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Photochemistry of Aliphatic Polyamides. 3. Mechanisms of Photooxidation of Polyamides 6, 11, and 12 at Short Wavelength

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ABSTRACT: An experimental and analytical study of the photooxidation of polyamide 6, 11, and 12 films carried out at short wavelength (254 nm) is reported. The photooxidation mechanisms imply the same intermediate photoproducts, which behave differently in the different films. The primary photoscission of the N–C bond, which is independent of the nature of the polyamide, accounts for the formation of the amine and aldehyde groups and for the initiation of the hydroperoxidation reaction. The hydroperoxides are shown to accumulate until a fairly low photostationary concentration higher in polyamide 12 (8 $\mathrm{mmol\cdot kg^{-1}}$) than in polyamides 6 and 11 (2–4 $\mathrm{mmol\cdot kg^{-1}}$). Photochemical decomposition of the hydroperoxides into N-1 hydroxylated groups is observed. The formation of imide groups, very photolabile at 254 nm, cannot be detected. Aldehyde groups appear as key products of the 254-nm photooxidation of polyamides. Formed through the direct photoscission and the photolysis of imide groups, they are converted competitively into α,β-unsaturated aldehyde and acidic groups. The behavior of aldehyde groups in the various matrices studied accounts for the major differences in the short-wavelength photooxidation of polyamides.

The behavior of aliphatic polyamides on exposure to UV irradiation has attracted much attention.[1,2] Photoaging of this class of thermoplastics is of greatest concern since many security devices are made with this high-performance material. However, up to 1982, the prediction of natural aging of aliphatic polyamides was difficult since the mechanism of photooxidation at wavelengths longer than 300 nm (i.e., under solar radiation) was at least partially unknown. Most of the reported research in this field concerns vacuum photolysis,[3] photooxidation at wavelengths shorter than 290 nm, and autoxidation and photooxidation of model compounds, i.e., low molecular weight amides.[4–6]

For several years, our group has been investigating the photochemistry of aliphatic polyamides in the solid state at short and long wavelengths.[7–10] Mechanisms were proposed that accounted for the behavior of the different intermediate photoproducts observed in the photooxidation of polyundecanamide. The hydroperoxides primarily formed were shown to be thermally unstable at 60 °C and photolyzed at short wavelengths. At long wavelengths ($\lambda > 300$ nm), they can accumulate until a photostationary concentration close to 15 $\mathrm{mmol\cdot kg^{-1}}$ is reached at 60 °C. Decomposition of hydroperoxide into imide groups and N-1 hydroxylated groups was observed and the imide groups were either hydrolyzed or photolyzed into acidic and amide groups. At short wavelengths ($\lambda = 254$ nm), products of a direct photoscission of the C–N bond, i.e., aldehydes and amines, were observed. In the wavelength range of daylight ($\lambda > 295 \pm 5$ nm), a dual mechanism is therefore implied in the photoinitiation of oxidation reactions. In the wavelength range of daylight ($\lambda > 295 \pm 5$ nm) direct absorption of the NHCO chromophore competes with the usual absorption of defect sites and impurities, indicating a dual mechanism in the photoinitiation of oxidation reactions. At short wavelengths, the direct photoscission is prevalent and photolability of various intermediate photoproducts is more pronounced than at long wavelengths.

In the present paper, we report results on the photochemical behavior of three aliphatic polyamides, polyhexanamide (PA6),[14] polyundecanamide (PA11),[14] and polydodecanamide (PA12),[14] with a special emphasis on the consequences of the photoscission at 254 nm in oxygenated matrices. Later, we will describe the characteristics of the photooxidation of these aliphatic polyamides at $\lambda > 300$ nm, i.e., the photooxidation directly related to natural aging.

Experimental Results

In Figure 1 are shown the absorption spectra of the three polyamides under investigation. Films with thicknesses of 40 μm were used. The actual absorption intensity was measured with a UV spectrophotometer equipped with an integration sphere for scattering corrections. Absorption of the chromophore group NHCO extends until 320 nm (polyamide extinction coefficient at 320 nm around 4 $\mathrm{cm^{-1}}$) and the observed maxima lie around 220 nm. At the excitation wavelength selected for this study, i.e., 254 nm, the absorbance of a 40-μm film was around 0.1 and invariant for all the polyamides under investigation. The absorption of the light was therefore homogeneous in the 40-μm film.

