Photochemistry of Aliphatic Polyamides. 4. Mechanisms of Photooxidation of Polyamides 6, 11, and 12 at Long Wavelengths

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ABSTRACT: An analytical study of the photooxidation of polyhexanamide (PA 6), polyundecanamide (PA 11) and polydodecanamide (PA 12), carried out at long wavelengths, is reported. The photooxidation mechanism implies the same intermediate photoproducts, i.e., hydroperoxide, imide, and *N*-1-hydroxylated groups, which behave differently in the various matrixes. Photoinitiation through direct excitation of NH–CO chromophores occurs up to 340 nm. At wavelengths longer than 340 nm, the rate of photooxidation, based for example on the rate of formation of imide groups, does not depend on the nature of the polyamide. At wavelengths longer than 300 nm, direct photoscission of NH–CO bonds and photoinitiation are 1.6 times faster in PA 6 and PA 12 than in PA 11. The stationary concentration of hydroperoxides differs notably in PA 6, PA 11, and PA 12 (respectively 10, 20, and 44 mmol·kg^{-1}); PA 6 hydroperoxides are more unstable than the corresponding species for PA 11 and PA 12. The three types of hydroperoxides convert essentially into imide groups, the *N*-1-hydroxylated groups being a minor photoproduct. Hydroperoxides are unable to initiate new oxidation processes. The main route of disappearance of the imide groups in the photooxidized matrixes, even under dry conditions, involves hydrolysis with the water that is formed in situ in close proximity to the imide groups. Imides formed in PA 6 hydrolyze faster than PA 11 and PA 12 imides. The role of water in the photooxidation of aliphatic polyamides is limited to reaction with the imides formed under oxidative conditions.

The natural aging of aliphatic polyamides has been for years a subject of great concern since many security devices are made of these high performance thermoplastics. However, most of the studies reported before 1982 dealt with vacuum photolysis or photooxidation at short wavelengths ($\lambda < 290$ nm) or with autooxidation or photooxidation of model compounds.[1-4]

As pointed out in reviews (see, for example ref 5 and 6) this work has provided useful information for understanding the behavior of polyamides exposed to oxidation. Nevertheless, the prediction of the fate of such materials under natural conditions is still difficult.

For several years our group has been investigating the photochemistry of polyundecanamide 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 mmol·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 wavelength ($\lambda = 254$ 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. Direct absorption of the light by the chromophores –NH–CO competed with the usual absorption by defects and impurities. At short wavelengths, the direct photoscission was prevalent and photolability of various intermediate photoproducts was more pronounced than at long wavelengths.

In a recent paper, we reported results on the photochemistry at 254 nm of polyhexanamide (PA 6), polyundecanamide (PA 11) and polydodecanamide (PA 12).[11] We are now reporting results on the photooxidation at wavelengths longer than 300 nm of PA 6, PA 11, and PA 12, results that are directly related to natural aging of PA in daylight ($\lambda > 295 \pm 5$ nm). Photoinitiation of the oxidation of PA 6,6 has recently been described by Allen et al.[12] In the present work, the photochemical evolution of PA 6,6 is briefly compared to the behavior of other aliphatic polyamides.

The aim of the present paper is not only to extend the photooxidation mechanism proposed for PA 11, but also to answer three essential questions. Is there any difference in the behavior of the various intermediate photoproducts (hydroperoxides, imides, *N*-1-hydroxylated groups) in the different matrices? What is the importance of chemical defects or impurities in the initiation at $\lambda > 300$ nm? What is the role of water in the course of the photooxidation? In the field of polymer aging, the role of water is often poorly understood and therefore overemphasized. This situation results from the experimental difficulties met in the control of water concentration in irradiated samples. A setup is proposed that overcomes this difficulty.

Experimental Results

Oxidation of PA 6, PA 11, and PA 12 Photoinduced at Wavelengths Longer than 340 nm under "Dry" Conditions. Films of PA 6, PA 11, and PA 12 (40-μm thickness) were irradiated in a SEPAP 12.24 setup; the temperature of the samples was kept at 45 ± 1 °C. Wavelengths shorter than 340 nm were cut off with a filter (3-mm thickness). Absorbed water, present at the initial time, was completely eliminated under irradiation. In such "dry" conditions, water was formed in situ through hydroperoxidation and decomposition of hydroperoxides into imides.

$$\sim\text{(HOO)CHNHCO}\sim \;\rightarrow\; \sim\text{CONHCO}\sim \;+\; \text{H}_2\text{O}$$

