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Photoageing of Aliphatic Polyamides

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The primary photophysical and photochemical processes in the amide group of polyamides and certain individual amides are examined. The mechanisms of the photolysis and photochemical oxidation of polyamides are analysed as a function of irradiation conditions. The problems of predicting the light stability of polyamides as well as the mechanisms of the stabilisation of polyamides with respect to the action of light and the sensitisation of their photochemical ageing are discussed. The bibliography includes 224 references.

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I. INTRODUCTION

When used under natural conditions, polyamides (PA) decompose under the influence of sunlight over periods ranging from half a year to one year[1]. Since the annual manufacture of polyamides runs into millions of tons, the problem of their photochemical ageing is of practical importance. It includes a wide range of questions concerning the nature of the primary and secondary photochemical process responsible for the photochemical ageing, the mechanisms of chemical and structural changes in polyamides, their relation with the changes in the characteristics of their mechanical strength, and the mechanisms of the stabilisation of polyamides with respect to the action of light and the sensitisation of their photochemical ageing.

In the present review an attempt is made at a systematic account of the experimental data on the above questions. Reviews already exist on individual aspects of the problem of the ageing of polyamides[2-7].

II. PRIMARY PHOTOPROCESSES IN ALIPHATIC POLYAMIDES AND MODEL COMPOUNDS

1. Primary Photophysical Processes

In contrast to polymers (for example, polyolefins), in which photoageing can be induced solely by the absorption of light by the chromophoric groups of impurities or oxidation products[8] and in contrast to aromatic polyamides which exhibit an intense intrinsic ultraviolet absorption[9], aliphatic polyamides absorb extremely weakly[10-13] in the region where the absorption spectrum of the chromophoric amide group of the polyamide overlaps the spectrum of sunlight at the Earth's surface (Fig.1). In the study of light-induced transformations of polyamides, one must therefore take into account both the absorption of light by impurities and the intrinsic absorption of amides.

The amide group $-CO-N\langle$ in different compounds in liquid and solid solutions has two absorption bands corresponding to the $^1\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ and $^1\Gamma_{n\pi} \leftarrow {}^1\Gamma_1$ transitions[14-17]. The short-wavelength absorption band associated with the $^1\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ transition can be assigned to charge transfer from the nitrogen atom to the carbonyl group[18-20]. The introduction of electron-donating substituents at the nitrogen atom shifts the $\pi\pi^*$-absorption maximum towards longer wavelengths, while the introduction of electron-donating substituents at the carbon atom of the carbonyl group causes a hypsochromic shift. Thus, the energies of the $^1\Gamma_{\pi\pi^*}$ state for *N*-dimethylformamide $HCON(CH_3)_2$, formamide $HCONH_2$, and acetamide CH_3CONH_2 are 6.22, 7.16, and 7.48 eV respectively[20]. With increase of solvent polarity, the $\pi\pi^*$ absorption shifts towards longer wavelengths[21]. The polyamides PA-3, PA-4, PA-6, PA-6,6, PA-6,10† and polyglycine have a $\pi\pi^*$ absorption maximum at a wavelength $\lambda_{max} = 190$ nm in the solid state[22,23], while a solution of the copolymer PA-548 in methanol has an absorption maximum at 205 nm.

The long-wavelength absorption of the amide group ($^1L_{n\pi^*} \rightarrow {}^1\Gamma_1$ transition) has small extinction coefficients $\varepsilon < 100$ litre mol^{-1} cm^{-1}.[17] According to some estimates[24], $\varepsilon \cong 0.02$ litre mol^{-1} cm^{-1} at ~300 nm for specially pure amides. The $n\pi^*$ absorption maximum is in the range 210–240 nm; thus $\lambda_{max} =$ 208 nm for the $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ transition of acetamide in water. A decrease of solvent polarity increases λ_{max} (Fig.1). The $n\pi^*$ absorption of the amide group in solid polyamides which are characterised by a low dielectric constant, should be similar to the absorption of solutions of *N*-alkylamides in hydrocarbons. Polyamides usually exhibit a more intense absorption in the long-wavelength region than in model compounds, which is evidently due to the absorption by impurities.

It has been shown that the isolated amide group does not fluoresce on excitation with light at wavelengths in the range $250 \leq \lambda \leq 300$ nm [24-26] in contrast to the amide group conjugated with an aromatic ring[27].

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† The numerals indicate the numbers of carbon atoms between the NH groups in the repeating elements of the chain in the case of the homopolymer. For example, PA-6,6 and PA-6 are polyhexamethyleneadipamide $-(CH_2)_6NHCO(CH_2)_4$. .$CONH-$~ and polycaproamide ~$-(CH_2)_5CONH-$~. The first of the two numerals separated by a comma characterises the amine component of the repeating unit, while the second numeral characterises the acid component. In naming mixed polyamides the numerals separated by an oblique stroke characterise components comprising the polymer. For example, PA-6,6/6,10/6 is the copolymer of ε-caprolactam ($\overline{(CH_2)_5CONH}$, the adipate of hexamethylenediamine $HOOC(CH_2)_4CONH(CH_2)_6$. .NH_2, and the sebacate of hexamethylenediamine $HOOC(CH_2)_8$. .$CONH(CH_2)_6NH_2$, known as PA-548.

The possibility of the phosphorescence of compounds with amide groups is controversial[24-26]. Larson et al.[25] investigated a large series of aliphatic amides and showed that the phosphorescence of these compounds (if it is observed after careful purification of the compounds) is very weak and is characterised by low quantum yields ($\Phi_p < 10^{-4}$–10^{-3}) and long lifetimes ($\tau_p > 0.1$ s); the phosphorescence spectrum depends on the excitation wavelength, which indicates the possibility of the phosphorescence of single crystals or of defects in vitrified solutions (the authors[25] used mainly EPA—mixtures of ether, pentane, and alcohol—as solvents). In another study[28] the phosphorescence of amides was not observed.

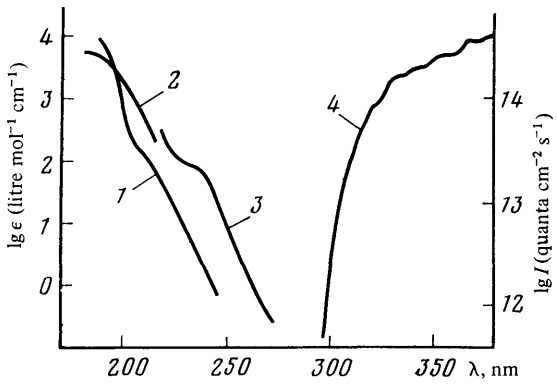


Figure 1. Ultraviolet absorption spectra[10-13] of acetamide solutions in water (curve *1*), of *N*-methylacetamide in cyclohexane (curve *2*), and of ε-caprolactam in n-heptane (curve *3*); curve *4* represents the spectrum of sunlight at the Earth's surface measured at 3 nm wavelength intervals (*I* represents the light intensity and ε is the extinction coefficient).

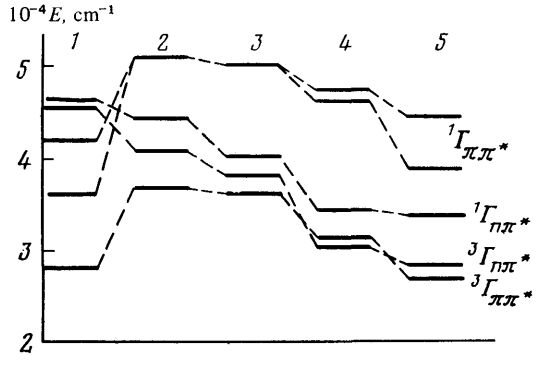


Figure 2. The energy levels (*E*) of the first electronically excited states of amides: 1) acetanilide ($\tau_p \approx 3$ s); 2) acetamide ($\tau_p > 0.1$ s, $\Phi_p < 10^{-4}$); 3) tetramethyloxamide ($\tau_p >$ 0.1 s, $\Phi_p < 10^{-4}$); 4) dimethyloxamide ($\tau_p = 0.1$ s, $10^{-4} \leq \Phi_p < 10^{-3}$); 5) 1-isopropyl-5,5-dimethyl 2,3-dioxopiperazine ($\tau_p = 0.1$ s, $10^{-4} \leq \Phi_p < 10^{-3}$).

It has been concluded[24] that the amide group is responsible for the observed weak phosphorescence of vitrified alcoholic solutions of α,ω-polymethylenebishexaneamides having the general formula $C_5H_{11}CONH(CH_2)_nNHCOC_5H_{11}$, where $n = 3$, 4, 5, 6, 7, 8, or 12. The amides have been synthesised under special conditions in order to avoid contamination; subsequent purification of the substance did not affect the phosphorescence and the phosphorescence spectrum was independent of the excitation wavelength. Depending on the value of *n*, the maximum in the excitation spectra has been observed in the range from 280 to 294 nm, i.e. in the region where the amides hardly absorb. By analogy with the phosphorescence of an isolated –CO–O– group (in carboxylic acids and their salts, for example, in HCOONa), which also has no singlet–singlet absorption in the region corresponding to excitation[29], it has been suggested[24] that there is direct excitation of the amide group to the triplet as a result of the $^3\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ transition. Bellinger and Roberts[24] determined from the excitation and phosphorescence spectra the energy of the lowest triplet state of the amide group: $3.35 \leq E_{T_1} \leq 3.44$ eV.

Table 1. Characteristics of the phosphorescence observed in polyamides and model compounds (77 K).

Compound	Excitation λ, nm	Emission, λ_{max}, nm	$\lambda_{0,0}$, nm	τ_p, s	Refs.
N-Hexylhexanamide	300*	440	360	0.6	26
N,N-Bishexyladipamide	265*	415	360	0.2	26
1,6-Hexamethylenebishexanamide	285*	460	370	0.2	26
1,5-Pentamethylenebishexanamide	295*	440	360	0.4	24
1,3-Trimethylenebishexanamide	294*	443	360	0.6	24
Hexamethylenediamineadipate	280*	430	—	1.0	41
PA-6,6	280	410	—	2.2	41
PA-6,6	290*	410	—	2.0	42
PA-6,6	295*	400	~365	2.0	28
PA-6,6	280*	420	~370	2.1	37
PA-6	280*	435	—	1.4	37
PA-11	270*	445	—	0.9	37
PA-12	270	450	—	1.0	37

*The value of λ at the maximum in the excitation spectrum.