The oxygen permeability of polyamides is fairly low. Relative values have been measured with an Oxtran apparatus.

	O_2 permeability, $(\mathrm{cm^3\cdot mm})/(\mathrm{cm^2\cdot s\cdot cmHg})$
PA6	0.15×10^{-10}
PA11	1.5×10^{-10}
PA12	3.3×10^{-10}
LDPE	$(20\text{–}25) \times 10^{-10}$

However, under the conditions of our experimental arrangement (incident light intensity 2×10^{13} $\mathrm{photon\cdot s^{-1}\cdot cm^{-2}}$, 25 ± 2 °C) no oxygen starvation effect was ever observed as a variation of the oxidation rate with sample thickness. In the range 40–100 μm, the oxidation rate remains proportional to the polymer mass, i.e., to the thickness of the film.

1. Analytical and Kinetic Study of the 254-nm Photooxidation of Aliphatic Polyamides. Films made of PA6, PA11, and PA12 supplied by Atochem, France, and containing no additives were exposed at 254 nm in the presence of oxygen in a Sepap 254 setup (see Experimental Section). The temperature of the samples was kept at 25 ± 2 °C. The analytic procedure was based on chemical titration of hydroperoxides and IR and UV spectrophotometry. The decomposition of the aldehyde groups

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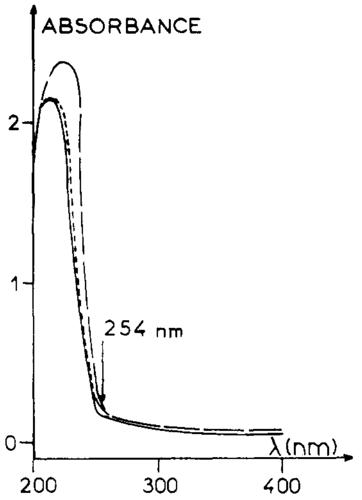


Figure 1. Absorption spectra of PA6 (–––), PA11 (- - -), and PA12 (—) films (thickness 40 μm).

Table I
Variation in the Hydroperoxide Concentration during Photooxidation at 254 nm and 25 °C

	Polyamide 6					
t, h	22	48	96	173	197	
[ROOH], mmol·kg^{-1}	0.7	4.8	2.9	2.7	4.7	
	Polyamide 11					
t, h	22	42	70	120	168	230
[ROOH], mmol·kg^{-1}	1.8	2.0	2.5	3.0	2.7	2.5
	Polyamide 12					
t, h	6	21	42	166		
[ROOH], mmol·kg^{-1}	7.9	6.3	6.6	7.9		

formed in the photooxidation was determined colorimetrically.

The concentration of hydroperoxide groups formed in the short-wavelength photooxidation was measured by the titration technique previously adapted to PA11. The titration was necessarily carried out at room temperature in hexafluoro-2-propanol since the hydroperoxides were shown to be fairly unstable above 60 °C (see Experimental Section). In Table I are reported the hydroperoxide concentrations measured after various exposure durations in PA6, -11, and -12. (In this range of low concentrations, the absolute error was estimated to be around 1–2 mmol·kg^{-1}.)

Considering the scatter of the data inherent in these low concentrations, it could be concluded that the stationary values observed for the ROOH concentrations are higher in PA12 than in PA11 and PA6. From Table I, it appears too that the hydroperoxide groups rapidly reached a photostationary concentration, lower than those observed in long-wavelength photooxidation. For example, in PA6, -11, and -12, respectively, ROOH concentrations up to 10, 20, and 45 mmol·kg^{-1} have been observed at $\lambda_{exc} > 300$ nm and 60 °C. This experimental fact is easily accounted for by the relative absorption of polyamide and hydroperoxide groups at short and long wavelengths.