Throughout the photooxidation course, it was observed that no UV absorption band peaking at 290 nm appeared. Also, no photoproducts absorbing around 3400 cm^{-1} in the hydroxyl region of IR spectra and stable above 120 °C were formed. These two facts show clearly that direct excitation of the amide group is not occurring in our setup in the time

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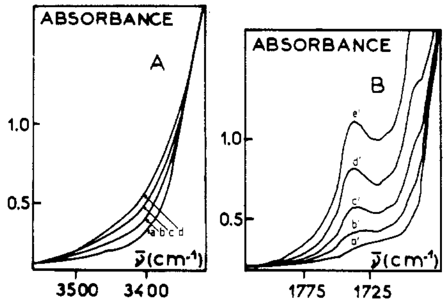


Figure 1. Infrared spectra of a 40-μm PA 12 film at various stages of photooxidation in polychromatic light λ > 340 nm and a sample temperature of 45 °C. Irradiation time: (a) 0 h; (b) 370 h; (c) 590 h; (d) 850 h; (a') 0 h; (b') 115 h; (c') 292 h; (d') 590 h; (e') 850 h.

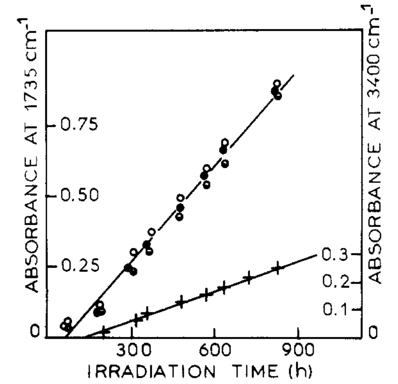


Figure 2. Variations in the absorbance at 3450 cm^{-1} during photooxidation in polychromatic light λ > 340 nm and at 45 °C: (+) PA 6, PA 11, and PA 12. Variations in the absorbance at 1735 cm^{-1} under the same experimental conditions: (O) PA 6; (●) PA 11; (◒) PA 12.

scale of our experiments (up to 1000 h). As reported recently direct photoscission of the amide chromophore leads to the formation of amines and aldehydes, which afterwards crotonize in the matrix.[10,11]

$$\sim\mathrm{NHCO}\sim \rightarrow \sim\mathrm{NH}\cdot + \cdot\mathrm{CO}\sim$$

$$\sim\mathrm{NH}\cdot + \sim\mathrm{CH_2NHCO}\sim \rightarrow \sim\mathrm{NH_2} + \sim\dot{\mathrm{C}}\mathrm{HNHCO}\sim$$

$$\sim\mathrm{CO}\cdot + \mathrm{CH_2NHCO}\sim \rightarrow \sim\mathrm{CHO} + \sim\dot{\mathrm{C}}\mathrm{HNHCO}\sim$$

$$\sim\mathrm{CHO} \rightarrow \sim(\mathrm{CH{=}CH})_n\text{-}\mathrm{CHO} \qquad n = 2 \text{ or } 3$$

Amines, which can be measured with IR spectroscopy as the only photoproducts absorbing at 3400 cm^{-1} and thermally stable above 120 °C,[13] are formed only through the direct photoscission.

As shown in Figure 1, the IR absorption spectra of PA 12 films, photooxidized at λ > 340 nm, showed an increase in the absorption bands at 1735 and 1690 cm^{-1}, previously attributed to the formation of imide groups.[8] An unstructured shoulder in the NH absorption band of PA appeared around 3400 cm^{-1}. This shoulder disappeared in a postirradiation thermal treatment at 120 °C and was attributed to *N*-1-hydroxylated groups.[8] In the UV spectra of the photooxidized samples, an absorption with no maximum developed as a shoulder on the PA band; no attribution is proposed for these absorbing groups, which cannot be identified as crotonized aldehydes.

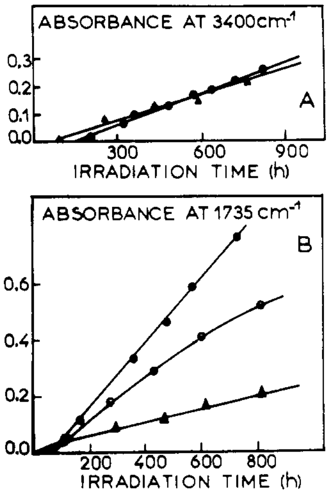


Figure 3. (A) Variations in the absorbance at 3400 cm^{-1} during photooxidation of PA 12 in polychromatic light λ > 340 nm at 45 °C in the presence of water (▲) or under "dry" conditions (●). (B) Variations in the absorbance at 1735 cm^{-1} throughout photooxidation of PA 12 in polychromatic light λ > 340 nm at 45 °C in the presence of water (◒), PA 12 in "dry" conditions (●), and PA 11 in the presence of water (▲).