The changes in the ultraviolet absorption spectra and luminescence properties of molecules containing amide groups have been investigated[25,30,31] as a function of the nature of the conjugation of the amide group with another chromophore, particularly with one or two amide groups. As a result, it was possible to estimate approximately the sequence of the energy levels for an isolated amide group (in relation to acetamide) (Fig.2). It was found that the lowest excited state is the triplet $^3\Gamma_{\pi\pi^*}$. The $^3\Gamma_{\pi\pi^*}$ state is characterised by long lifetimes ($\tau_p > 0.01$ s) in relation to emission[32], which makes it possible to explain the low values of Φ_p. The phosphorescence of simple molecules can be observed if the vibrational levels of the $^3\Gamma_{\pi\pi^*}$ and $^3\Gamma_{n\pi^*}$ states are mixed, which leads to a decrease of τ_p (for example, in oxamides—Fig.2).

It has been concluded[22] that the luminescence of aromatic amides is caused by the influence of the aromatic ring, which reduces the probability of radiation-less transitions; the lowest triplet level of acetamide has been estimated[31] as $E_{T_1} = 4.6$ eV. As mentioned above[20], electron-donating substituents lower the energy of the $^1\Gamma_{\pi\pi^*}$ level by ~1 eV. Under conditions where the ST-splitting is retained, one may expect that the $^3\Gamma_{\pi\pi^*}$ level of N-alkylamides (modelling the PA chain) has an energy $E_{T_1} \cong 3.6$ eV, which agrees best with the estimate $E_{T_1} \cong 3.4$ eV.[24,30,33]. It is interesting to note that similar values $E_{T_1} = 3.2$–4.0 eV have been found for the lowest $^3\Gamma_{\pi\pi^*}$ level of the –CO–O– group, which has the same number of electrons as in the –CO–NH– group[30].

Table 1 presents for comparison the parameters of the phosphorescence spectra of polyamides[28,34–44] and model compounds[24,26]. The authors of all the investigations noted that the phosphorescence observed in polyamides can be induced by impurities. It has been suggested[41] that the phosphorescence in PA-6,6 is caused by the polymer oxidation products formed under the polymerisation conditions, because, with increase of the degree of polymerisation, the intensity of the phosphorescence rises and its maximum shifts towards shorter wavelengths with a simultaneous increase of the phosphorescence lifetime. However, on thermal oxidation of PA-6 at 180 °C, a bathochromic shift of the phosphorescence λ_{max} is observed with a simultaneous decrease of the phosphorescence intensity[43].

The change in the characteristics of the phosphorescence on passing from amides to polyamides can be accounted for by the intrinsic phosphorescence of polyamides. It is known[21] that the state of aggregation of a substance has almost no influence on the energy of the triplet level. Similar values of $\lambda_{0,0}$ for amides and polyamides therefore show that the energy of the luminescent state in PA is equal to the energy of the $^3\Gamma_{\pi\pi^*}$ level of the amide group. Polar solvents increase the phosphorescence intensity, because they decrease the degree of association of the aromatic amide molecules[27] or molecules containing the –CO–O– group[29], which reduces the probability of radiationless processes. With decreased probability of radiation less deactivation, the lifetime of the excited state τ_p approaches the limiting lifetime τ_p^0 corresponding to emission in the absence of radiation less deactivation. In the amorphous regions of the polyamide specimen the association of the amide groups in the macromolecular chain is less effective than in solutions of model amides. This is the reason for the appearance of non-associated amide groups, for which the lifetime of the excited state τ_p is close to τ_p^0. Indeed, in model compounds $\tau_p = 0.2$–0.6 s whereas in polyamides $\tau_p \cong 2$ s; the increase of phosphorescence intensity on passing from amides to polyamides is associated with this factor. Thus the available experimental data do not rule out the possibility of both an intrinsic phosphorescence of polyamides and the possibility of the "superposition" on the latter of the phosphorescence due to impurities and oxidation products.

Polyamides frequently exhibit a fluorescence[37,39,41,45], which is characterised by values of λ_{max} of 365 and 445 nm in excitation and fluorescence spectra respectively. Evidently, the fluorescence of polyamides is due to impurities. The most probable impurities can be the products of the oxidation of polyamides and the initial monomers[39].

2. Primary Photochemical Processes

In the early studies on the photochemistry of polyamides and model compounds a wide variety of reactions was proposed as the possible primary photochemical processes in amides:

$$\mathrm{R(CH_2)_3CONHCH_2CH_2R'} \xrightarrow{h\nu} \begin{cases} \rightarrow \mathrm{R(CH_2)_3\dot{C}O + \dot{N}HCH_2CH_2R'}, & (1) \\ \rightarrow \mathrm{R(CH_2)_3CONH\dot{C}HCH_2R' + \dot{H}}, & (2) \\ \rightarrow \mathrm{R(CH_2)_3C\dot{O}NH + \dot{C}H_2CH_2R'}, & (3) \\ \rightarrow \mathrm{R(CH_2)_3NHCH_2CH_2R' + CO}, & (4) \\ \rightarrow \mathrm{RCH{=}CH_2 + CH_3CONHCH_2CH_2R'}, & (5) \\ \rightarrow \mathrm{RCH_2CH{=}CH_2 + HCONHCH_2CH_2R'}, & (6) \\ \rightarrow \mathrm{R(CH_2)_3CONH_2 + CH_2{=}CHR'}, & (7) \\ \xrightarrow{\text{amide}} \mathrm{R(CH_2)_3\dot{C}(OH)NH(CH_2)_2R' + R(CH_2)_3CONH\dot{C}HCH_2R'} & (8) \end{cases}$$

($\dot{R}$ and $\dot{R}'$ are alkyl radicals or terminal alkyl macroradicals).

Reactions (5)–(8) have been suggested[46,47] by analogy with the Norrish type II and III reactions, i.e. reactions involving intramolecular and intermolecular abstraction of a hydrogen atom by the oxygen atom of the carbonyl group in ketones in an electronically excited state[10]. The data concerning the nature of the excited state of the amide group suggest that reactions (5)–(8) are unlikely owing to the differences in the nature of the excitation of the carbonyl and amide groups. Thus in formaldehyde the $n\pi^*$ excitation is accompanied by the transfer of a charge of 0.64e from the oxygen atom to the carbon atom[32]. The decrease of electron density at the oxygen atom promotes the abstraction of a hydrogen atom. The $\pi\pi^*$ excitation in formamide is accompanied by the transfer of a charge of 0.7e from the nitrogen atom to the carbon atom, while the electron density at the oxygen atom remains almost unchanged[17]. The oxygen atom of the amide group in the $^3\Gamma_{\pi\pi^*}$ state does not therefore exhibit an enhanced reactivity in respect of abstraction reactions. (There is evidence[48] that on $n\pi^*$ excitation, the main contribution to absorption comes from the transfer of a non-bonding electron from an atomic orbital of nitrogen to the π orbital of the amide.)

It has been shown experimentally[49] that Norrish type II and III processes do not occur in the photolysis of N-alkylpyrrolidinones and N-alkylamides[50]. The products of reactions (5)–(7) have been detected in extremely small amounts on irradiation of N-alkylamides[46], PA-6,6, and PA-6.[51]

Investigators of the photochemical oxidation of amides[11] and polyamides[3,51] put forward reactions (2) and (3) to account for the formation of products with terminal amide groups and hydrogen. Estimates have shown[52] that the quantum yield of hydrogen formed via reaction (2) is extremely low ($\Phi_2 < 7 \times 10^{-5}$). The large yields of hydrogen, usually observed in the photolysis of amides and polyamides, have been explained by the photolysis of the products, since, with increase of the degree of photochemical reaction, the rate of accumulation of H_2 also increases significantly[52,53]. It is difficult to determine the probability of reaction (3), since unsubstituted amides have not been detected in the photolysis of N-alkylamides[53] and, as will be shown below, the main pathway leading to the formation of unsubstituted amides in photochemical oxidation involves oxidation processes.

Since the excitation of the amide group entails a partial separation of electrons forming the amide bond, presumably the most probable reaction of the amide group in an electronically excited state is dissociation of the amide linkage [reaction (1)]. Reaction (4) can be regarded as a result of reaction (1), which is followed by the elimination of CO from the acyl group and recombination of the amino and alkyl radicals in the cage.

In aromatic amides the photodissociation of the amide bond is the main primary process, which proceeds with a high quantum yield ($\Phi_1 = 0.25$).[54,55] The reverse reactions of the

acyl and amine radicals reduce the quantum yield of the photochemical reaction to 0.13 when acetanilide is irradiated in cyclohexane. High values of Φ_1 have also been observed for aliphatic amides: when *N*-alkylpyrrolidinones are irradiated in alcoholic solutions, $\Phi_1 = 0.02-0.1$ depending on the substituent[49,50], while on photolysis of *N*,*N*-dialkylamides in cyclohexane and dioxan, $\Phi_1 = 0.1-0.15$.[56] In the photolysis of solid PA-6 [7] the quantum yield of the radicals which have emerged from the cage as a result of reaction (1) is 0.01.

The primary photochemical process in both aromatic and aliphatic amides is apparently the photodissociation of the peptide bond. This conclusion does not rule out the occurrence of a multiplicity of other reactions which proceed at a significantly lower rate and give rise to a set of a wide variety of secondary products. Thus analysis of the products of the photolysis of polyamides[46,51,57-61] indicates approximately identical probabilities for the dissociation of all the C–C bonds of the polyamide and the possibility of a non-radical decomposition via reaction (5). The evolution of small amounts (less than 1% of the main volatile products—H_2 and CO) of hydrocarbons (ethane, ehtylene, propane, and propene) has also been observed in the photolysis.

The formation of the photochemical oxidation products from polyamides[2,7,62-66] has been explained by the dark reactions of radicals and by secondary photochemical processes.