The IR spectra of the photooxidized sample, recorded after various exposure durations, showed the same features as those previously reported for PA11, i.e., (i) a development of an unstructured shoulder of the NH absorption band of PA around 3500–3400 cm^{-1} related to the appearances of amines and N-1 hydroxylated groups (as pointed out later, in section 2.1, the concentration of amine groups was determined from the residual absorbance at 3400 cm^{-1} after a 120 °C thermolysis treatment; the concentration of N-1 hydroxylated groups was derived from the absorbance variation in this posttreatment (see Figure 2)) and (ii) a fast increase of the absorption band, peaking at 1710 cm^{-1} and attributed to the formation of acidic groups.

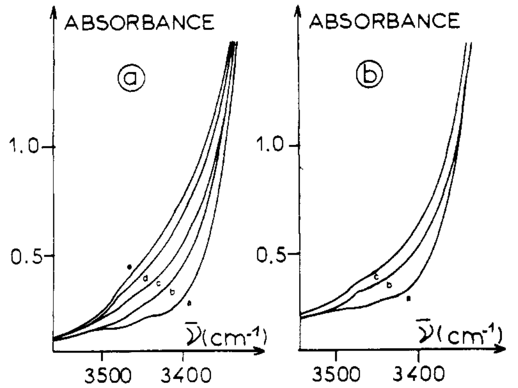


Figure 2. (a) Infrared spectra of 40-μm PA6 film at various stages of photooxidation at 254 nm. Irradiation times: (a) 0, (b) 145, (c) 210, (d) 350, and (e) 470 h. Sepap 254; sample temperature 25 °C. (b) Infrared spectra of preoxidized 40-μm PA6 film treated at 120 °C under vacuum: (a) initial sample; (b) after 30 min at 120 °C; (c) sample photooxidized for 230 h in a Sepap 254 at 25 °C.

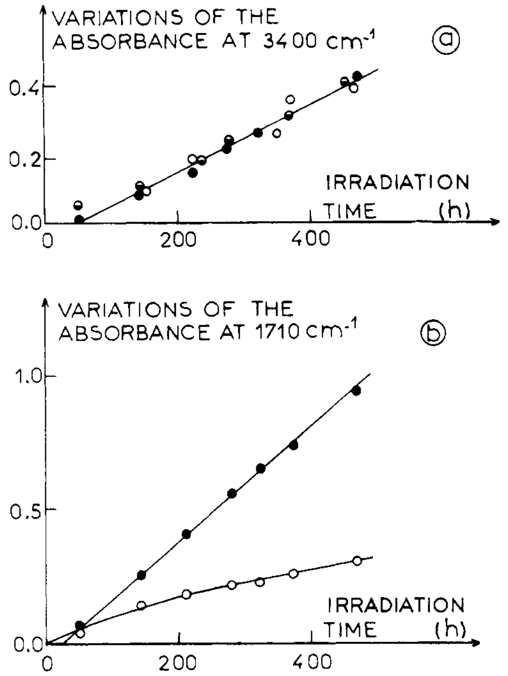


Figure 3. (a) Variations in the residual absorbance at 3400 cm^{-1} of PA films at various stages of photooxidation at 254 nm and 25 °C after a thermal treatment at 120 °C: (○) PA6; (●) PA11; (◒) PA12. (b) Variations in the absorbance at 1710 cm^{-1} of PA films at various stages of photooxidation at 254 nm and 25 °C: (○) PA6; (●) PA11 and -12.

Throughout the photooxidation, the concentration of amines and acidic groups increased continuously with a concurrent loss of the mechanical properties of the samples (see Figure 3). The concentration in N-1 hydroxylated groups reached a stationary value. In PA6, -11, and -12, the initial rate of formation and the photostationary concentration of N-1 hydroxylated groups were practically the same. The formation of amines was independent of the nature of the polyamide. However, the rate of formation of the acidic groups was 3 times higher in PA11 and PA12 than in PA6 (see Figure 3).