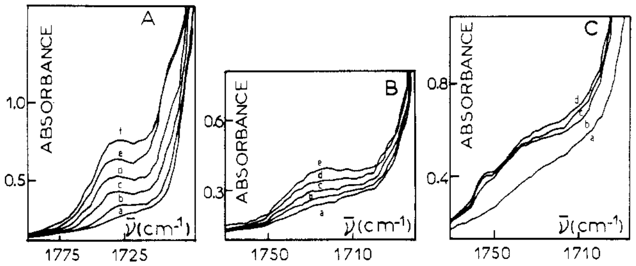


Figure 4. Infrared spectra of a 40-μm PA film at various stages of photooxidation in polychromatic light of λ > 340 nm and a sample temperature of 45 °C. (A) PA 12 irradiation time: (a) 0 h; (b) 152 h; (c) 260 h; (d) 420 h; (e) 530 h; (f) 801 h. (B) PA 11 irradiation time: (a) 0 h; (b) 96 h; (c) 270 h; (d) 430 h; (e) 610 h. (C) PA 6 irradiation time: (a) 0 h; (b) 96 h; (c) 200 h; (d) 320 h.

Similar phenomena were observed in PA 6 and PA 11 exposed under the same conditions. The incident light is essentially absorbed in chromophoric defects and impurities that cannot be effectively controlled. However, it must be pointed out that the formation of *N*-1-hydroxy and imide groups occurred with the same rate throughout the course of the photoinduced oxidation of the three polyamides studied (see Figure 2).

Oxidation of PA 6, PA 11, and PA 12 Photoinduced at λ > 340 nm in the Presence of Water. Films of PA 6, PA 11, and PA 12 (40-μm thickness) were exposed while immersed in well-oxygenated water, the temperature of which was kept constant at 45 °C. In the SEPAP 12.24 setup, wavelengths shorter than 340 nm were filtered off.

In PA 12, it was observed that the rate of formation of *N*-1-hydroxy groups, measured as the rate of increase of the absorbance at 3400 cm^{-1} in the photooxidized samples, was the same under "dry" and immersed conditions. The initial rate of formation of imide groups, measured as the initial rate of increase of the absorbance at 1735 cm^{-1}, was not modified by the presence of water (Figure 3). The photoinduced oxidation into *N*-1-hydroxy and imide groups is not significantly affected by water.

It was anticipated, however, that the imide groups formed in the photooxidation would be more hydrolyzed into acidic groups in the immersed film than under dry conditions. As shown in Figure 3, the hydrolyzed fraction of imides was an increasing function of exposure time to radiation, oxygen, and water. Nevertheless, more than 60% of the imide formed remained unhydrolyzed in an 800-h experiment.

Table I
Variations in the Hydroperoxide ROOH Concentrations during the Photooxidation (Irradiation Time *t*) of PA 6, PA 11, and PA 12

Polyamide PA 6

t, h	22	38	56	94	114	122	139	162	195	210
(ROOH), mmol·kg^{-1}	0	2.5	5.4	7.7	9.5	10.8	11.2	10.1	13.0	10.2

Polyamide PA 11

t, h	22	50	73	120	165	195	210
(ROOH), mmol·kg^{-1}	9.0	14.1	17.9	19.5	19.8	20.9	20.2

Polyamide PA 12

t, h	7	16	24	30	45	58	69	77	106	120	180
(ROOH), mmol·kg^{-1}	3.3	7.9	9.4	14.5	18.5	25.6	27.9	30.8	46.6	42.4	44.2

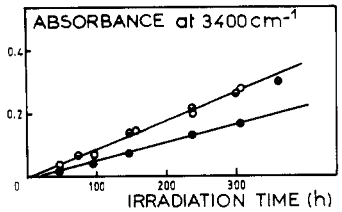


Figure 5. Variations in residual absorbance at 3400 cm^{-1} of a 40-μm PA film prephotooxidized at various stages in polychromatic light (λ > 300 nm) at 60 °C and submitted to 30-min thermolysis at 120 °C. (◒) PA 12; (●) PA 11; (○) PA 6.

In Figure 4, the IR spectra of photooxidized samples of PA 12, PA 11, and PA 6 can be compared in the range of the carbonyl stretching vibration. PA 11 behaved like PA 12, the rate of the photooxidation into imides being somewhat lower in PA 11. In PA 6, the absorption at 1735 cm^{-1} of the imide groups very soon reached stationary intensity. It will be shown that PA 6 imides are very easily hydrolyzed into acids and amides in immersed samples. The growth of the acid absorption bands is not very apparent on the spectra of PA 6 films; these acid groups can indeed be neutralized in the immersed samples.