III. THE FORMATION OF RADICALS IN POLYAMIDES AND IN MODEL COMPOUNDS

The results of studies by Refikov and coworkers[58], who first observed the EPR spectrum of PA-6 irradiated by ultraviolet light, indicate a radical mechanism of the photoageing of polyamides. The EPR spectrum of a single radical $RCONH\dot{C}HR'$, which we shall designate by $\dot{P}_1$, has been observed for γ-irradiated PA-6.[67] However, the EPR spectra observed on ultraviolet irradiation of polyamides are very complex and are poorly resolved, which hinders their interpretation. The situation is complicated by possible photochemical reactions of free radicals[68], which absorb light very strongly. Thus the ultraviolet spectrum of the radical P_1 has two absorption maxima[69,70]—in the regions 245–248 and 350 to 380 nm with extinction coefficients of 7000 and 2000 litre mol^{-1} cm^{-1} respectively[71]. Under the influence of light at the above wavelengths, the radicals $\dot{P}_1$ readily undergo secondary photochemical reactions[72]. The radicals $\dot{P}_1$ are therefore most conveniently observed either in the presence of photoinitiating additives[73-76], which react under the influence of light with $\lambda > 380-400$ nm, or in the absence of light, when polyamides are acted upon by high-energy radiations[72,77-79], or under mechanical degradation[80,81]. Thus the concentration of $\dot{P}_1$ can reach 0.04 mol kg^{-1} on γ-irradiation of PA-6 at 30 °C.[82]

The photochemical reactions of the radicals in PA-6 films with added iron(III) chloride have been investigated[73-76]. The radicals were initiated by reactions (9) and (10) involving the abstraction of a hydrogen atom from the PA-6 molecule (P_1H) by a chlorine atom with formation of either the radical $\dot{P}_1$ or the radical $RCONHCH_2\dot{C}HR'$ ($\dot{P}_2$). Almost all the radicals detected were identified and the sequence of their formation was found:

$$Cl + P_1H \longrightarrow \dot{P}_1 + HCl \quad (9)$$

$$Cl + P_1H \longrightarrow \dot{P}_2 + HCl \quad (10)$$

$$\dot{P}_1 + h\nu \xrightarrow{\lambda \approx 365\ nm} R\dot{C}O + NH{=}CHCH_2R' \quad (11)$$

$$\dot{P}_1 + h\nu \xrightarrow{\lambda \approx 365\ nm} \dot{P}_2 + P_1H \quad (12)$$

$$R\dot{C}O + h\nu \xrightarrow{\lambda > 365\ nm} \dot{R} + CO \quad (13)$$

$$\dot{R} + P_1H \xrightarrow{T \approx 77K} RH + \dot{P}_1 \quad (14)$$

$$\dot{R} + P_1H \xrightarrow{T \approx 77K} RH + \dot{P}_1 \quad (15)$$

$$\dot{P}_2 + P_1H \xrightarrow{T > 150K} P_1H + \dot{P}_2 \quad (16)$$

$$R\dot{C}O + P_1H \xrightarrow{T \approx 273K} RCHO + \dot{P}_1 \quad (17)$$

The concentration of $\dot{P}_1$ is extremely low even under the conditions of sensitised photolysis owing to the important reactions (11) and (12); the accumulation of $\dot{P}_1$ becomes appreciable only on irradiation with light in the region of 313 nm, to which corresponds the minimum absorption. Measurements of the stabilities of the radicals $\dot{R}$, $\dot{P}_2$, $R\dot{C}O$, and $\dot{P}_1$ showed that they begin to disappear at appreciable rates at 117, 150, 273, and 300 K respectively. Thus the radical $\dot{P}_1$ shows the greatest thermal stability among the PA radicals identified; with increase of temperature, a quantitative conversion of various radicals into $\dot{P}_1$ via reactions (14)–(17) has been observed[73-76].

The EPR spectra of the radicals $R\dot{C}O$ or $\dot{R}$ have been observed in the non-sensitised photolysis of polyamides, which indicates the occurrence of reaction (1), involving the photolysis of the amide linkage, but the possibility of secondary photolysis hinders the interpretation of the EPR spectra[58,77,78,83-85].

In the presence of oxygen, the radicals $\dot{P}_1$, which accumulated during the mechanical degradation of polyamides are converted into the corresponding peroxy-radicals $P_1\dot{O}_2$.[80] An analogous reaction has not been observed in γ-irradiated PA-6 fibres following exposure to air[78]. The exposure of γ-irradiated thin (2–5 μm) PA-6 films to a O_2 atmosphere at room temperature leads to the rapid disappearance of $\dot{P}_1$, although peroxy-radicals are not then detected[86]. It has been suggested that the diffusion time of O_2 in the polyamide specimen is longer than the lifetime of the peroxy-radicals, so that the $P_1\dot{O}_2$ species are not formed in appreciable concentrations. On mechanical degradation, the radicals are formed on the surface of the specimen where diffusion-dependent limitations are insignificant.

Ultaviolet irradiation of PA-6 in air at room temperature led to the detection[87] of radicals of two types: $\dot{P}_1$ and the radical responsible for an unidentified singlet. Since films 80 μm were used for irradiation, one cannot rule out the possibility of the presence of $\dot{P}_1$ owing to the diffusion-dependent limitations to the photochemical oxidation.

The EPR spectra of the radicals in polyamides have also been discussed in other studies[88-90].

IV. THE MECHANISM OF THE PHOTOAGEING OF POLYAMIDES

1. The Mechanism of the Photolysis of Polyamides

When polyamides are irradiated with ultraviolet light at room temperature in the absence of O_2, the following reactions can take place[7]:

$$RCONHCH_2R' \xrightarrow{h\nu} \dot{R} + CO \quad (\Phi_{18} = 5\cdot10^{-4}) \quad (18)$$

$$RCONHCH_2R' \xrightarrow{h\nu} R\dot{C}O + \dot{N}HCH_2R' \quad (\Phi_1 = 5\cdot10^{-3}) \quad (1)$$

$$RCONHCH_2R' \xrightarrow{h\nu} \dot{P}_1 + \dot{H} \quad (\Phi_2 \leqslant 7\cdot10^{-6}) \quad (2)$$

$$\dot{R} + P_1H \rightarrow \dot{P}_1 + RH \quad (14)$$

$$R\dot{C}O + P_1H \rightarrow \dot{P}_1 + RCHO \quad (17)$$

$$R'CH_2\dot{N}H + P_1H \rightarrow \dot{P}_1 + R'CH_2NH_2 \quad (19)$$

$$\dot{H} + P_1H \rightarrow \dot{P}_1 + H_2 \quad (20)$$

$$\dot{P}_1 \xrightarrow{h\nu} \left\{ \begin{array}{l} \longrightarrow R\dot{C}O + NH{=}CHR' \\ \longrightarrow \dot{H} + RCON{=}CHR' \end{array} \right\} (\Phi_{11,21} \simeq 1) \quad , \qquad (11)$$

$$(21)$$

$$\dot{P}_1 + \dot{P}_1 \rightarrow P_1{-}P_1 \quad . \qquad (22)$$

Here $\dot{P}_1$ denotes the central macroradical RCONHĊHR′ and $\dot{R}$ and $\dot{R}'$ are the terminal alkyl macroradicals.

Reactions (1), (2), and (18) have already been discussed. Reactions (14), (17), (19), and (20) reflect the fact that different radicals are readily converted in polyamides into the more stable radical $\dot{P}_1$. Reaction (20) proceeds very efficiently (the minimum value of the rate constant is $k_{20} = 2 \times 10^{-3}$ litre mol^{-1} s^{-1}),[91] so that no other reactions of atomic hydrogen, for example, the recombination of H atoms, compete with it. Reaction (11) has been detected[76] by EPR. Reaction (21) cannot be detected by EPR, since the disappearance of the radicals $\dot{P}_1$ via reaction (21) leads to their regeneration via reaction (20). Nevertheless, evidence for the occurrence of reaction (21) has been obtained by comparing the photolysis products of deuterated and non-deuterated alanine peptides[92]. The rate of formation of H_2 in the photolysis of polyamides corresponds to a reaction order with respect to light intensity which is intermediate between the first and the second, which also indicates the formation of hydrogen in the photolysis of the radicals[52]. As a rule, the photolysis of the radicals proceeds with high quantum yields ($\Phi \simeq 1$).[68]

The cross-linking of polyamides on photolysis is explained by reaction (22), whose occurrence has been proposed by Zimmerman[70] on the grounds that the radical $\dot{P}_1$ is the most stable among all those present. The recombination of $\dot{P}_1$ with formation of a C–C bond is sterically impossible when there are free valences at the atoms of adjacent chains when the neighbouring amide groups are hydrogen-bonded[93]. The probability of cross-linking should therefore be greater in the amorphous regions of the polymer, where the hydrogen bonds are partly disrupted and where the radicals can migrate as a result of segmental diffusion or successive hydrogen atom abstraction reactions. Indeed polyamide copolymers with a degree of crystallinity lower than in PA-6,6 are cross-linked much more readily than the latter[93]. It has been noted that polyamides are cross-linked to a lesser extent than other polymers, for example, polyethylene[94–96]. Direct evidence for the occurrence of reaction (22) has been obtained in a study[97] where the formation of a C–C bond between the α-methylene groups adjoining the nitrogen atom was observed. We may note that cross-linking via the formation of C–N bonds has been observed by NMR in the thermal degradation of polyamides[98].

2. Model Polyamide Photochemical Oxidation Reactions

In the presence of oxygen, the composition of the products of the photochemical reactions of polyamides and low-molecular-weight *N*-alkylamides, which provide the most effective models of the polyamide chain, differ from the products characteristic of photolysis. Analysis of the composition of the photochemical oxidation products (as well as thermal oxidation products[99]) indicates the important role of the oxidative reactions of a single free radical, namely $\dot{P}_1$.