The IR spectra of the photooxidized samples did not reveal the presence of imide groups, which are key products

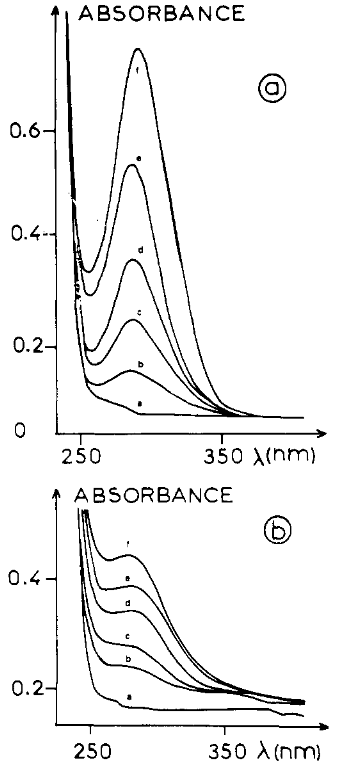


Figure 4. (a) UV spectra of a 40-μm PA6 film during a photooxidation at 254 nm. Irradiation time: (a) 0, (b) 22, (c) 45, (d) 68, (e) 104, and (f) 231 h. (b) UV spectra of 40-μm PA11 and PA12 films during a photooxidation at 254 nm. Irradiation time: (a) 0, (b) 70, (c) 95, (d) 196, (e) 280, and (f) 312 h.

of the long-wavelength oxidation of aliphatic polyamides. The same observation was reported for PA11 photooxidation at 254 nm.[8] The imide groups were shown to be photolabile at 254 nm by postexposure of groups built up during long-wavelength oxidation (λ > 300 nm).

As shown in Figure 4, the variations in the UV spectra of the photooxidized samples of PA6, -11, and -12 were essentially characterized by the increase of an absorption band around 290 nm. The UV absorption band appearing under photooxidation increased continuously (see Figure 5). The initial rate of formation of the photoproduct absorbing around 290 nm was dependent on the polyamide studied. This initial rate was roughly 3 times higher in PA6 than in PA11 and PA12.

Vacuum photolysis at 254 nm of PA6, -11, and -12 also caused the formation of photoproducts that absorbed at 290 nm. However, the initial rate of formation of this photolysis product was 2–3 times lower than in the presence of oxygen.

The "290-nm" band observed in PA11 was previously attributed to saturated aldehyde terminal groups formed through direct photoscission and abstraction of a hydrogen atom by the ketyl radicals.[8] At 254 nm, this photoproduct was assumed to be photochemically protected by the polymer itself; it indeed disappeared as the excitation radiation shifted to longer wavelengths (λ > 300 nm). The more detailed results in section 2 of the present study lead us to reassign this absorption band.

Finally, a colorimetric titration of the aldehyde groups formed in the 254-nm photooxidation was carried out, based on the dinitrophenylhydrazine reagent.[8] Results are presented in Table II and Figure 5. In PA11 and -12, the stationary concentration of aldehyde groups was reached more rapidly than in PA6. However, these stationary values were practically independent of the PA type and, in any case, fairly low.

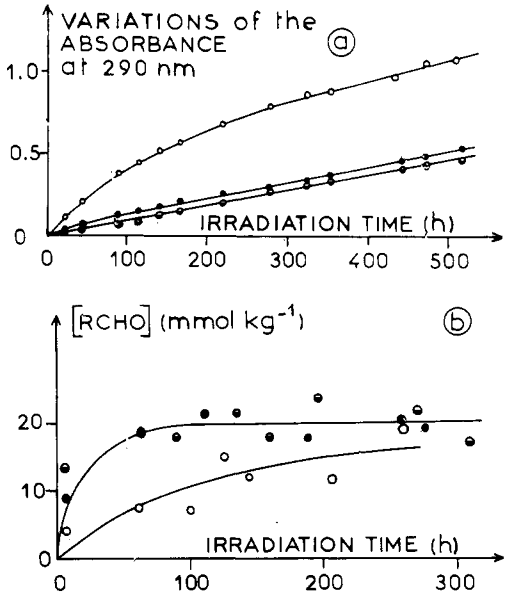


Figure 5. (a) Variations of the absorbance at 290 nm of 40-μm PA films during a photooxidation at 254 nm: (○) PA6; (●) PA11; (◒) PA12. (b) Variations in the RCHO concentrations during a photooxidation at 254 nm: (○) PA6; (●) PA11; (◒) PA12.