The rate of formation of *N*-1-hydroxy groups was independent of the PA matrix under dry conditions under an excitation at long wavelengths (λ > 340 nm). In the presence of water, differences appeared: in PA 12, similar concentrations of *N*-1-hydroxy groups were formed in the presence or in the absence of water. However, in the photooxidation of PA 11 and PA 6 films, no *N*-1-hydroxy groups could be detected. This experimental results can only be explained by the thermal decomposition at 45 °C of *N*-1-hydroxy groups in PA 6 and PA 11. As will be pointed out, this decomposition is rather slow at 45 °C, it can however proceed in the long-exposure time.

Photooxidation of PA 6, PA 11, and PA 12 at λ > 300 nm under "Dry" Conditions. As pointed out in the Introduction, photooxidation at λ > 300 nm is induced by direct excitation of the amide chromophores and of defects and impurities. Photochemistry observed at 254 nm and at λ > 340 nm is indeed implicated.

Films of PA 6, PA 11, and PA 12 (40-μm thickness) were irradiated in a conventional Sairem SEPAP 12.24 unit; the temperature of the samples was kept at 60 ± 1 °C. The incident light contains no wavelengths shorter than 300 nm.

The formation of the amine groups has been measured from the residual absorbance at 3400 cm^{-1} of the irradiated sample, after a 30-min thermal treatment at 120 °C. Figure 5 shows the variations in this residual absorbance during the photooxidation of PA 6, PA 11, and PA 12 films. It will be recalled that amine groups are specifically formed through a direct photoscission. The rate of the primary photodissociation of the amide groups is 1.6 times higher in PA 6 and PA 12 than in PA 11.

Table II
Variations in ROOH Concentrations (mmol•kg^{-1}) during Vacuum Photolysis at 45 °C of PA Films Prephotooxidized

	t, h					
film	0	8	15	23	35	42
PA 6	11.5	5.2	1.7	2.0	0	0
PA 11	20	15.6	10.3	8.5	8.5	3.1
PA 12	44	26	20.9	14.2	16.0	12.7

Table III
Variations in ROOH Concentrations (mmol•kg^{-1}) during Thermal Treatment, under Vacuum, at 60 °C of PA Films

	t, h				
film	0	5	24	46	70
PA 6	11	0	0	0	0
PA 11	20	9.8	3.1	2.4	1.1
PA 12	44	20.9	5.0	1.1	0

Formation and Decomposition of Hydroperoxides. With chemical titration at room temperature in hexafluoro-2-propanol solution, the concentrations of hydroperoxidic groups were measured at various irradiation times.

Accuracy and reproductibility of the chemical titration were fairly good. Considering the order of magnitude of the concentrations measured absolute errors were estimated to be 2 mmol·kg^{-1}. From the values reported in Table I, it appears that hydroperoxide rapidly reached a stationary concentration $(ROOH)_\infty$(irradiation time around 120 h) that was dependent on the nature of the matrix; $(ROOH)_\infty$ was found respectively equal to 11 ± 2, 20 ± 2, and 44 ± 2 mmol·kg^{-1} in PA 6, PA 11, and PA 12.

The photochemical and thermal stabilities of ROOH in the various matrices have been examined as follows:

(i) Film samples were photooxidized at λ > 300 nm and 60 °C until $(ROOH)_\infty$ was obtained (around 120 h). Then, the various films were irradiated under vacuum at λ > 300 nm and at 45 °C (to limit the thermal decomposition). In Table II, the results of the chemical titration of ROOH after various irradiation times (within 42 h) are reported. Apparent first-order kinetics were observed. The higher photolability of PA 6 hydroperoxides at 254 nm has been pointed out in a later part of the same series.[11]

(ii) Samples prephotooxidized at the same extent as above were maintained under vacuum at 60 °C. As shown in Table III, the thermal stabilities of PA 11 and PA 12 hydroperoxides were found to be very similar. PA 6 hydroperoxides were more unstable. These results account for the lower stationary concentrations of ROOH found in PA 6 and show that the main disappearance route for ROOH in the irradiated PA 6 films is essentially the thermal decomposition. In PA 11 and PA 12, hydroperoxides decompose photochemically and thermally.