In the first study on the photochemical oxidation of model compounds[47] the products of prolonged (285 h) non-sensitised photochemical oxidation of *N*-pentylcaproamide at 38 °C were investigated and measurements were made of the absorption of oxygen; the different positions in the amide $C_4H_9{-}\overset{a}{C}H_2{-}\overset{b}{C}O{-}\underset{c}{N}H{-}CH_2{-}C_4H_9$ were labelled with ^{14}C. It was noted that CO is evolved from the α-methylene group adjoining the nitrogen atom (position *c*). When position *a* was labelled with ^{14}C, the only radioactive product was caproic acid, labelling of position *b* gave caproic acid and CO_2, while labelling of positions *c* gave valeraldehyde, valeric acid, CO, and CO_2. Substitution of the hydrogen atoms of the α-methylene group adjoining the nitrogen atom by methyl groups suppressed the photochemical oxidation. These findings led to the conclusion that amides are oxidised via a stage in which a hydrogen atom is abstracted from the α-methylene group with formation of the radical $\dot{P}_1$. In order to account for the composition of the final products, Sharkey and Mochel[47] postulated (by analogy with the oxidation of hydrocarbons) a mechanism in which the following reactions involving the radical $\dot{P}_1$ take place after reaction (1) and the exchange of primary radicals in dark processes:

$$\dot{P}_1 + O_2 \rightarrow P_1\dot{O}_2 \quad , \qquad (23)$$

$$P_1\dot{O}_2 + P_1H \rightarrow P_1OOH + \dot{P}_1 \quad , \qquad (24)$$

$$P_1OOH \rightarrow P_1\dot{O} + \dot{O}H \quad . \qquad (25)$$

The radicals $P_1\dot{O}$ and $\dot{O}H$ formed in the radical decomposition of the hydroperoxide [reaction (25)] lead to the reformation of the radical $\dot{P}_1$, giving rise at the same time to N_1-(1-hydroxyalkyl)amide (P_1OH), which is a precursor of the products detected—the unsubstituted amide, aldehydes, and acids.

It was found subsequently that the probability of the radical decomposition of P_1OOH is low. The amide hydroperoxide was isolated for the first time[100] in the oxidation of fused ε-caprolactam. The formation of the products of the decomposition of ε-hydroperoxycaprolactam, adipimide, and water indicated the occurrence of the non-radical decomposition $\overbrace{(CH_2)_4CONHC}(OOH)H \rightarrow \overbrace{(CH_2)_4CONHCO} + H_2O$. The addition of ε-hydroperoxycaprolactam did not accelerate the oxidation of caprolactam[101,102]. The polymerisation of diallyl phthalate cannot be initiated by the hydroperoxides of *N*-alkylamides at 131 °C over a period of 6 h, while the addition of di-t-butyl peroxide or dibenzoyl peroxide under the same conditions causes the formation of a polymer after 40 and 5 min respectively[103]. It has been shown by the inhibitor method that more than 97% of P_1OOH decomposes via a non-radical mechanism at 131 °C.[104]

Analysis of the products of the thermo- and photo-sensitised oxidation of 89 different *N*-alkylamides led to a mechanism[103–106] of the model oxidation of polyamides in which the $\dot{P}_1$ initiation stage and reactions (23) and (24) are followed by the processes

$$P_1OOH \rightarrow \delta\,(P_1\dot{O} + \dot{O}H) \xrightarrow[2\dot{P}_1H]{} \delta\,(P_1OH + H_2O + 2\dot{P}_1) \quad , \qquad (25')$$

$$P_1\dot{O}_2 + P_1\dot{O}_2 \left\{ \begin{array}{l} \longrightarrow 2RCONHCOR' + H_2O_2 \quad , \qquad (26) \\ \longrightarrow P_1OOP_1 + O_2 \quad , \qquad (27) \\ \longrightarrow P_1OH + RCONHCOR' + O_2 \quad , \qquad (28) \end{array} \right.$$

$$P_1OH \rightarrow RCONH_2 + R'CHO \quad , \qquad (29)$$

$$P_1OOH \left\{ \begin{array}{l} \longrightarrow RCONHCOR' + H_2O \quad , \qquad (30) \\ \longrightarrow RCONHCHO + R'OH \quad , \qquad (31) \\ \longrightarrow RCONHCH{=}CHR' + H_2O_2 \quad , \qquad (32) \\ \longrightarrow RCONH_2 + R'CHO \quad . \qquad (33) \end{array} \right.$$

At low temperatures (below 100 °C) the chain propagation reaction (24) is insignificant: the main products are formed in reactions (26)–(28) involving the destruction of peroxy-radicals. In photochemical oxidation at 0 °C the hydroperoxide P_1OOH was not detected. The high activation energies for reaction (24) $E_D > 13$ kcal mol^{-1} also shows that the chain

propagation reaction is difficult at low temperatures. In thermal oxidation the chain length increases under the experimental conditions from three units at 70 °C to 20–30 at 130 °C, where the main product becomes the hydroperoxide; its decomposition via reactions (30)–(33) gives rise to the final set of stable products. The probability δ of the liberation of radicals from the cage in the decomposition of P_1OOH is extremely low ($\delta < 0.015$ at 130 °C). When the temperature is reduced and after passing from solutions to a solid polymer, a considerable decrease of δ is to be expected as a result of the decrease of the mobility of molecules.

A similar mechanism of the photosensitised non-chain oxidation of *N*-alkylamides at 30 °C has been proposed by other workers[107], who wanted to explain the formation of the main products by the recombination reactions of the peroxy-radicals $P_1\dot{O}_2$.

Having determined all the products of prolonged (685 h) non-sensitised photochemical oxidation of *N*-butylcaproamide and their proportion relative to the amount of oxygen absorbed, Lánska and Šebenda[11] showed that the principal products are the imide, unsubstituted amides, water, CO, CO_2, hydrocarbons, and carboxylic acids. Peroxides, aldehydes, butylamine, and H_2 are formed in significantly smaller amounts. Pyrrole derivatives were present in trace amounts; other products were not detected.

3. The Influence of Experimental Conditions on the Photochemical Oxidation

The differences in the conditions of the photochemical experiments lead to differences in the composition of the products of the photochemical oxidation of *N*-alkylamides and polyamides. Thus, the main products in the non-sensitised photochemical oxidation are acids, the unsubstituted amides $RCONH_2$ and $R'CONH_2$, and the volatile products CO, CO_2, etc., but *N*-formylamide RCONHCHO was not detected. In the sensitised photochemical oxidation *N*-formylamide was detected together with the main products—imides and unsubstituted amides, but acids and volatile products were not found. It is not possible to account for the above differences by the inadequacy of the analytical methods[11].

We believe that the dependence of the composition of the products on the method of photoinitiation can be explained by differences between the primary photochemical reactions, by the competition between photochemical and dark processes, and also by the competition between primary and secondary photochemical reactions. Whereas photoinitiation as a result of the rupture of the amide bond, leading to the formation of an acyl radical whose oxidation gives rise to acids, is more probable in the non-sensitised process, in the sensitised photochemical oxidation reactions involving the abstraction of a hydrogen atom from the α-methylene group adjoining the nitrogen atom and leading to the formation of $\dot{P}_1$ are more likely. In the absence of oxidation chains, the composition of the products is determined by the photoinitiation mechanism.

The oxidation products formed can be extremely unstable. Thus the slow formation of acetone has been observed[105] on storage in the dark of preirradiated *N*-isopropylamides even at 0 °C; the liberation of acetone ceased only after 26 h. One can therefore postulate that, after very prolonged irradiation (in non-sensitised photochemical oxidation the duration of irradiation amounts to hundred of hours, while in sensitised photochemical oxidation its duration is only 1–3 h), the dark processes in certain cases compete with the photochemical processes, which alters the proportions of the products.

Finally, competition between the absorption of light by the initiating chromophoric group and the oxidation products can play an extremely important role, because in the wavelength range of the light incident on the amide usually employed ($\lambda > 250$–260 nm) amides absorb extremely weakly ($\varepsilon_{PA} < 1$–3 litre mol^{-1} cm^{-1}), while the products have extinction coefficients ε_P greater by three–four orders of magnitude than the amides. By irradiating thick layers of the amide (as a rule >1 cm), it is possible to increase the role of the secondary photolysis, since by shielding the amide from light, the products formed decrease the amount of light which it absorbs. The use of photoinitiating additives makes it possible to reduce the role of secondary photolytic reactions.

In order to assess the role of secondary photolytic reactions in the nonsensitised photochemical oxidation of polyamides, one can use[7] the equation

$$[P]_{min} = \Phi_{form} K_{PA}/\varepsilon_P, \qquad (34)$$

where $[P]_{min}$ is the minimum concentration of the product for which the rates of its formation and consumption via secondary photolysis are equal, Φ_{form} is the quantum yield in the formation of the product, ε_P the extinction coefficient of the product, and $K_{PA} = \varepsilon_{PA}[PA]$ is the absorption coefficient of PA. At 254 nm we have $K_{PA} = 32$ cm^{-1} [108] and the quantum yield in the formation of radicals is $\Phi_{form} = 0.01$. Assuming that the extinction coefficient of the radicals $\dot{P}_1$ and $P_1\dot{O}_2$ is $\varepsilon_P \cong 7 \times 10^3$ litre mol^{-1} cm^{-1},[68,71] we find from Eqn.(34) that the photolysis of radicals under the influence of light at $\lambda = 254$ nm can be come appreciable at radical concentrations of $\sim 4 \times 10^{-5}$ mol kg^{-1}. Such radical concentrations are indeed observed, for example, in the irradiation of PA-6.[109] It is possible to determine similarly the concentrations at which the photolysis of peroxides, aldehydes, etc. becomes significant.

For the photoageing of polyamides sensitised by an additive D, Eqn.(34) can be written in the form

$$[P(sens)]_{min} = \Phi_{form}\varepsilon_D [D]/\varepsilon_P. \qquad (35)$$

Compounds whose extinction coefficients $\varepsilon_D \cong 10^4$ litre mol^{-1} cm^{-1}, and whose quantum yields for the formation of radicals are extremely high ($\Phi_{form} \cong 0.1$–1), are usually employed as the initiating additives. Evidently, by selecting a suitable sensitiser and its concentration, it is possible to reduce to zero the role of secondary photolytic reactions. In this case photoageing is determined solely by initiation and dark reactions.

