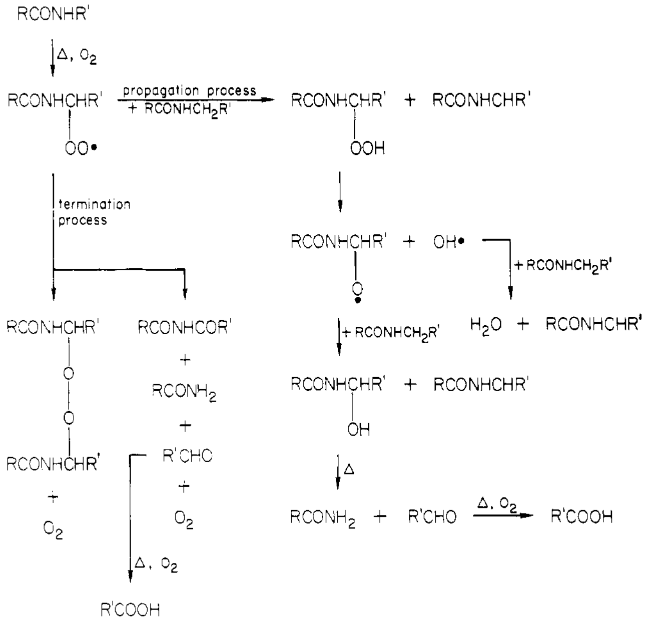
$$\text{-CO}\cdot + \text{-CONH-} \rightarrow \text{-CHO} + \text{-CONH}\dot{\text{C}}\text{H-} \qquad \text{(II)}$$

$$\text{-NH}\cdot + \text{-CONH-} \rightarrow \text{-NH}_2 + \text{-CONH}\dot{\text{C}}\text{H-} \qquad \text{(III)}$$

Aldehydic and amine groups have indeed been observed.

The same primary process is observed at wavelengths shorter than 290 nm in the presence of oxygen.[3] However, oxygen traps the two macroradicals, forming peroxy radicals and hydroperoxides.

Scheme I
Autoxidation of *N*-Alkyl Amides



Autoxidation of model compounds of *N*-alkyl amides $RCH_2CONHCH_2R'$ has been studied by Sagar et al.[4,5] at temperatures lower than 100 °C. *N*-Acyl amides, *N*-formyl

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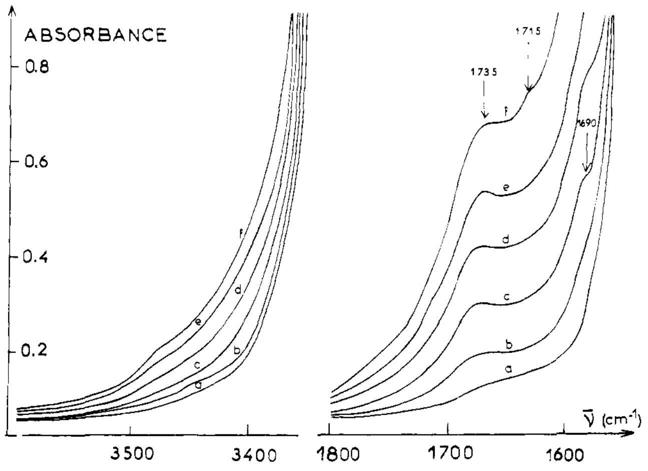


Figure 1. Infrared spectra of a 40-μm polyundecanamide film at various stages of photothermal oxidation. Irradiation times: (a) 0 h; (b) 20 h; (c) 40 h; (d) 60 h; (e) 80 h; (f) 100 h. SEPAP 40.07, polychromatic light λ >300 nm, sample temperature 60 °C.

amides, and products resulting from a C–N scission (amides, aldehydes, and acids) have been identified. As shown in Scheme I, a conventional autoxidation mechanism has been proposed in which the chain carrier macroradical is formed through the abstraction of a hydrogen atom α to the nitrogen. The C–N scission occurs in the disproportionation of peroxy radicals and in the thermal decomposition of hydroxylated compounds.