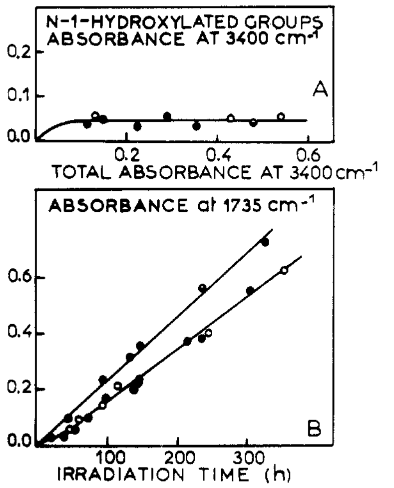


Figure 6. (A) Variations in the absorbance at 3400 cm^{-1} of *N*-1-hydroxylated groups as a function of the total absorbance at 3400 cm^{-1} during the photooxidation of a 40-μm PA film with polychromatic light $\lambda > 300$ nm and a sample temperature of 60 °C: (◒) PA 12; (●) PA 11; (○) PA 6. (B) Variations in the absorbance at 1735 cm^{-1} during the photooxidation of a 40-μm film in polychromatic light $\lambda > 300$ nm and a sample temperature of 60 °C.

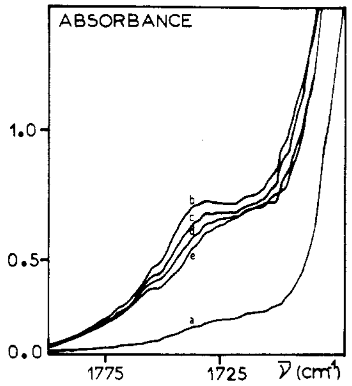


Figure 7. Infrared spectra of a 40-μm PA 12 film prephotooxidized in polychromatic light $\lambda > 300$ nm at 60 °C and submitted to hydrolysis at 100 °C during (b) 0 h; (c) 0.5 h; (d) 1.4 h; (e) 3.7 h. (a) Nonexposed sample.

The ability of ROOH to induce, by decomposition, new oxidative propagation processes in the matrices has been studied with the following procedure: 40-μm films of PA 6, PA 11, and PA 12 were photooxidized for 120 h at 60 °C and $\lambda > 300$ nm. In each film, the stationary concentration in ROOH was observed, and, as shown in Figure 6, the imide concentration was still increasing linearly with irradiation time. Then the films were exposed to the same polychromatic light in borosilicate reactors, either under vacuum or in the presence of air. The exposure time was 25 h, i.e., long enough to observe an important decomposition of ROOH in the vacuum photolysis (checked by chemical titration). The rate of formation of imides, which was derived from the variations in absorbance at 1735 cm^{-1}, was exactly equal in the film photolyzed under vacuum and in the film for which the photooxidation was resumed during 25 h. This meant that, in oxidative conditions, ROOH had no inductive effects since imides were only formed in the photolysis of ROOH.

Formation and Decomposition of N-1-Hydroxy Groups. The contribution of *N*-1-hydroxy groups to the IR absorption at 3400 cm^{-1} was measured after thermal treatment at 120 °C of the photooxidized samples.[14] In Figure 6, it appeares that the concentrations of these groups rapidly reached a stationary value, which was not dependent on the matrix considered. The stationary values were far lower than those observed in the same films irradiated at 254 nm and room temperature (30 °C).[11]

If samples prephotooxidized at 254 nm and 30 °C were afterwards photolyzed under vacuum at $\lambda > 300$ nm and 45 °C, the concentration of *N*-1-hydroxylated groups did not decrease significantly over a period of 200 h. If samples prephotooxidized at 254 nm and 30 °C are heated at 60 °C in the dark, the *N*-1-hydroxy groups disappear completely in 60 h. The main reason for the low stationary value observed in photooxidation at $\lambda > 300$ nm and 60 °C is therefore the thermal decomposition of these intermediate products. In photooxidation at λ 254 nm and 30 °C, the stationary value observed is controlled by the photooxidation at short wavelengths of *N*-1-hydroxy groups.

Formation and Decomposition of Imide Groups. The variations in absorbance at 1735 cm^{-1}, a main absorption band of imide groups, throughout the course of photooxidation are shown on Figure 6. In PA 6 and PA 11, the rate of formation of imide is 80% of the rate in PA 12. No variations in this rate of appearance was observed over 300 h of irradiation.

The difference between PA 11 and PA 12 is easily accounted for by differences in the rate of hydroperoxidation, which is lower in PA 11 than in PA 12; it will be recalled that hydroperoxides decompose thermally and photochemically with the same rates in both matrices.