Table II
Variation in Aldehyde Concentration in the 254-nm Photooxidation of Various Aliphatic Polyamides

Polyamide 6

t, h	7	60	60	100	126	144	206	206	260
[RCHO], mmol·kg^{-1}	4	7.4	7.5	7.1	15.2	11.8	11.5	11.7	19.3

Polyamide 11

t, h	7	64	112	188	258	276
[RCHO], mmol·kg^{-1}	9.2	18.8	21.5	18	20.8	19.4

Polyamide 12

t, h	7	90	134	160	196	274	310
[RCHO], mmol·kg^{-1}	13.5	18.4	21.7	18	24	22.1	15.5

2. Properties of the Photooxidation Products in Postirradiation Treatments. 2.1. Vacuum Thermolysis. PA6, -11, and -12 photooxidized samples were maintained at a constant temperature (25, 90, 120, and 140 °C) under vacuum. IR and UV spectra were recorded throughout the thermal treatment. It was observed that thermolysis at 90 °C provoked a partial decrease of the absorption in the OH–NH stretching range. The residual absorption remained invariant even after a thermal treatment at 140 °C. The unstable and stable photoproducts were identified as amine and N-1 hydroxylated groups, as previously proposed in PA11 photooxidation.[8] N-1 hydroxylated groups are thermolyzed into aldehyde and amide groups, i.e., into products that are not absorbing around 3500–3400 cm^{-1}.

The photoproducts absorbing around 290 nm were observed to be unstable in vacuum thermolysis at 90 °C. Even at room temperature, the maximum of the absorption band shifted in the dark to shorter wavelengths. For example, in PA6, the absorption maximum was at exactly 292 nm immediately after the incident light was cut off. The sample maintained at room temperature (25 °C) showed a hypsochromic shift to 288 nm which paralleled a hyperchromic effect (the intensity of the band increased by a factor of 1.4). A postirradiation at 254 nm of the same sample restored the initial absorbing properties of the film. This series of experiments has been carried out at various

Table III
Thermal Treatment of PA6 Film Photooxidized at 254 nm

t, h	66	114	186	257	329
A(292 nm)	0.180	0.355	0.540	0.685	0.840
A(288 nm)[a]	0.260	0.500	0.740	0.940	1.26
hyperchromicity	1.44	1.41	1.37	1.37	1.50

[a] After thermolysis.

stages of the short-wavelength photooxidation (see Table III).

In the solid state, the conversion

$$P_{288} \underset{\Delta\ (t\, >\, 25\ ^\circ\mathrm{C})}{\overset{h\nu\ (254\ \mathrm{nm})}{\leftrightarrows}} P_{292}$$

$$\epsilon_{\max}(P_{288}) = 1.4\epsilon_{\max}(P_{292})$$

could be repeated many times. In PA11 and PA12 films a conversion of the initial photoproducts P_{290} could only be observed through the hyperchromic effect (the intensity of the 290-nm band being multiplied by 1.4).

2.2. Long-Wavelength Photolysis or Photooxidation. As PA6, -11, and -12 films prephotooxidized at 254 nm are exposed to long-wavelength radiation ($\lambda >$ 300 nm), the photoproduct absorbing around 290 nm disappears more rapidly in the presence of oxygen than in its absence.

3. Reactions of Low Molecular Weight Aldehydes in PA Matrices. The results presented in the previous section suggested that the saturated aldehydes primarily formed in PA photooxidation reacted in the matrix. To assess this assumption, these reactions were modeled by immerging 40-μm films of the various polyamides in methanolic or aqueous solutions of methanal, propanal, 1-butanal, and 1-pentanal. After 30-min immersion, the films were dried, their UV spectra were recorded, and the aldehyde concentrations were determined by using dinitrophenylhydrazine reagent.[11] The phenomena observed with PA6 films are summarized in Table IV.