The photooxidation of *N*-pentylhexanamide, studied by Sharley et al.,[6] leads to similar products. The nature of the observed products also showed that hydroperoxidation is occurring α to the nitrogen atom.

Each of these previous studies has provided useful information for understanding behavior of polyamides exposed to oxidation. Obviously, the mechanism of photooxidation cannot be deduced from the vacuum photolysis experiments, since the involvement of oxygen is ambiguous. And, though the photooxidation of model compounds may follow the same primary mechanisms as the parent polymer, it is often observed that the intermediate photoproducts behave differently in the two cases. A detailed experimental study of the photooxidation at long wavelengths (λ >300 nm) appears to be necessary for predicting the natural aging of polyamides. In the present work, an investigation of the photothermal oxidation of films of polyundecanamides of the Rilsan type (i.e., poly(iminocarbonyldecamethylene), $[NHCO(CH_2)_{10}]_n$) under excitation at short and long wavelengths is reported. In the following article, the TiO_2-photocatalyzed oxidation of these polymers is described and compared to a photothermal oxidation. Preliminary results of this work have been recently reported.[7]

Experimental Results

(i) Analytical Study of the Photothermal Oxidation of Polyundecanamides at Wavelengths Longer Than 300 nm. The photothermal oxidation of polyundecanamide films (thickness 40 μm) at long wavelengths has been carried out in a SEPAP 40.07 device (described in the Experimental Section). The temperature of the samples was kept constant at 60 ± 2 °C and the light was carefully filtered through a solarized borosilicate filter (λ >300 nm). Absorbed water was completely eliminated under irradiation. A preliminary study of the rate of dehydration of the thin samples in an IR beam has shown that the water was absorbed and not adsorbed. Dehydration was a fast process in our irradiation device. The consecutive oxidation reactions have been followed by IR and UV spectrophotometry and the hydroperoxides formed have been chemically titrated.

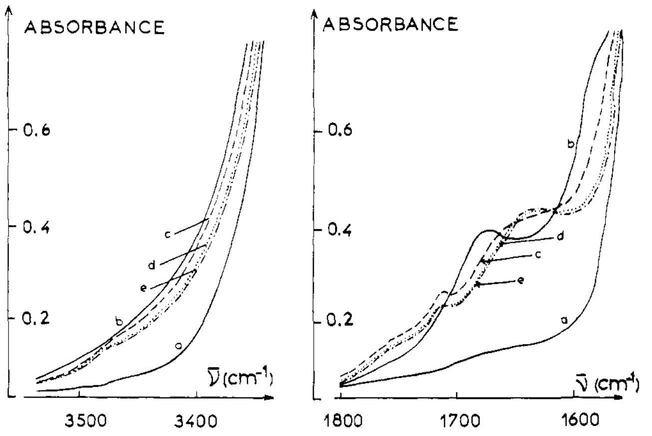


Figure 2. Infrared spectra of preoxidized 40-μm polyundecanamide films heated at 90 °C under vacuum: (a) initial sample; (b) sample photooxidized during 50 h in a SEPAP 40.07 (λ >300 nm, 60 °C); (c) after 15 h at 90 °C; (d) after 36 h at 90 °C; (e) after 116 h at 90 °C.

In the first stages of the photothermal oxidation of polyundecanamides (PA11) carried out in a SEPAP 40.07 setup, an IR absorption band appears at 1735 cm^{-1} (see Figure 1). A shoulder on the main polyamide carbonyl band was also observed at 1690 cm^{-1}. After long irradiation, an absorption at 1715 cm^{-1} could be observed. A shoulder of the NH absorption band of PA11 at 3400–3500 cm^{-1} increased continuously during irradiation without any significant deformation. In the UV spectra of the photooxidized sample, a continuous absorption in the 250–350-nm range appeared as an unstructured shoulder of the amide band (λ_{max} around 200 nm).