Differences between PA 6 and PA 12 is accounted for neither by the rate of hydroperoxidation (equal in both matrices) nor by the rate of decomposition of ROOH (higher in PA 6; accordingly the rate of formation of imide would be higher too). Variations in imide stabilities can only be anticipated.

Thermal treatment at 60 °C or vacuum photolysis at $\lambda > 300$ nm and 45 °C did not cause the decomposition of imide groups over several hundred hours. Differences in imide stabilities were observed as photooxidized samples were immersed in water at 100 or 60 °C. Imides in PA 6 were hydrolyzed faster than imides in PA 11 and PA 12 at both temperatures, and differences in reactivity were easily observed at 60 °C. As an example, the IR spectra of a PA 12 sample photooxidized under dry conditions and then submitted to hydrolysis at 100 °C are shown in Figure 7. The intensity of the absorption peaking at 1735 cm^{-1} decreased progressively as the imide groups were converted into acidic groups.

The differences in hydrolytic reactivity of the imide groups accounted for the significant variations in imide concentrations observed throughout photooxidation under dry conditions. In that particular case, a partial hydrolysis was indeed provoked by water which was simultaneously formed in the decomposition of hydroperoxides.

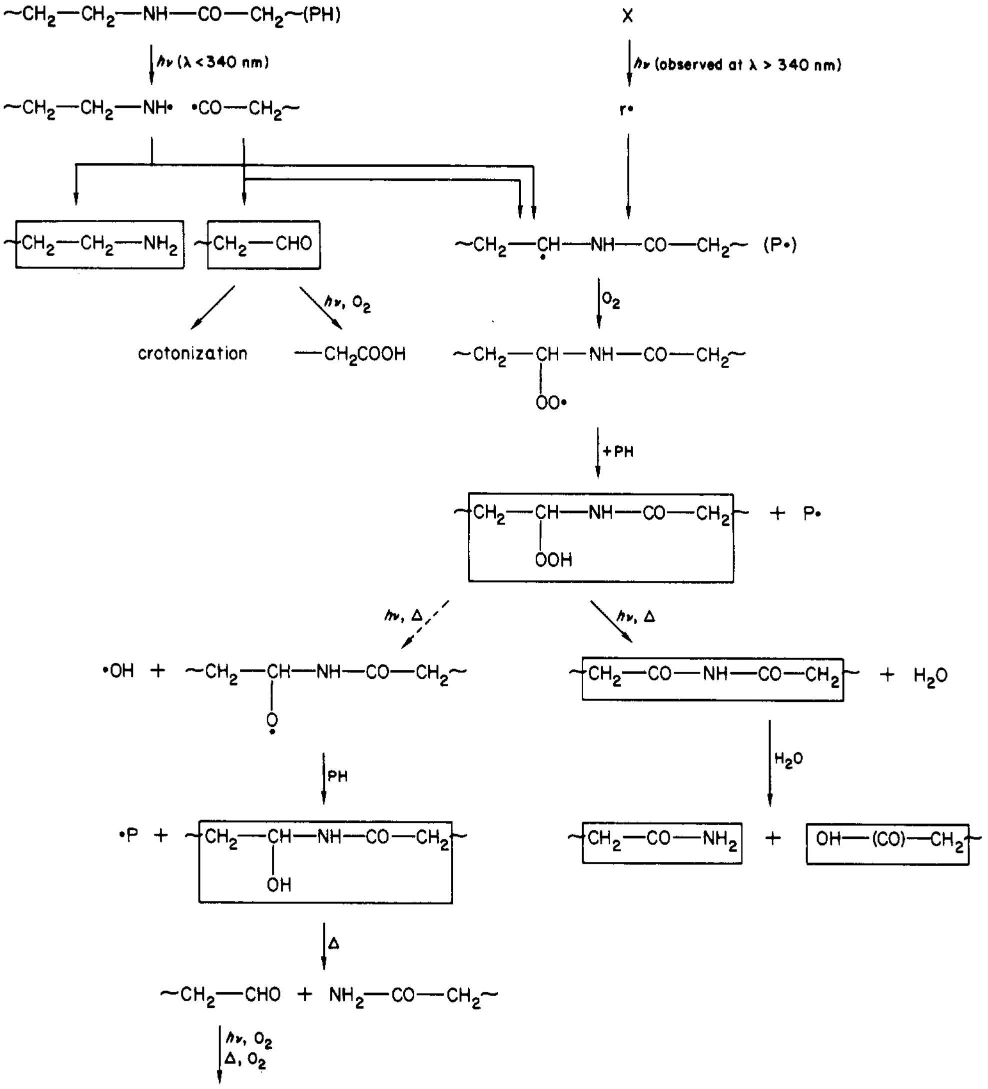
$$\sim\mathrm{(HOO)CHNHCO}\sim \;\rightarrow\; \sim\mathrm{CONHCO}\sim \; + \mathrm{H_2O}$$

$$\sim\mathrm{CONHCO}\sim \; + \mathrm{H_2O} \rightarrow \; \sim\mathrm{CONH_2} + \mathrm{HO(CO)}\sim$$

The photooxidation of a PA 66 film (40-μm thickness) has been studied, the sample being either immersed and submitted to long wavelengths ($\lambda > 340$ nm) or exposed under "dry" conditions at $\lambda > 300$ nm.