An additional factor influencing the photochemical oxidation—diffusion-dependent limitations—appears in the photochemical oxidation of polyamides. Even in the liquid-phase oxidation diffusion-dependent limitations can play a significant role[110]. In solid polymers the diffusion coefficients of O_2 are several orders of magnitude smaller than in the liquid phase. The range of the permissible rates of oxidation of the polymer, where the diffusion of O_2 does not limit the reaction, is therefore restricted to more severe conditions. It has been found[7] that the oxidation must proceed in the kinetic region when

$$w < 10^{11}(P/L^2)p_{O_2}, \qquad (36)$$

where w is the rate of absorption of oxygen (mol $litre^{-1}$ h^{-1}), P the constant of the permeability of the polymer to O_2#, L

The permeability constant P is expressed[111] in cubic centimetres, adjusted to the standard temperature and pressure, of the gas which has passed in 1 s through 1 cm^2 of the area of a membrane 1 mm thick when the pressure drop is 1 cmHg.

the thickness of the film or the diameter of the fibre (μm), and p_{O_2} is the partial pressure of oxygen (atm). The values of P for different polymers have been published[111]; $P = 3.8 \times 10^{-11}$ for PA-6 at 30 °C.

Examples of the influence of diffusion-dependent limitations on the photochemical oxidation of polyamides have been published in a number of communications[112-114] and discussed by Margolin et al.[7]

4. The Sequence of the Formation of Photochemical Oxidation Products

In the liquid-phase oxidation of hydrocarbons, the primary product is as a rule the hydroperoxide whose reactions determine both the initiation and the composition of the main products[110]. As shown above, the same situation obtains also in the oxidation of *N*-alkylamides at temperatures above 100 °C, but, when the temperature is reduced, the oxidation of *N*-alkylamides proceeds via a non-chain mechanism and the primary products arise from the recombination of peroxy-radicals. In polymers, the peroxy-radical recombination reaction is difficult owing to the restricted molecular ability; the radicals can therefore participate in other reactions leading to an increased chain length for oxidation[115]. The problem of the sequence of the polyamide photochemical oxidation products therefore requires special consideration.

The first study on the accumulation of peroxides in the photochemical oxidation of polyamides was carried out by Anton[64]. When PA-6,6 fibres are irradiated in air by light at $\lambda > 270$ nm, the concentration of peroxides increases from 1.7×10^{-3} to 4.2×10^{-3} mol kg^{-1} over a period of 60 h; the polymer is then almost completely decomposed long before the attainment of a steady-state concentration of peroxides. Under the influence of light at $\lambda > 300$ nm and also $\lambda > 340$ nm, the decrease in stability takes place at lower rates but peroxides accumulate almost as much as under the influence of light at $\lambda > 270$ nm. On illumination with light at $\lambda > 415$ nm, the decrease in the stability of the polyamide is not accompanied by an appreciable change in the concentration of peroxides. We believe that the results obtained show that the main pathway in the photochemical decomposition of polyamides is unrelated to the peroxide formation reaction under the given experimental conditions.

It is of interest to note that, in the radiation-induced oxidation of PA-6 [65,116] and model *N*-alkylamides[82], peroxy-radicals are converted via parallel pathways into peroxide, carbonyl, and carboxy-compounds, which has been explained by the non-chain oxidation of PA-6 at temperatures below 100 °C.

The results of studies[108,112-114,117-120] on the kinetics of the accumulation of the non-sensitised photoageing of polyamides under the influence of light at $\lambda = 254$ nm are presented in Fig. 3 and in Table 2. Table 2 shows that the main contribution to the photodecomposition of polyamides comes from oxidation processes. Thus the increase in the quantum yield for the chain dissociation process following an increase of the O_2 partial pressure indicates that, apart from the primary ruptures S_{prim} caused by the photolysis of the amide linkage [reaction (1)], secondary ruptures S_{sec}, due to oxidative processes, also arise. The formation of peroxides does not then constitute the only pathway in the photochemical oxidation. Separate experiments have shown[121] that, for concentrations in the range 0–0.02 mol kg^{-1}, peroxides do not initiate the photochemical oxidation of polyamides. The quantum

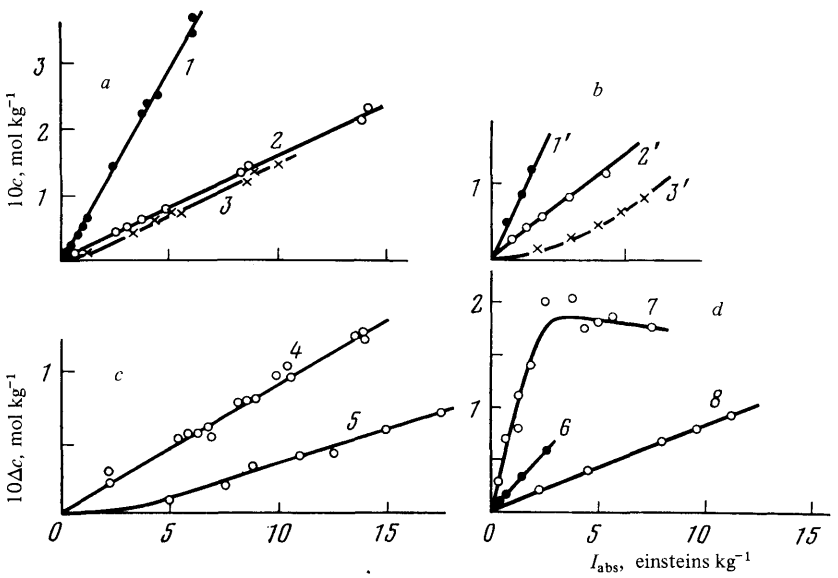


Figure 3. Photochemical oxidation of PA-6 and PA-548 films 3–6 μm thick under the influence of light at $\lambda = 254$ nm as a function of the irradiation dose I_{abs} at 25–30 °C: *a*) kinetic curves for the absorption of oxygen (curve *1*), the accumulation of breaks (curve *2*), and the evolution of CO (curve *3*) on irradiation of PA-6 (curves *1*–*3*) and PA-548 (curve *1*) in air; *b*) kinetic curves for the absorption of oxygen (curve *1'*), the accumulation of breaks (curve *2'*), and the evolution of CO (curve *3'*) on irradiation of PA-6 (curve *1'*) and PA-548 (curves *1'*–*3'*) in an O_2 atmosphere; *c*) kinetic curves for the accumulation of aldehydes (curves *4*) and carboxylic acids (curve *5*) on irradiation of PA-6 and PA-548 in air; *d*) kinetic curves for the accumulation of peroxy-compounds in air (curve *6*) and in an oxygen atmosphere (curve *7*) on irradiation of PA-548 and for the accumulation of pyrrole derivatives (curve *8*) on irradiation of PA-6 in air.

yields of a number of processes in PA-6 are identical with the yields of the corresponding processes in PA-548, which is explained by the fact that in both PA-6 and PA-548 the photoageing is caused by the absorption of light by the amide group.

A schematic sequence of the formation of products (the numbers over the arrows indicate the quantum yields of the corresponding processes in the photochemical oxidation of polyamides in air) has been proposed[7] on the basis of a comparison of the kinetic curves in Fig. 3:

Scheme I

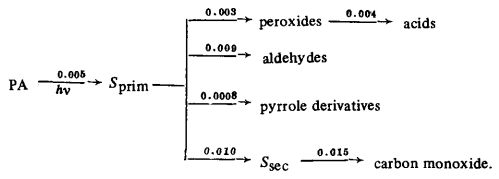


Table 2. The quantum yields of the photolysis and photochemical oxidation processes in the kinetic region on irradiation of PA-6 ($\lambda = 254$ nm; 25–30 °C).

Chemical process	Quantum yield of process (Ref.7)		
	photolysis	photochemical oxidation	
		air	oxygen
Formation of radicals	0,01[a]	—	—
Formation of carbon monoxide	$5\cdot10^{-4}$	0.015	0.030[c]
Formation of hydrogen	$7\cdot10^{-5}$	0.000[c]	0.000[c]
Ruptures in main PA chain	$5\cdot10^{-3}$[b]	0.015[c]	0.030[c]
Absorption of oxygen	—	0.060[c]	0.090[c]
Formation of carboxylic acids	$1.5\cdot10^{-4}$	0.004[c]	—
Formation of aldehydes	—	0.009[c]	—
Consumption of amino-groups	$1.5\cdot10^{-4}$	0.001[d]	—
Accumulation of peroxides	—	0.003[e]	0,007[e]
Accumulation of pyrrole derivatives	$2\cdot10^{-4}$[a]	0.0008	—

Note. [a]Estimate. [b]Estimated on the assumption that the primary process involves the dissociation of the amide bond. [c]The same value, within the limits of experimental error (10%), was obtained on irradiation of PA-548. [d]Determined from the initial rate of consumption of amino-groups. [e]Determined on irradiation of PA-548.

5. The Mechanisms of the Formation of the Products of the Photochemical Oxidation of Polyamides

The photoageing of polyamides is characterised by a large number of reactions, the relative rates of which depend on the experimental conditions. Since the same product can be formed in different reactions in the photoageing of polyamides, it is necessary to examine the possible mechanisms of the formation of the most important products: carboxylic acids, aldehydes, pyrrole and pyridine derivatives, peroxides, and carbon monoxide. Aparte from the composition of the products, in the study of the photoageing of polyamides one determines the number of breaks in the macromolecules and the decrease of stability, which, like the chemical products, characterise the process. Such processes, leading to the rupture of polyamide macromolecules and a decrease of the stability of polyamides, are examined below.