Through HPLC measurements in hexafluoro-2-propanol solution, the aldehydes have not reacted with the polymer. The only reaction occurring in the polymer was aldehyde condensation.

The absorption bands detected in polyamide films after immersion in aldehyde solution were very similar to those observed in photooxidized PA samples. As the total concentration of aldehydes was found to be less than 2×10^{-2} mol·kg^{-1} and the optical path was 40 μm, the observed absorption bands must be attributed to compounds with high molar extinction coefficients and not to the saturated aldehydes initially formed in the sample. In a PA matrix, aldolization and crotonization of aliphatic aldehydes are occurring as shown by comparing the absorption bands reported in Table IV with the following data:[12] $CH_3CH{=}CHCHO$, $\lambda_{\max} = 220$ nm, $\epsilon_{\max} = 14\,800$ mol·L^{-1}·cm^{-1}; $CH_3(CH{=}CH)_2CHO$, $\lambda_{\max} = 271$ nm, $\epsilon_{\max} = 24\,500$ mol·L^{-1}·cm^{-1}; $CH_3(CH{=}CH)_3CHO$, $\lambda_{\max} = 315$ nm, $\epsilon_{\max} = 37\,100$ mol·L^{-1}·cm^{-1}; $CH_3(CH{=}CH)_4CHO$, $\lambda_{\max} = 353$ nm, $\epsilon_{\max} = 40\,700$ mol·L^{-1}·cm^{-1}.

In photooxidized samples, saturated aliphatic aldehydes are indeed formed through the direct excitation of the NHCO groups. These aldehydes are crotonized afterward in the polyamide matrix and the condensation is limited to the formation of two or three conjugated double bonds ($\lambda_{\max} \simeq 290$ nm, $\epsilon_{\max} = 16\,000$ mol·L^{-1}·cm^{-1}). The formation of such compounds accounts for the reversibility described in section 2.1. On short-wavelength exposure, trans → cis isomerization occurs in the α,β-unsaturated aldehydes. The cis form absorbs generally at longer wavelengths than the all-trans form and a hypochromic effect is generally observed. In the dark, the cis forms were converted back to all-trans forms with a hyperchromic effect and a hypsochromic shift (292 → 288 nm in PA6). Moreover, it is known that excitation of unsaturated aldehydes in $\pi\pi^*$ transition provokes mainly isomerization as opposed to long-wavelength excitation in $n\pi^*$ transition, which leads to photoscission into radicals. This explains the disappearance of these unsaturated aldehydes at wavelength longer than 300 nm in the presence of oxygen.

The thermal and photochemical oxidation of nylon 66 films has been studied recently[13] using second-order derivative UV spectroscopy. The 290-nm absorption was associated with an intense absorption band at 230 nm and attributed to α,β-unsaturated carbonyl groups initially present in the sample; these two bands disappeared on exposure and were restored in the dark. No precise structure was assigned to this absorbing species.

Discussion and Conclusions

The previous proposal of the photoproduct absorbing around 290 nm in PA11 as saturated aldehydes formed on a direct photoscission mechanism suggested that the relative importance of the photoscission in polyamides was dependent on the nature of the polyamide considered, i.e., on the length of the carbon chain. Two contradictions to this proposal have appeared in the study. Evaluated from the rate of formation of the amine groups, the rate of the direct photoscission was invariant in PA6, -11, and -12. The concentration of saturated aldehydes as determined by absorbance at 290 nm was too high when compared with the available nitrogen atoms.

The experimental results described in the previous sections show that the aldehydes groups formed in the matrix crotonize progressively in the polyamide matrices. In the presence of oxygen, the aldehyde groups are converted competitively either into α,β-unsaturated aldehydes such as $(CH{=}CH)_2CHO$ or into acidic groups through oxidation. The absorption band peaking around 290 nm must now be attributed to the crotonized aldehydes. It appeared that aldehyde condensation occurred 3 times faster in PA6 than in PA11 and PA12. Acidic groups are therefore more rapidly formed in PA11 and PA12.