The hydroperoxide groups formed in the samples exposed to long-wavelength photooxidation at 60 °C in a SEPAP 12.24 setup were titrated after different times of irradiation. As described in the Experimental Section, the titration was carried out in hexafluoro-2-propanol solution and was based on the oxidation of Fe^{2+}. Our results were as follows (irradiation time (h), hydroperoxide concentration (10^{-2} mol·kg^{-1})): 22, 0.50 ± 0.08; 42, 0.84 ± 0.08; 70, 1.22 ± 0.12; 120, 1.44 ± 0.14; 168, 1.58 ± 0.16; 230, 1.47 ± 0.15.

If the presence of hydroperoxide groups can be readily ascertained by chemical titration, the identification of the other photoproducts cannot be made solely on the basis of their spectral properties. Therefore, the thermal stability and the photostability at short wavelength of the different products have been studied. Chemical titration of hydroperoxides in samples photooxidized at 60 °C and then maintained at 60 °C under vacuum showed that the hydroperoxide groups formed in PA11 decomposed slowly, as revealed by the following data (treatment time at 60 °C (h), hydroperoxide concentration (10^{-2} mol·kg^{-1})): 0, 150 ± 0.15; 18, 0.80 ± 0.08; 40, 0.30 ± 0.10; 60, <0.10; 80, <0.10. If the preoxidized samples were heated at 110 °C, hydroperoxides decomposed completely in 10 min.

When the IR spectra of samples were recorded during the thermal treatment at 60 °C, a small but significant increase of the absorption bands at 1735 and 1690 cm^{-1} was observed. The IR absorption spectra of photooxidized samples heated under vacuum at 90 °C showed the disappearance of the 1735- and 1690-cm^{-1} bands. In the OH–NH stretching range, a partial decrease of the shoulder around 3450 cm^{-1} was observed (Figures 2 and 3). The same evolution in the IR absorption bands occurred if the preoxidized samples were heated at 90 °C in the presence of oxygen. Thermooxidation proceeded too

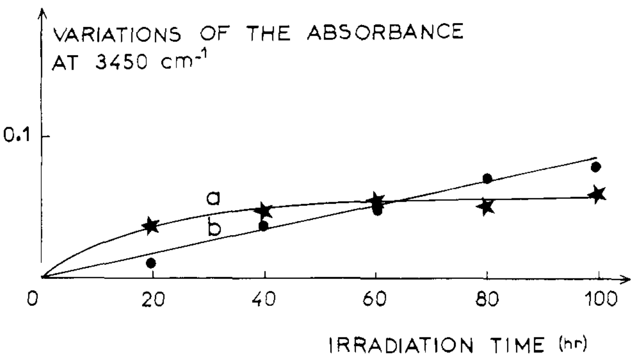


Figure 3. Variations in the absorbance at 3450 cm^{-1} in thermal treatments of a sample photooxidized at long wavelengths: (a) total decrease in the absorbance at 3450 cm^{-1} after heating at 90 °C; (b) residual absorbance at 3450 cm^{-1} after heating at 90 and 140 °C. SEPAP 40.07 setup; temperature of samples during the photooxidation, 60 °C.

slowly to be detected under such conditions.

If the photooxidized samples heated 116 h at 90 °C were then heated to 140 °C, no significant change in the IR spectra was observed. The carbonyl absorption at 1715 cm^{-1} and the residual NH–OH absorption around 3450 cm^{-1} must be attributed to stable products.

The same thermal treatments were performed on samples photooxidized at different time intervals. It was shown that the photoproducts which were unstable at 90 °C and absorbed at about 3450 cm^{-1} reached a photostationary concentration after 60 h of irradiation in a SEPAP 40.07 device (a 60-h irradiation in a SEPAP 40.07 setup is roughly equivalent to a 180-h irradiation in a SEPAP 12.24 device) and that the concentration of the thermally stable photoproduct absorbing at about 3450 cm^{-1} increased continuously (see Figure 3).