The formation of carboxylic acids. The formation of acids is attributed either to the oxidation of the acyl radical $R\dot{C}O$, which arises when the amide bond is ruptured[62], or to the oxidation (at advanced stages of the process) of aldehydes (Scheme II):[47]

Scheme II

$$R\dot{C}O + O_2 \rightarrow RC(O)O\dot{O}\ , \quad (37)$$

$$RC(O)O\dot{O} + P_1H \rightarrow RC(O)OOH + \dot{P}_1\ , \quad (38)$$

$$RC(O)OOH \rightarrow RC(O)\dot{O} + \dot{O}H\ , \quad (39)$$

$$RC(O)\dot{O} + P_1H \rightarrow RCOOH + \dot{P}_1\ , \quad (40)$$

$$RC(O)\dot{O} \rightarrow \dot{R} + CO_2\ , \quad (41)$$

$$2RC(O)OOH \rightarrow 2RCOOH + O_2\ , \quad (42)$$

$$R'CHO + RC(O)OOH \rightarrow R'COOH + RCOOH\ , \quad (43)$$

$$RCHO + O_2 \rightarrow RCOOH\ . \quad (44)$$

As in the oxidation of hydrocarbons[122], the radical decomposition of the peracid via reaction (39) hardly leads to the formation of acids owing to the rapid decomposition of the radical $RC(O)\dot{O}$ [reaction (41)], with which reaction (40) cannot compete ($k_{41}/k_{40} \cong 100$ at 85 °C). Therefore reactions (42) and (43), involving a non-radical transformation of the peracid, make the main contribution to the formation of acids and explain the low quantum yields in the formation of peroxides and acids in Scheme I. Reaction (39) should occur particularly effectively under the influence of light, resulting in the evolution of CO_2, as has been observed, for example, on irradiation of *N*-alkylamides by light at $\lambda > 300$ nm. However, in conformity with Eqn. (34) and the data in Fig. 3, the photolysis of the peracid at $\lambda = 254$ nm cannot compete with the dark reactions of the peracid, which agrees with the absence of CO_2 from the products and with the induction period with respect to the absorption of oxygen (Fig. 3, line *1*). At advanced stages of the photochemical oxidation the additional pathways leading to the formation of acids consist of photochemical and dark reactions of aldehydes and other oxidation products[11].

The formation of aldehydes. It has been suggested[7,11,123,124] that there is a possibility of the formation of aldehydes in parallel processes, which include the dark reactions of the radicals $R\dot{C}O$, $P_1\dot{O}_2$, and $P_1\dot{O}$ as well as the photochemical reaction of $P_1\dot{O}_2$ (Scheme III)

Scheme III

$$R\dot{C}O + P_1H \rightarrow RCHO + \dot{P}_1\ , \quad (17)$$

$$P_1\dot{O}_2 + P_1\dot{O}_2 \rightarrow P_1OH + RCONHCOR' + O_2 \quad (28)$$

$$\rightarrow RCONH_2 + R'CHO\ , \quad (29)$$

$$P_1OOH \rightarrow P_1\dot{O} + \dot{O}H\ , \quad (25)$$

$$P_1OOP_1 \rightarrow P_1\dot{O} + P_1\dot{O}\ , \quad (45)$$

$$P_1\dot{O} + P_1H \rightarrow P_1OH + \dot{P}_1\ , \quad (46)$$

$$P_1\dot{O}_2 \rightarrow RCONHCHO + CH_2O + \dot{R}'\ , \quad (47)$$

$$P_1\dot{O}_2 \xrightarrow{h\nu} RCONHCHO + R'\dot{C}HOH\ , \quad (48)$$

$$P_1\dot{O}_2 + R'\dot{C}HOH \rightarrow RCONHCOR' + R'CHO + H_2O\ . \quad (49)$$

The $P_1\dot{O}_2$ isomerisation reaction [reaction (47)] is significant only at high temperatures[123]. It has been suggested[7] that the photolysis of radicals via reaction (48) can lead to the formation of aldehydes in reaction (49).[124] The fact that, under the influence of light at $\lambda = 254$ nm, aldehydes are formed independently of peroxy-compounds makes it possible to rule out a significant contribution of reactions (25), (45), and (46) to the formation of aldehydes under the experimental conditions of Margolin et al.[7] However, under other irradiation conditions, these reactions may prove to be highly important.

The formation of pyrrole and pyridine derivatives. It has been suggested[65] that pyrroles are formed in the photochemical oxidation of PA-6,6 as a result of the condensation of dicarbonyl compounds with primary amines. Peebles and Hoffman[66] explained the formation of pyridine derivatives in the ageing of PA-6,6 and PA-10.6 by the condensation reactions of carbonyl compounds with the terminal amide groups and subsequent cyclisation. Owing to the structural characteristics of the molecule, in PA-6 the analogous reactions lead to pyrrole derivatives. The suggested derivatives explained to some extent the extremely low quantum yields in their formation (Scheme I).

The formation of peroxy-compounds. It is believed[2,7,11,47,100,101,103-107] that there is a possibility of the formation of five peroxy-compounds. There are peracids [reaction (38)], the hydroperoxide P_1OOH [reaction (24)], hydrogen peroxide [reactions (26) and (32)], the peroxide P_1OOP_1 [reaction (27)], and the terminal alkyl hydroperoxide of the type RCH_2OOH, which is formed on oxidation of the terminal alkyl radical. The above reactions result from processes involving different radicals and functional groups, which explains the dependence of the composition of the peroxy-products on the method of photoinitiation and temperature.

Breaks in the main polyamide chain and the formation of carbon monoxide. These can occur in the following reactions (Scheme IV):[7,11]

Scheme IV

$$P_1H \xrightarrow{h\nu} R'CH_2\dot{N}H + R\dot{C}O \quad , \qquad (1)$$

$$RCONHCOR' \xrightarrow{h\nu} \begin{cases} \longrightarrow RCO\dot{N}H + R'\dot{C}O \quad , & (50) \\ \longrightarrow R'CO\dot{N}H + R\dot{C}O \quad , & (51) \end{cases}$$

$$\dot{P}_1 \xrightarrow{h\nu} \begin{cases} \longrightarrow R'CH{=}NH + R\dot{C}O \quad , & (11) \\ \longrightarrow RCON{=}CHCH_2R'' + \dot{H} \quad , & (21) \end{cases}$$

$$P_1OOH \rightarrow RCONHCH{=}CHR'' + H_2O_2 \quad , \qquad (32)$$

$$RCON{=}\overset{\uparrow}{C}HCH_2R'' \xrightarrow{H_2O} \underset{RCONHCH=CHR''}{} RCONH_2 + R'CHO \quad , \qquad (52)$$

$$P_1OOH \rightarrow RCONH_2 + R'CHO \quad , \qquad (33)$$

$$P_1\dot{O}_2 \rightarrow RCONHCHO + R''\dot{C}HOH \quad , \qquad (48)$$

$$P_1\dot{O}_2 + P_1\dot{O}_2 \rightarrow RCONH_2 + R'CHO + RCONHCOR' + O_2 \quad , \qquad (28)$$

$$P_1\dot{O} \rightarrow RCONHCHO + \dot{R}' \quad , \qquad (53)$$

$$P_1OOH \rightarrow RCONHCHO + R'OH \quad , \qquad (31)$$

$$P_1OOP_1 \rightarrow RCONHCHO + RCONHCOR' + R''CH_3 \quad , \qquad (54)$$

$$RCONHCHO \rightarrow RCONH_2 + CO \quad , \qquad (55)$$

$$RCHO \xrightarrow{h\nu} RH + CO \quad , \qquad (56)$$

$$R\dot{C}O \rightarrow \dot{R} + CO \quad . \qquad (18)$$

The secondary breaks can occur in the photolysis of imides [reactions (50) and (51)], alkyl radicals [reactions (11) and (21)], and peroxy-radicals [reaction (48)], as a result of the decomposition of peroxy-compounds [reactions (31)–(33) and (54)] and the radicals $P_1\dot{O}$ [reaction (53)], and the recombination of peroxy-radicals [reaction (28)]. The breaks in the polyamide macromolecules are accompanied by the evolution of CO either in the decomposition of acyl radicals [reaction (18)], or in the photolysis of aldehydes [reaction (56)], or in the decomposition of the unstable *N*-formylamide [reaction (55)][107,123]. At reduced temperatures the occurrence of reaction (55) under the influence of light is more likely. In this case it is analogous to the photolysis of aldehydes[10].

Scheme IV shows clearly that in the oxidation process all the reactions involving the rupture of the main polyamide chain lead ultimately to the formation of unsubstituted amides; the latter are obtained either directly in the dissociation reaction or on further reactions of the radicals and the unstable products formed when the chain is broken. In the oxidation process the number of breaks in the polyamide should therefore be close to the number of terminal amide groups obtained. The second product of the majority of dissociation reactions is an aldehyde or the oxidation product of the acyl radical—a peracid and an acid.

The photolysis of imides, which is significant at advanced stages of the oxidation process, leads to the rupture of the polyamide chain with formation of an unsubstituted amide and an aldehyde or acid in subsequent reactions. The unstable products of reactions (21) and (32) (enamides or their tautomers) lead to breaks via the formation of the intermediate P_1OH, the decomposition of which also gives rise to an unsubstituted amide and an aldehyde [reaction (52)]. The most probable product of the oxidation of the amino-radical, formed in reaction (1), is a primary amide.

The mechanism of reaction (53), involving the decomposition of the radical $P_1\dot{O}$, has been formulated by analogy with the decomposition reaction of secondary alkoxy-radicals, which usually constitutes the main pathway in their transformation on oxidation of hydrocarbons[110]. There is no reason to believe that the radicals $P_1\dot{O}$ are less reactive in the decomposition reactions. On the other hand, the reactivity of the radicals $P_1\dot{O}$ in the reactions involving the abstraction of a hydrogen atom should be lower than for alkoxy-radicals owing to the influence of the nitrogen atom, which increases the electron density around the oxygen atom. The analogous influence of the nitrogen atom leads to an appreciable diminution of the reactivity of the radical $\dot{P}_1$ compared with alkyl radicals. The formation of $P_1\dot{O}$ is most probable in the photolysis of peroxides.