Immersed in water and exposed at $\lambda > 340$ nm at 45 °C, PA 66 behaved exactly like PA 6. A significant concentration of amine or *N*-1-hydroxy groups could not be observed. Imide groups were formed that rapidly reached a stationary concentration. The intensity of the 1735 and 1690 cm^{-1} absorption bands was observed to be the same as in PA 6. Acid groups accumulate afterwards in the matrix.

Scheme I



The variations in the IR spectrum of a PA 66 film photooxidized at λ > 300 nm under "dry" conditions are represented in Figure 8a (for comparison, the IR spectra of a PA 6 film photooxidized under the same experimental conditions are presented in Figure 8b). The formation of amine and *N*-1-hydroxy groups is apparent in the range 3500–3350 $\mathrm{cm^{-1}}$; *N*-1-hydroxy groups are unstable as the corresponding groups in PA 6. The buildup of imide groups is observed at 1735 $\mathrm{cm^{-1}}$ (and 1690 $\mathrm{cm^{-1}}$); these groups are partially hydrolyzed in the matrix into acid groups. PA 66 imide groups present the same hydrolytic reactivity as PA 6 imides.

Discussion and Conclusions

It is known that the photooxidative phenomena, which are the most relevant to natural photoaging of the solid material, are those observed in the solid state. But it is also necessary to limit the extent of oxidation to the level just required for a significant degradation of the physical properties of the polymer. It is recommended that one study the photooxidation mechanism at a very low degree of oxidation. The concentration of the intermediate photoproducts must be kept very low. These restrictions make the experimental study of the properties of the intermediate products rather difficult.

The photooxidation mechanism previously proposed for PA 11 and presented in Scheme I can be extended to PA 6 and PA 12.

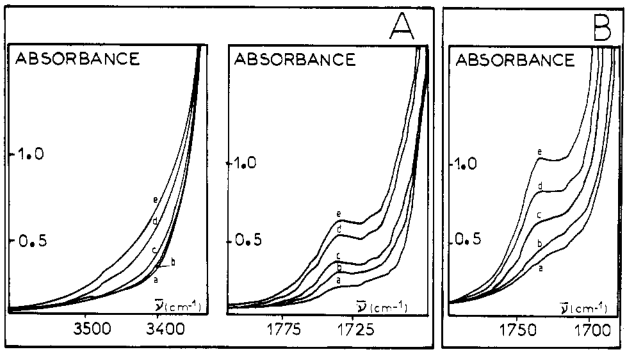


Figure 8. (A) Infrared spectra of a 40-μm PA 66 film at various stages of photooxidation in polychromatic light λ > 300 nm and a sample temperature of 60 °C. Irradiation time: (a) 0 h; (b) 48 h; (c) 96 h; (d) 209 h; (e) 297 h. (B) Infrared spectra of a 40-μm PA 6 film at various stages of photooxidation under the same conditions. Irradiation time: (a) 0 h; (b) 66 h; (c) 142 h; (d) 233 h; (e) 300 h.

This scheme prompts the following comments:

(i) Photoinitiation through direct excitation of the –NHCO– chromophore occurs up to 340 nm. At λ > 340 nm and 45 °C, chromophore defects, and impurities initiate hydroperoxidation, and no difference was observed between PA 6, PA 11, and PA 12. A recent interpretation of the initiation in PA 66 photooxidized in the Microscal unit is consistent with this conclusion.[12] (The incident light in the Microscal unit contains only wavelengths longer than 365 ± 25 nm.)

(ii) At $\lambda > 300$ nm, a dual initiation mechanism is involved, implying excitation of defects and impurities and direct excitation of –NHCO–chromophores. From the rate of formation of amine groups, it is derived that the direct photoscission is 1.6 faster in PA 6 and PA 12 than in PA 11.