When samples photooxidized at long wavelengths were then exposed to short-wavelength radiation (λ_{exc} = 254 nm in a SEPAP 254 device), the following observations could be made:

(i) The hydroperoxide groups were photochemically decomposed. Results of the chemical titration were as follows (time of irradiation at 254 nm (h), hydroperoxide concentration (10^{-2} mol·kg^{-1})): 0, 1.50 ± 0.15; 4, 0.89 ± 0.09; 20, 0.72 ± 0.07; 48, 0.24 ± 0.10; 60, 0.32 ± 0.10; 80, 0.28 ± 0.10.

(ii) In the IR absorption spectra, the parallel disappearance of the 1735- and 1690-cm^{-1} absorptions and the increase of the 1715-cm^{-1} band were observed again.

(iii) In the UV absorption spectra, the long-wavelength shoulder of the amide band disappeared and was replaced by a new absorption band with a maximum at 290 nm.

(ii) Analytical Study of the Photooxidation of Polyundecanamides at 254 nm. Films of PA11 (thickness 40 μm) were irradiated at 254 nm in the presence of oxygen in a SEPAP 254 setup. The temperature of the samples was kept at 30 ± 2 °C. As shown in Figure 4, the IR absorption spectra of these films showed a fast increase in the absorption band at 1715 cm^{-1}, and an unstructured shoulder in the NH absorption band of PA11 appeared simultaneously. An increase in the 1420-, 1220-, 1190-, and 935-cm^{-1} absorption bands was observed, too. None of these absorption bands reached a photostationary intensity. A continuous increase was observed during the irradiation until the mechanical properties of the samples were deteriorated completely. In the UV spectra of the same samples photooxidized under the same experimental conditions, an absorption band at 290 nm increased initially and reached a photostationary intensity (see Figure 5).

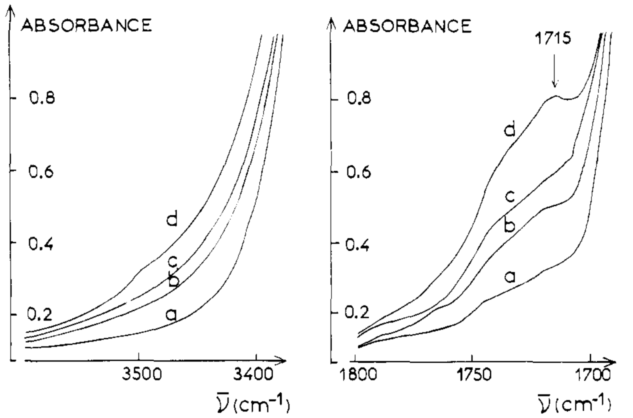


Figure 4. Infrared spectra of a 40-μm polyundecanamide film during photooxidation at 254 nm. Irradiation times: (a) 0 h; (b) 72 h; (c) 98 h; (d) 188 h. SEPAP 254 setup; sample temperature 30 °C.