The major initial mechanism of the 254-nm photooxidation of aliphatic polyamides is the direct photoscission, which is independent of the length of the carbon chain

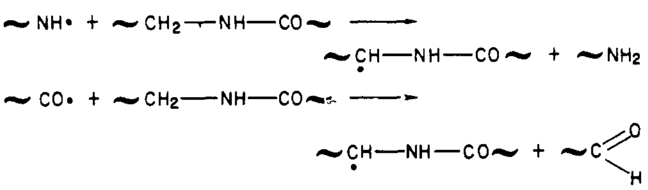
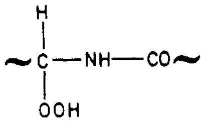


Table IV
Conversion of Aliphatic Saturated Aldehydes in PA6 Matrix

	methanal	ethanal	propanal	butanal	pentanal
spectrophotometric observations on 40-μm film after immersion and drying	no absorption detected	slow formation of 3 absorption bands peaking at 270, 310, 340 nm	no absorption detected	fast formation of absorption bands at 240 and 295 nm	slow formation of absorption band peaking at 280 nm

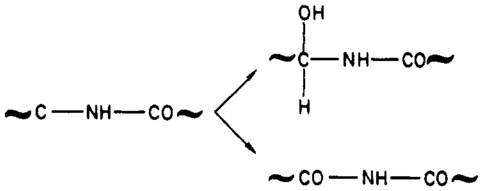
The rate and quantum yield of formation of the amine group is indeed independent of the polyamide considered. The formation of aldehyde groups is 2 times faster in the presence of oxygen than in its absence. The photoscission mechanism obviously cannot alone account for this result; the oxidation mechanism must also be considered.

The major photoproducts of oxidation, i.e., the hydroperoxide groups



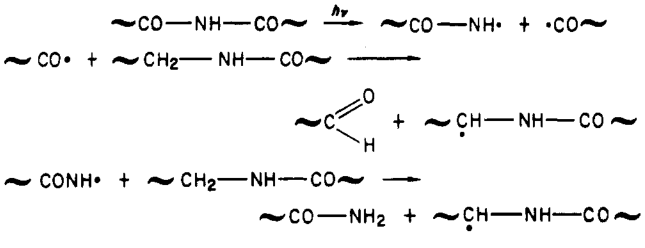
$$\sim\overset{\displaystyle H}{\underset{\displaystyle OOH}{C}}-NH-CO\sim$$

are photolabile at 254 nm. As shown through chemical titrations, the photostationary concentration in hydroperoxides were found to be very low (around a few mmol·kg^{-1}). A competitive phototransformation of hydroperoxide groups into N-1 hydroxylated and imide groups, faster in PA6 and PA11 than in PA12, can account for the variations of the concentration of these intermediate photoproducts.



The initial rate of formation of N-1 hydroxylated groups was shown to be independent of the nature of the polyamide.

The imide groups, which can be directly observed in the IR spectra of samples photooxidized at long wavelengths,[8,10] are highly photolabile at 254 nm. On exposure at 254 nm, the photostationary concentration is below IR detection. The photolability of imides was checked as follows. For example, on exposure of PA6 film at λ > 300 nm, imide groups accumulated in the presence of oxygen. When the excitation wavelength was shifted to 254 nm, the imide groups disappeared rapidly, while the 292-nm absorption band developed in the UV spectra. In this experiment, the exposure duration was short enough to prevent the formation of aldehydes through the direct photoscission mechanism (duration <20 h). The photolysis of imides gives rise to crotonized aldehydes.



In conclusion, aldehyde groups appear to be key products for the understanding of the 254-nm photooxidation of aliphatic polyamides. Formed through a dual mechanism, photoscission and photolysis of imide groups, aldehydes are converted competitively into α,β-unsaturated aldehydes and acidic groups, both final products being observed spectrophotometrically. The behavior of aldehyde groups in the various matrices accounts essentially for the major differences observed in the short-wavelength photooxidation of polyamides.