The wide variety of alternative reactions leading to the formation of the same products via different pathways provides an idea of the complexity of the mechanism of the photochemical oxidation of polyamides in which particular reactions occur depending on the experimental conditions and the ratios of the final products differ very widely. In photochemical oxidation, where virtually all the alkyl radicals are converted into peroxy-radicals, reactions (11) and (21) are insignificant. At reduced temperatures, where the photochemical oxidation of polyamides is a non-chain process, one can neglect the contribution of the hydroperoxide decomposition reactions (31)–(33) to the chain dissociation processes. However, there remains the possibility of the formation of the peroxides P_1OOP_1, whose pohotolysis can lead to chain breaks either via the formation of the radicals $P_1\dot{O}$ or via reaction (54).

In the sensitised photochemical oxidation it is possible to neglect the photolysis of the peroxy-radicals $P_1\dot{O}_2$ via reaction (48), since the principal breaks at reduced temperatures occur on recombination of $P_1\dot{O}_2$, according to the observations of Lock and Sagar[105]. In the non-sensitised photochemical oxidation of PA-6 under the influence of light at $\lambda = 254$ nm, for small extents of oxidation (Fig.3 and Table 2) when it is possible to neglect the photolysis of aldehydes but not the photolysis of peroxy-radicals, the quantum yields of the secondary dissociation processes and the formation of aldehydes and CO have similar values. Considering the possible dissociation reactions, these relative amounts of the products can be accounted for by the photolysis of the peroxy-radicals [reaction (18)], this being followed by the evolution of CO in the decomposition of *N*-formylamide via reaction (55) and the formation of an aldehyde on recombination of the radicals [reaction (49)].

In the non-sensitised photochemical oxidation under the influence of the total light of the PRK-2 lamp aldehydes undergo vigorous photolysis at advanced stages of the oxidation process, so that their yield is extremely low and that of CO is somewhat lower than the yield of unsubstituted amides[11]. Under these conditions, the imides are photolysed via reactions (50) and (51), which makes an additional contribution to the number of breaks, and the oxidation of acyl radicals to peracids and the subsequent photolysis of the latter lead to the evolution of CO_2. In the sensitised photochemical oxidation at reduced temperatures there is no evolution of CO, despite the formation of breaks, *N*-formylamide, and aldehydes, owing to the shielding effect of the sensitiser on the photolytic reactions of *N*-formylamide and the aldehyde [reactions (55) and (56)].

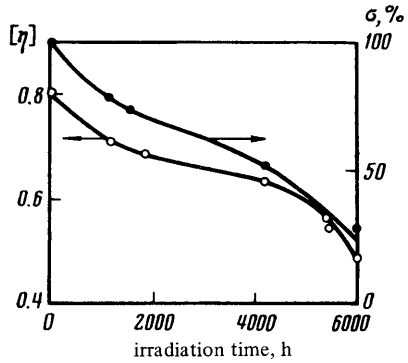


Figure 4. Photochemical ageing of PA-6.6 fibres under natural conditions {variation of the intrinsic viscosity (η) and of the loss of strength σ as a function of the duration of irradiation by sunlight with $\lambda > 300$ nm}.

6. The Decrease of the Strength of Polyamides

The impairment of the mechanical strength characteristics of polyamides on photoageing is associated with chemical processes[46]. For example, the simultaneous decrease of the tensile strength of the polymer and of its molecular weight are observed in the photoageing of PA-6,6 [46] (Fig. 4).

In order to elucidate the nature of the strength of polyamides, the dependence of their lifetime τ on the applied load σ, described by Zhurkov's equation[126]

$$\tau = \tau_0 \exp[(U_0 - \gamma\sigma)/kT], \qquad (57)$$

was investigated. For polyamides, the empirical parameters are $\tau_0 = 10^{-12}$ s and $U_0 = 45$ kcal mol^{-1}. The influence of the change of the molecular weight of the polyamide on the parameters τ_0, U_0, and γ has been investigated[127]. By irradiating PA-6 with different doses of ultraviolet light, the authors obtained specimens with different molecular weights; subsequently, the lifetimes of the specimens were measured in the dark. Preliminary irradiation affected only the parameter γ. A linear relation was observed[127] between $1/\gamma$ and the molecular weight and its theoretical validity was demonstrated[128]. Thus one may conclude that the breaks in the main polyamide chain lead to an increase of γ and hence to a decrease in the strength of the polymer.

The strength of the polyamide is influenced not only by the molecular weight of the polymer but also by the nature of the supermolecular structure. For example, the tensile strength of the highly oriented PA-6 is twelve times greater than that of the non-oriented material[129]. It follows from the theory[130–133] and has been confirmed by experiment[134], that $1/\gamma$ is directly proportional to the degree of extrusion. The structural changes in the photoageing of polyamides are observed as an increase in the density, the degree of crystallinity, and the surface microrelief; they are explained by the fact that the breaks in the main polyamide chain facilitate the movement of the macromolecules, which leads to more ordered structures[135–139]. Thus in this case too the breaks in the main polyamide chain lead ultimately to an alteration of the mechanical and stength characteristics of the polymer.

During use, polyamide articles can be subjected to different loads. The joint influence of the light intensity *I* and of the load σ, resulting in a decrease of the lifetime τ_I of the polyamide, has been investigated[140–143]. It has been shown that, for a certain load σ_{lim}, a characteristic break is observed in the experimental lg τ–σ linear plots:

$$\tau_I = \tau_0 \exp[(U_0 - \gamma\sigma)/kT] \text{ for } \sigma > \sigma_{lim}; \qquad (58)$$

$$\tau_I = B(T)/IK\Phi_{0,s} \exp(m\gamma\sigma) \text{ for } \sigma < \sigma_{lim}, \qquad (59)$$

where *K* is the light absorption coefficient of the polyamide, *m* a constant coefficient, $\Phi_{0,S}$ the quantum yield of the dissociations in the main polyamide chain in the specimen not subjected to a load, and *B(T)* a function which only slightly depends on temperature.

For $\sigma > \sigma_{lim}$, the action of light is weak compared with that of the load and can be neglected, so that the lifetime of the specimen is described by Zhurkov's equation (57). The quantity $\Phi_{0,S} \exp(m\gamma\sigma)$ is regarded as the quantum yield for dissociation in the molecules subjected to a load. It is believed that the increase of the quantum yield of the dissociation under the influence of the load occurs mainly as a result of the suppression of the cage recombination of the radicals formed on rupture of the macromolecule subjected to extending forces[144–150]. It is readily seen that the expression $IK\Phi_{0,S} \exp(m\gamma\sigma)$ in Eqn. (59) represents the number of breaks in the main polyamide chain. Thus for $\sigma < \sigma_{lim}$, the lifetime of the polyamide on irradiation in the loaded state is inversely proportional to the number of breaks.

The influence of ultraviolet irradiation and oxygen[142,143] and of nitrogen dioxide[151] on the lifetime of polyamide specimens subjected to a load has been investigated. In all the investigations a relation has been observed between the number of breaks in the main polyamide chain and the decrease of their strength. This relation makes it possible to regard the changes in the mechanical and strength characteristics as a result of chemical changes determined by the mechanism of the photoageing of the polyamide.

7. Kinetics of the Photochemical Oxidation of Polyamides

The kinetics of the destruction of macroradicals in polyamides of different structure have been studied[70,77,152,153]. It has been established that the destruction of macroradicals $\dot{P}_1$ is of second order with respect to concentration. The quadratic termination of macroradicals, including peroxy-radicals, has been observed in various polymers[154]. Presumably, peroxy-radicals $P_1\dot{O}_2$ in polyamides are also destroyed via a second-order reaction, as happens in the oxidation of model *N*-alkylamides[155,159].

The rate of photochemical oxidation of polyamides with quadratic termination can be represented by the expression

$$w = \frac{1}{2} w_{in} + (k_p/\sqrt{k_t})[P_1H]\sqrt{w_{in}}, \quad (60)$$

where $w_{in} \cong I$ is the rate of photoinitiation and k_p and k_t are the chain propagation and termination rate constants respectively.

Experiment shows[7] that the rates of absorption of O_2 and of accumulation of polyamide photochemical oxidation products under the influence of light at $\lambda = 254$ nm are proportional to the light intensity I at 20–30 °C and that with increase of temperature the order of the reaction based on the rate of initiation diminishes. Thus at 100 °C the rate of photochemical oxidation of PA-6 is proportional to $I^{1/2}$. These results can be accounted for by the absence of oxidation chains in the low-temperature oxidation owing to the unduly high rates of photoinitiation under the experimental conditions where it is possible to neglect the second term of the sum on the right-hand side of Eqn.(60). With increase of temperature, the photochemical oxidation at the same rates of photoinitiation acquires a chain mechanism as a result of the increase of $k_p/\sqrt{k_t}$.

It might have been supposed that the reaction is first order with respect to light intensity because it is a chain oxidation process with linear termination and that the decrease of the reaction order with increase of temperature is caused by a change in the termination mechanism. For long oxidation chains, the rate of absorption of O_2 determines the concentration of the radicals. It is known[70] that the efficiency of the destruction of macroradicals in polyamides depends very markedly on the supermolecular structure of the polymer. The dependence of the destruction of radicals on the supermolecular structure should influence also the rate of oxidation, as has been observed, for example, in the thermal oxidation of different polyamides[160] and other polymers[161]. However, it has been found that the rate of photochemical oxidation of PA-6 is independent of the degree of orientation and the degree of crystallinity of the specimen[162,163], which conflicts with the hypothesis of chain oxidation with linear termination.

At the same time, in the low-temperature non-sensitised photochemical oxidation of polyamides the rate of photochemical oxidation exceeds by a factor of nine the rate of the primary photoinitiation (Table 2). Under the experimental conditions, there is apparently additional initiation as a result of secondary photolysis. Indeed, a different relation between the rates of photochemical oxidation and photoinitiation is observed in the photochemical oxidation of polyamides sensitised by benzophenone under conditions where, according to Eqn.(35), secondary photolysis can be neglected[7]:

$$w \simeq w_{in} \simeq 0.11 \text{ mol kg}^{-1} \text{ h}^{-1}. \quad (61)$$

The parameter $k_p/\sqrt{k_t} = 2.7 \times 10^{-4}$ litre mol^{-1} s$^{-1/2}$ at 30 °C can be estimated from Eqns.(60) and (61); it is of interest to compare it with the kinetic parameters of the oxidation of model *N*-alkylamides and other compounds (Table 3).