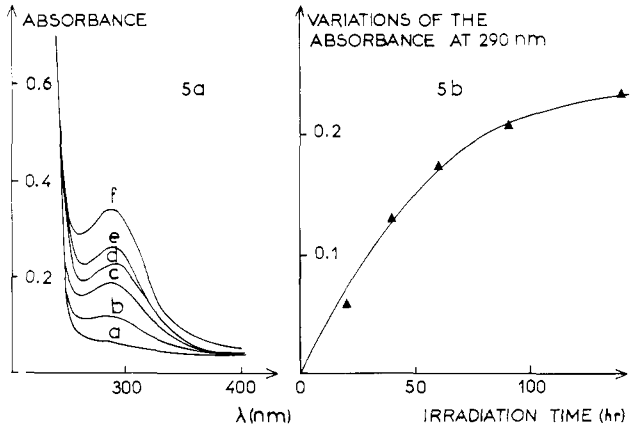
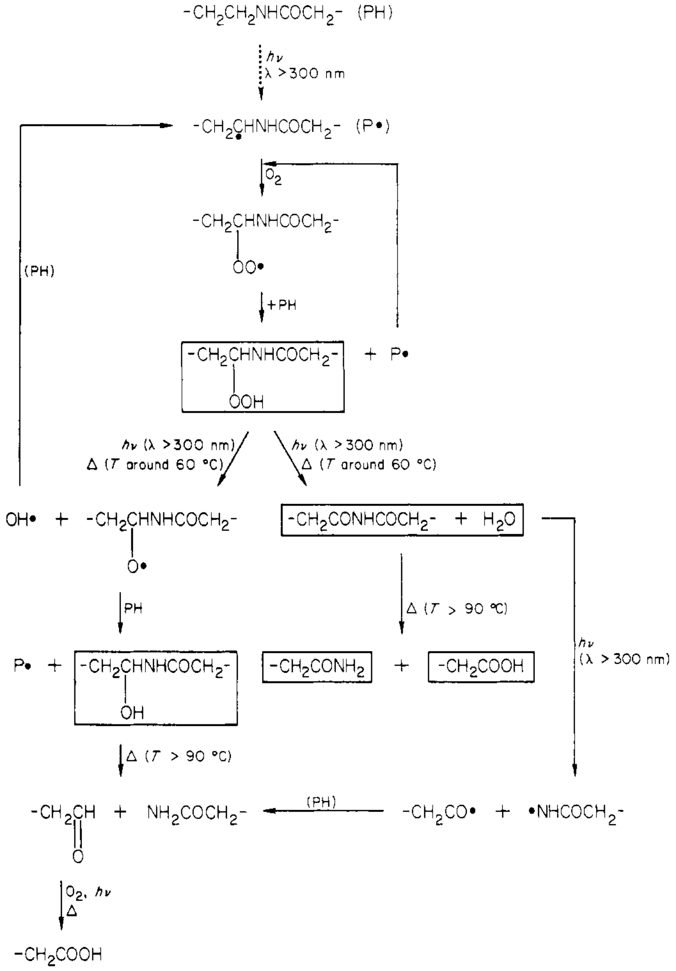


Figure 5. (a) UV spectra of a 40-μm polyundecanamide film during photooxidation at 254 nm. Irradiation times: (a) 0 h; (b) 20 h; (c) 40 h; (d) 60 h; (e) 90 h; (f) 140 h. SEPAP 254 setup; sample temperature 30 °C. (b) Variations in the absorbance at 290 nm during photooxidation at 254 nm.

Chemical titration of the hydroperoxide groups formed in the sample was carried out in hexafluoro-2-propanol solution. Results are as follows (irradiation time (h), hydroperoxide concentration (10^{-2} mol·kg^{-1})): 6, 0.12 ± 0.10; 40, 0.32 ± 0.10; 45, 0.16 ± 0.10; 68, 0.28 ± 0.10; 113, 0.18 ± 0.10; 138, 0.16 ± 0.10; 160, 0.28 ± 0.10. The reproducibility is low since the measured concentrations are close 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.

Again, the thermal stability of the observed photoproducts has been examined. After photooxidation, the samples were heated at 90 and 140 °C in the presence of oxygen. At 90 °C, a partial decrease of the absorption around 3450 cm^{-1} was readily observed and the 1715-cm^{-1} absorption band increased simultaneously. The thermal oxidation at 90 °C of a nonirradiated control sample over the same period of time has been shown to induce any significant increase in the IR absorption at 1715 cm^{-1}. The 290-nm band of the UV spectrum of the photooxidized sample disappeared on heating at 90 °C. Identical testing of the thermal stability of photoproducts formed under excitation at 254 nm carried out after different times of irradiation showed that the photoproduct unstable at 90 °C reached a photostationary concentration and that the photoproduct stable at 140 °C accumulated. If the photooxidized sample heated at 90 °C was then heated at 140 °C, the IR absorption around 3450 cm^{-1} remained constant.

Scheme II
Photothermal Oxidation of Polyundecanamide
at λ >300 nm



Discussion

(i) Mechanism of Photothermal Oxidation of PA11 at Long Wavelengths. The mechanism proposed in Scheme II prompts the following comments.