Experimental Section

The PA6, -11, and -12 films of the Rilsan type were processed and supplied by Atochem, Serquigny, France. PA6 (Organamide R) was made by hydrolytic polycondensation of ϵ-caprolactam (hexahydro-2*H*-azepin-2-one). PA11 (Rilsan type B) was made by hydrolytic polycondensation of 11-aminoundecanoic acid using phosphoric acid as a chain regulator. PA12 (Rilsan type A) was made by hydrolytic polycondensation of ω-dodecalactam (azacyclotridecane-2-one) using adipic acid as a chain regulator. The films were obtained by conventional extrusion techniques (flat film on a chill roll).

The experimental results reported in the present study were carried out with 40-μm films. The experimental apparatus, i.e., Sepap 254 and Sepap 12.24 (from Service d'Etudes du Photovieillissement Accélêré des Polymêres), has been described in previous papers of this series.[8,9]

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 was based on the oxidation at room temperature of Fe^{2+} and the complexation of Fe^{3+} by SCN^- anions. As stressed previously, this method gives only correct results in good solvents of polyamides, e.g., hexafluoro-2-propanol. The photooxidized polyamide (5 mg) was dissolved in 1 mL of hexafluoro-2-propanol. After complete dissolution of the film, 1 mL of a 50/50 mixture of a methanolic solution of $(NH_4)_2SCN$ (2×10^{-1} mol·L^{-1}) and a methanolic solution of Mohr's salt (10^{-2} mol·L^{-1}) and H_2SO_4 (4.5×10^{-2} mol·L^{-1}) was added. The solution volume was increased to 25 mL through addition of benzene (PA11 and PA12) or methanol (PA6). The concentration of the complexed ion $(Fe(SCN)_6)^{3-}$ was determined spectrophotochemically ($\lambda_{max} = 512.5$ nm, $\epsilon_{max} = 1.68 \times 10^4$ L·mol^{-1}·cm^{-1}).

The ROOH concentration was calculated based on the stoichiometry

$$ROOH + 2Fe^{2+} + 2H^+ \rightarrow ROH + 2Fe^{3+} + H_2O$$

A colorimetric titration of the aldehyde groups present in the matrix was based on the formation of the 2,4-dinitrophenylhydrazone through the reaction[11]

$$2,4\text{-}(NO_2)_2C_6H_3NHNH_2 + RCHO \rightarrow 2,4\text{-}(NO_2)_2NHNHCHR + H_2O$$

The photooxidized polyamides (5 mg) were dissolved in 1 mL of hexafluoro-2-propanol. Two milliliters of a methanolic solution of DNPH (2.5 mg) and HCl (0.05 mL of 36 M HCl) was added. After standing 40 h, the polymer containing the diphenylhydrazone group was centrifuged off and dissolved in a known volume of hexafluoro-2-propanol. A spectrophotometric titration was carried out at $\lambda_{max} = 357$ nm ($\epsilon = 23\,000$ mol^{-1}·L·cm^{-1}).

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) Tang, L.; Lemaire, J.; Sallet, D.; Mery, J. M. *Makromol. Chem.* **1981**, *182*, 3467.
(8) Tang, L.; Sallet, D.; Lemaire, J. *Macromolecules* **1982**, *15*, 1432.
(9) Tang, L.; Sallet, D.; Lemaire, J. *Macromolecules* **1982**, *15*, 1437.
(10) Roger, A. Ingênieur-Docteur Thesis, University of Clermont-Ferrand, Oct 1984.
(11) Sawicki, E.; Sawicki, C. R. "Aldehydes: Photometric Analysis"; Academic Press: London and New York, 1975; Vol. I, p 34.
(12) Rao, C. N. R. "Ultraviolet and Visible Spectroscopy"; Butterworths: London, 1961; p 34.
(13) Allen, N. S. *Polym. Degrad. Stab.* **1984**, *55*, 63.
(14) PA6, -11, and -12 are respectively poly(imino(1-oxo-1,6-hexanediyl)), poly(imino(1-oxo-1,11-undecanediyl)), and poly(imino(1-oxo-1,12-dodecanediyl)).