(iii) The primary hydroperoxidation in PA 6, PA 11, and PA 12 differs notably, particularly in the stationary state. Differences between PA 11 and PA 12 are accounted for by differences in photoinitiation essentially due to direct excitation of the amide groups. Differences between PA 6 and PA 12 can only be explained by differences in ROOH stabilities. It was observed that the hydroperoxide groups formed in PA 6 were more thermally (and photochemically) unstable than hydroperoxides formed in PA 12. (In both cases, the main decomposition route was thermolysis.)

(iv) Thermal and photochemical decomposition of ROOH occurs through the homolysis of the peroxidic bond

$$\sim(\mathrm{HOO})\mathrm{CHNHCO}\sim \;\rightarrow\; \sim\dot{\mathrm{O}}\mathrm{CHNHCO}\sim \; + \mathrm{OH}\cdot \quad (1)$$

However, it has been shown that ROOH did not initiate any new oxidative propagation process, i.e., has no photoinductive effect. This is consistent with a preferential recombination of the radicals formed (especially the very reactive OH· radicals), leading to imide groups.

$$\sim\dot{\mathrm{O}}\mathrm{CHNHCO}\sim \; + \mathrm{OH}\cdot \rightarrow \mathrm{H_2O} + \; \sim\mathrm{CONHCO}\sim \quad (2)$$

The secondary formation of *N*-1-hydroxy groups through the process

$$\sim\dot{\mathrm{O}}\mathrm{CHNHCO}\sim \; + \; \sim\mathrm{CH_2NHCO}\sim \;\rightarrow\; \sim(\mathrm{HO})\mathrm{CHNHCO}\sim \; + \; \mathrm{CHNHCO}\sim$$

must therefore be of minor importance. The *N*-1-hydroxy groups were shown to be thermally unstable above 60 °C.

These intermediate photoproducts are maintained at a low stationary concentration in the matrices studied. No firm conclusions can be derived from the fact that they are observed at the same absorbance in the various PA studied.

(v) The main route of disappearance of the imide groups in the photooxidized matrices, even under "dry" conditions, involves hydrolysis with water that is formed in situ in close vicinity of the imide groups (process 2). It has been shown that imides formed in PA 6 matrices were hydrolyzed at 60 °C faster than the corresponding imides in PA 11 and PA 12.

(vi) The eventual role of water in natural photoaging is limited to the hydrolysis of imide groups formed. This role can only be observed under oxidative conditions.

As a general conclusion, it appears that although the aliphatic polyamides studied behave very similarly, intermediate photoproducts such as hydroperoxides and imides were more unstable in PA 6 than in PA 11 and PA 12.

Experimental Methods

The PA 6, PA 11, and PA 12 films of the Rilsan type were processed and supplied by Atochem, Serquigny, France.

PA 6 (Organamide R) was made by the hydrolytic polycondensation of ϵ-caprolactam (hexahydro-2*H*-azepin-2-one).

PA 11 (Rilsan Type B) was made by the hydrolytic polycondensation of 11-aminoundecanoic acid using phosphoric acid as a chain regulator.

PA 12 (Rilsan Type A) was made by the 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 chilled roll).

The experimental results reported in the present study were carried out with 40-μm films. The experimental setup Sairem SEPAP 12.24 (from Service d'Etudes du Photovieillissement Accéléré des Polymères) has been described in the previous papers of the same 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 $\mathrm{Fe^{2+}}$ and the complexation of $\mathrm{Fe^{3+}}$ by $\mathrm{SCN^-}$ anions. As stressed previously, this method gives correct results only in good solvents for polyamides such as hexafluoro-2-propanol. Photooxidized PA (5 mg) was dissolved in 1 mL of hexafluoro-2-propanol. After the complete dissolution of the film, 1 mL of a 50/50 mixture of a methanolic solution of $\mathrm{(NH_4)_2SCN}$ (2×10^{-1} mol·L^{-1}) and a methanolic solution of Mohr salt (10^{-2} mol·L^{-1}) and $\mathrm{H_2SO_4}$ (4.5×10^{-2} mol·L^{-1}) was added. The solution volume was extended to 25 mL through the addition of benzene (PA 11 and PA 12) or methanol (PA 6). The concentration of the complexed ion $\mathrm{(Fe(SCN)_6)^{3-}}$ 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

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

Registry No. PA 6, 25038-54-4; PA 11, 25035-04-5; PA 12, 24937-16-4; poly(11-aminoundecanoic acid), 25587-80-8; poly(azacyclotridecan-2-one), 25038-74-8.

References and Notes

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(13) Acidic groups do not absorb significantly at 3400 cm^{-1} at the low degree of oxidation considered in our study.
(14) It is recalled that *N*-1-hydroxy groups decompose at 120 °C as opposed to stable amine groups.