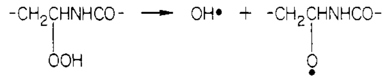
Photoinitiation through excited impurities or defects in nonabsorbing polymers leads to a radical attack on the polymer chain and the formation of hydroperoxide groups. As mentioned in the introduction, it is well-known that the hydroperoxidation of amides occurs in the α position to the NH amide group.[4-6] At our present stage of knowledge, photooxidation occurring to a significant extent on the other CH_2 groups of the polymer cannot be definitively excluded. However, no experimental proof of this possibility has been obtained so far.

The hydroperoxide groups are revealed only by chemical titration in solution in a very special solvent. Since these hydroperoxides are fairly unstable at temperatures higher than 60 °C, this titration must be carried out at room temperature. Hexafluoro-2-propanol appears to be the only suitable solvent for polyundecanamide at room temperature.

The hydroperoxide groups are thermally unstable at temperatures near 60 °C and photochemically unstable under excitation at 254 nm. It has to be stressed that under excitation at long wavelengths, these hydroperoxides can accumulate in the polymer at fairly high concentrations. Hydroperoxides are usually photolabile since excitation in the nσ* transition of the hydroperoxide bond induces a photodissociation of this bond with a high quantum yield. In aliphatic polyamides, hydroperoxides absorb 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 concentrations.

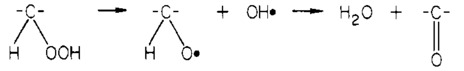
The IR absorption spectra of photooxidized samples at 1735 and 1690 cm^{-1} can be attributed to the presence of imide groups $-CH_2CONHCOCH_2-$. The IR spectra of an acyclic imide is composed of absorption bands peaking at 3289, 1787–1735, 1695–1690, and 1503 cm^{-1}. In the polymer studied, the only observable bands are at 1735 and 1690 cm^{-1}.

According to our data, hydroperoxides decompose thermally above 60 °C and photochemically at short wavelengths into the imide groups. The homolytic cleavage of the peroxide bond leads to hydroxyl radicals and corresponding macroradicals.



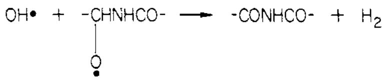
$$\text{-CH}_2\underset{\text{OOH}}{\underset{|}{\text{CH}}}\text{NHCO-} \longrightarrow \text{OH}\bullet + \text{-CH}_2\underset{\text{O}\bullet}{\underset{|}{\text{CH}}}\text{NHCO-} \qquad (1)$$

In previous work, it was shown that secondary hydroperoxides formed in the chain of low-density polyethylene were unable to initiate secondary oxidative processes during decomposition. This experimental observation was explained by a reaction between the two radicals formed.[9]



$$\underset{\text{H}\quad\text{OOH}}{\text{-C-}} \longrightarrow \underset{\text{H}\quad\text{O}\bullet}{\text{-C-}} + \text{OH}\bullet \longrightarrow \text{H}_2\text{O} + \underset{\text{O}}{\underset{\|}{\text{-C-}}}$$

The conversion of hydroperoxides into imides observed in polyamides may obey the same mechanism.



$$\text{OH}\bullet + \text{-}\underset{\text{O}\bullet}{\underset{|}{\text{CH}}}\text{NHCO-} \longrightarrow \text{-CONHCO-} + \text{H}_2\text{O} \qquad (2)$$

In the polymer matrix, the imide groups are hydrolyzed into acidic and amide compounds at a temperature around 90 °C.

$$\text{-CONHCO-} \xrightarrow{H_2O} \text{-CONH}_2 + \text{-COOH} \qquad (3)$$

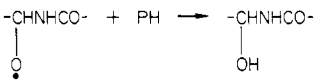
The acidic compounds are very easily observed by their IR absorptions at 1715, 1420, 1220, 1190, and 935 cm^{-1}. At such a high temperature and in a dry atmosphere, hydrolysis should proceed by the water formed in the decomposition of the hydroperoxides.

Our experimental results lead to the conclusion that the imide groups can be excited by wavelengths longer than 300 nm and then photodissociate:

$$\text{-CONHCO-} \rightarrow \text{-CONH}\cdot + \cdot\text{CO-} \qquad (4)$$

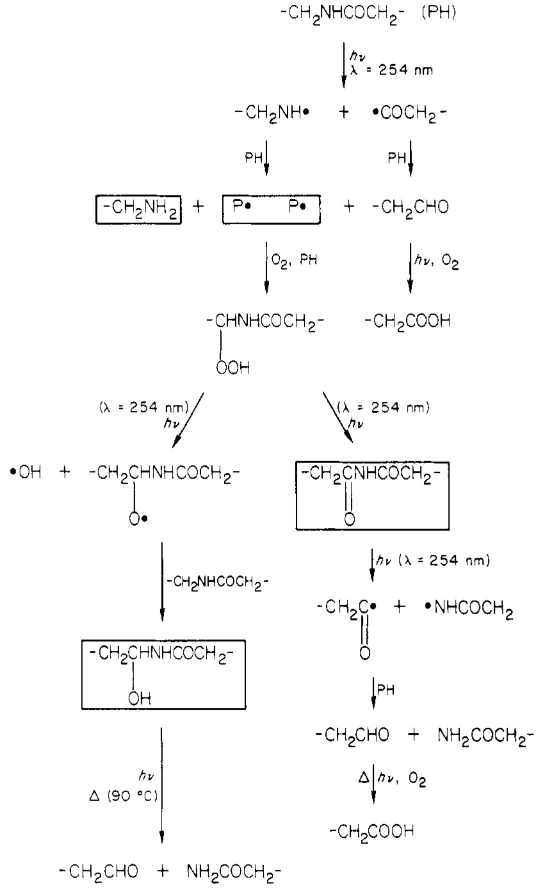
Aldehyde and amide groups are formed through abstraction of hydrogen atoms from the chain.[12] Aldehyde groups are immediately oxidized into acids. These consecutive reactions explain why the imide concentration passes through a maximum during irradiation and why acids are observed at temperatures lower than 90 °C.

Finally, we have observed a photoproduct that absorbs around 3450 cm^{-1} and decomposes around 90 °C. This photoproduct cannot be identified as any of the described photoproducts (hydroperoxides, imides, amides, and acids). As a matter of fact, the macroradical formed in reaction 1 may abstract a hydrogen atom[12] (in competition with reaction 2); a hydroxylated derivative is then formed:

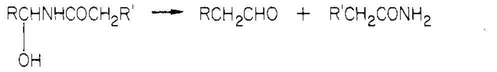


$$\text{-}\underset{\text{O}\bullet}{\underset{|}{\text{CH}}}\text{NHCO-} + \text{PH} \longrightarrow \text{-}\underset{\text{OH}}{\underset{|}{\text{CH}}}\text{NHCO-} \qquad (5)$$

Scheme III
Photooxidation of Polyundecanamide at 254 nm



According to Sagar et al., the *N*-(1-hydroxyalkyl) amides formed in the autoxidation of *N*-alkyl amides decompose around 100 °C into amides and aldehydes.[4,5]



$$RCH(OH)NHCOCH_2R' \longrightarrow RCH_2CHO + R'CH_2CONH_2 \qquad (6)$$

The observed absorption can therefore be attributed to such a hydroxylated group, which is thermally unstable in the polymer matrix.

As discussed later, the photoproduct absorbing at 3400–3500 cm^{-1} and stable at 140 °C was identified as an amine group resulting from a direct photodissociation of the polyamide bond (see section ii).

(ii) Mechanism of Photooxidation of PA11 at 254 nm. The proposed degradation mechanism, shown in Scheme III, is as follows:

A primary photodissociation is induced by the 254-nm radiation, which is directly absorbed by the amide chromophore.[1] A C–N scission occurs and the two macroradicals formed through abstraction of a hydrogen atom from the polymer chain are transformed into aldehyde and amide groups, with production of secondary macroradicals.

The aldehyde groups are easily observed in the UV spectra of a photooxidized sample ($\lambda_{max} \simeq 290$ nm). Their concentration is close to 10^{-1} mol·kg^{-1} and reaches a photostationary value that 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 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 photoxidation of aldehydes.

The amine group formed in the first steps are thermally stable at 140 °C and are observed in the IR spectra around 3400–3500 cm^{-1}. Indeed, the NH absorption band of a primary amine hydrogen bonded with the polymer chain must appear between 3470 and 3410 cm^{-1}. It can be easily checked through IR spectrometry that such amine compounds are not formed in thermal oxidation of PA11.

As shown by chemical titration, the photostationary concentration of hydroperoxide is far lower under excitation at 254 nm than under long-wavelength irradiation. Both hydroperoxides and the polymer absorb the 254-nm radiation, and the hydroperoxides photolyze into imides and *N*-1-hydroxypolyamides (reactions 1, 2, and 5). 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, as shown previously, the imide groups formed during long-wavelength photooxidation are readily destroyed by subsequent short-wavelength excitation. Therefore, under 254-nm irradiation their concentration is too low to be detected by means of IR.

Thus a detailed mechanism of photooxidation of polyundecanamide has been proposed based on an analysis of the different intermediate photoproducts and a study of their stability in the polymer matrix. At long wavelengths ($\lambda > 300$ nm) and at a temperature higher than room temperature, a photoinduced oxidation is observed. The primary formation of hydroperoxides is followed by various photochemical or thermal steps leading finally to scission of the backbone of the polymer. At short wavelengths, photooxidation occurs through the same intermediate products. Differences resulting from long-wavelength irradiation are associated with relative photostationary concentrations. A strategy for photostabilization of polyamides is currently being developed in our laboratory based on the proposed mechanism.

Experimental Section

Processing of Samples. The polyundecanamide films of the Rilsan type were supplied by Ato Chimie, Serquigny, France. They were made by polycondensation of 11-aminoundecanoic acid, either with an acidic catalyst (PA11 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 this article were carried out with type B. No additive was introduced into any of the samples.

Films of 40-μm thickness were irradiated in different setups (see below). Preliminary experiments have shown that the rate of photooxidation is independent of thickness in the range 30–50 μm. The controlling factor is not, therefore, the diffusion of oxygen in 40-μm films.

Experimental Setup. Two polychromatic devices used in this analytical study were built in our Service d'Etudes du Photovieillissement Accéléré des Polymères (SEPAP). Designed for testing natural photoaging as well as for fundamental research, these devices present the following common features:

(1) The polychromatic incident beam is filtered in order to eliminate radiation of wavelengths shorter than 300 nm. The main reason for such a limitation is its relevance to natural photoaging. However, in fundamental research, under these radiation conditions it is also easier to control the initiation rate. In the condensed phase of a "pure" polymer, internal conversions and vibrational relaxation in an isolated chromophore group often annihilate short-wavelength effects. In mixtures, irradiated at short wavelengths ($\lambda < 300$ nm), excitation of different chromophores of impurities or additives can occur and wavelength effects can be observed. Various initiation processes can interfere. If the incident light contains only long wavelengths, it is easier to

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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).

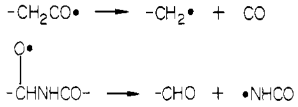
A SEPAP 254 setup equipped with a monochromatic low-pressure mercury arc ("resonance" lamp) was used for short-wavelength irradiation (254 nm). In that case, a cylindrical reflector with an elliptical base was built. The source was located along the first focal axis and the rotating support for the samples 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:



$$-CH_2CO\bullet \longrightarrow -CH_2\bullet + CO$$

$$-\overset{\displaystyle O\bullet}{\overset{|}{C}}HNHCO- \longrightarrow -CHO + \bullet NHCO$$

(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

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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.

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