The values of $k_n\sqrt{k_t}$ for different amides recalculated per reactive α-C–H, bond are similar and equal to $(0.2–0.3)\times10^{-4}$. On passing from low-molecular-weight amides to solid polyamides, the parameter $k_n\sqrt{k_t}$ increases by a factor of approximately 6. An analogous situation has been observed also for polypropylene and its low-molecular-weight analogue 2,4-dimethylpentane, mainly owing to the appreciable decrease of the termination rate constants k_t as a result of the limitation of molecular mobility on passing from the liquid phase to the solid polymer.

V. PROBLEMS OF CONTROLLED PHOTOAGEING

1. Prediction of the Resistance to the Action of Light

Prediction of the resistance to the action of light makes possible a fairly well-founded approach to the selection of the material for use under specific conditions. A direct prediction procedure is based on natural tests, which make it possible to estimate the time during which the useful properties of the polymer are retained when it is employed under natural conditions. The main operational property of polyamides is their strength. Therefore in tests of the resistance of polyamides to the action of light under natural conditions one investigates the changes in the mechanical strength characteristics. Fig.5 presents data[1] concerning the changes in relative elongation on rupture and of the ultimate tensile strength under conditions of natural photoageing of specimens of different polymers. Fig.5 shows that polyamides exhibit a low resistance to the action of light: all aliphatic polyamides lose their useful operational properties in all climatic zones during less than one year. A significant impairment of properties occurs after only one–two months[4,164–166].

Table 3. Kinetic parameters of the oxidation of a series of compounds at 30 °C*.

Compound	k_p, litre mol^{-1} s^{-1}	$10^{-7}k_t$ litre mol^{-1} s^{-1}	$10^4(k_p/\sqrt{k_t})$, litre$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$	Refs.
N,N-Dimethylacetamide	1.44	14	1.2	155
N-Isopropylacetamide	0.05	0.9	0.16	155
N-Isopropylacetamide	—	—	0.38	104
N-n-Butylacetamide	0.22	2.3	0.47	155
N-n-Propylpropionamide	—	—	0.62	104
PA-548**	—	—	2.7	—
Polypropylene (60°)	0.015	$5.7\cdot10^{-5}$	6.3	154
2,4-Dimethylpentane (60°)	0.014	$2.2\cdot10^{-3}$	0.9	154

*Determined by extrapolation of the temperature variations of k_p and k_t to 30 °C.
**Estimated from Eqns.(60) and (61).

The photoageing of polymers during their use (and in tests under natural conditions) takes place under conditions characterised by significant changes in operating factors: the intensity and spectral composition of light, temperature, humidity, and level of corrosive impurities in the atmosphere, etc. Fig.5 shows that humidity has a significant influence on certain polymers. It has been found that humidity retards somewhat the evolution of CO in the photolysis of PA-669[167] but has almost no influence on strength when polyamide fibres are irradiated by light at $\lambda > 340$ nm and retards slightly the loss of strength by polyamides after irradiation by light at shorter wavelengths at room temperature; however, one should note that at higher temperatures (100 °C) and in the presence of titanium dioxide humidity accelerates appreciably the photoageing processes of polyamides[4,46,168,169]. The decrease of the strength of polyamides on photoageing in the vicinity of cities proceeds at higher rates than in the country[4], which indicates the possible influence of corrosive impurities in the atmosphere. Nitrogen dioxide and ozone also accelerate the photoageing of PA-6,6.[170] However, the most significant factor influencing the photoageing of polyamides is evidently the intensity and spectra composition of sunlight.

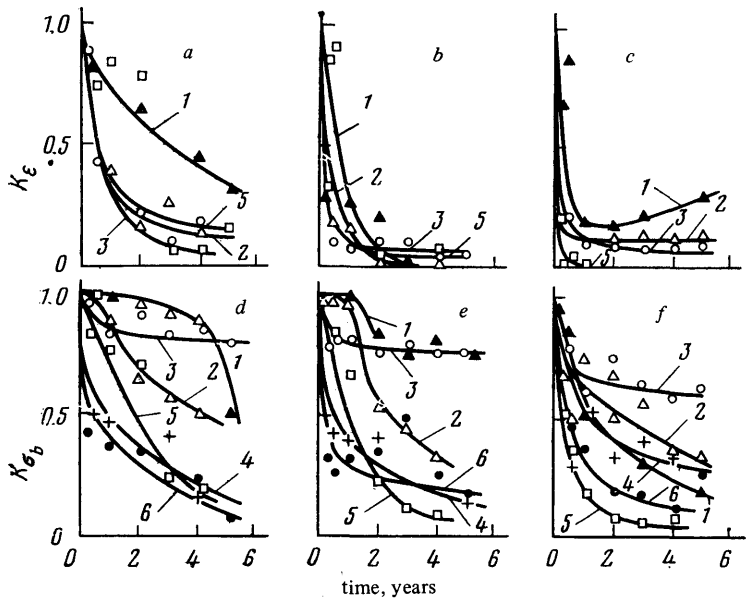


Figure 5. Dependence of the relative elongation (K_ε) on rupture (*a*, *b*, and *c*) and of the ultimate tensile strength (K_{σ_b}) (*d*, *e*, and *f*) as a function of the ageing time in moderately cold (*a* and *d*), warm and humid (*b* and *e*), and hot and dry (*c* and *f*) climatic zones for specimens of the trioxan-dioxolan copolymer (curves *1*), the formaldehyde–dioxolan copolymer (curves *2*), polycarbonate (curves *3*), PA-6 (curves *4*), PA-12 (curves *5*), and PA-6,10 (curves *6*).

A second way of predicting photoageing involves prediction based on the rsults of accelerated tests. Empirical relations, which describe with a greater or lesser degree of approximation the result of both natural and accelerated tests, are of great assistance in such tests[1,171]. In order to be able to extrapolate the results of accelerated tests to conditions corresponding to the photoageing of polyamides under natural conditions, one takes into account during the accelerated tests the factors which are significant in natural tests. Allowance for the influence of temperature, atmospheric humidity, and the content of ozone in air is achieved by a modelling procedure. An essential condition for a correlation between the results of natural and accelerated tests is also believed to be complete identity of the spectral composition of sunlight and artificial light[139,172–176]. It has been found[176] that photochemical activity is not shown by light over the entire spectral range but only by the short-wavelength part of the spectrum with $\lambda < 315$ nm; the nature of the spectra composition of light at $\lambda < 315$ nm is therefore most significant.

The intensity of sunlight in the region corresponding to absorption by polyamides, i.e. at $\lambda < 290$–300 nm, is extremely low ($I < 3.6 \times 10^{12}$ quanta cm^{-2} s^{-1}).[12] This suggests that secondary photolysis makes a major contribution to the initiated photoageing of polyamides under natural conditions. A wide variety of photochemical oxidation products—aldehydes, peroxy-compounds, and nitrogen-containing compounds (for example, imides or pyrrole derivatives, the absorption spectra of which differ)—can be involved in secondary photolytic reactions. This explains in its turn the necessity for maintaining the identity of the spectral composition of light as a condition for a correlation between the results of natural and accelerated tests.

At the same time one should note that the use of a high light intensity in accelerated tests with the remaining operating factors unchanged affects the form of chemical process occurring and alters the relative roles of different reactions. Thus, for fairly high light intensities I, the polyamide oxidation reaction has a non-chain mechanism and is determined solely by the initiation and radical destruction reactions. For very low values of I, the chain propagation stage may prove to be significant. The study of the influence of light intensity on the photoageing of polyamides therefore constitutes a more valid approach to the solution of the problem of a correlation between accelerated and natural tests.

Quantitative allowance of the factors already examined makes it possible to approach on a sounder basis the search for a correlation between the reults of natural and accelerated tests. The accuracy of such correlation is however inevitably limited by the uncertainty in the weather conditions (cloud cover, humidity, etc.). The study of the resistance of polyamides to the action of light in the presence of a wide variety of additives is of greatest interest. However, additives can influence the mechanism of the photoageing of polyamides, which also limits the scope of the correlation and of the theoretical predictions.

2. The Influence of Additives on the Photoageing of Polyamides

Titanium dioxide[46,51,62,65,177,178], which is used to etch fibres, is an active photosensitiser of the oxidation of polyamides. It has been shown[42] that the action spectrum of light on PA-6,6 in the presence of titanium dioxide is identical with the absorption spectrum of the latter and a number of possible mechanisms for the photosensitised oxidation of polyamides by titanium dioxide have been discussed.

Anthraquinone derivatives are believed to be the most powerful photosensitisers of the oxidation of polyamides[179]. Sodium anthraquinone-2-sulphonate at concentrations of 0.02 to 0.04 mol kg^{-1} increases the rate of photochemical oxidation of *N*-alkylamides by three orders of magnitude[107]. Initiation

in *N*-alkylamides takes place as a result of the abstraction of a hydrogen atom from the amide molecule by the excited sensitiser molecule and subsequent oxidation of the semiquinone radical by molecular oxygen.

Dyes such as β-Hydroxyethylsulphonium Red and Yellow and Monochlorotriazine Red and Yellow increase the rate of formation of radicals when PA-6 is irradiated by light at $\lambda = 254$ nm in air[87], the increase in the yield of radicals being directly proportional to the increase in the yield of carboxy-groups[109,180,181]. The impurities present in the initial monomers and formed in the synthesis of polyamides can also accelerate photoageing[182]. For a controlled acceleration of photoageing of polyamides, one can employ a wide variety of radical initiators, for example, iron(III) chloride, peroxides, etc.

The extensive experimental data accumulated hitherto on the stabilisation of PA with respect to the action of light have been published in reviews[3,4,6,183]. There exist literally thousands of substances and compositions which retard by factors of 2–5 the photoageing of polyamides. Apart from the large class of u.v. shields and u.v. absorbers, the action of which consists in the simple shielding of the polymer from light, among the most widely used light-stabilisers of polyamide mention may be made of copper and manganese compounds[3]. There is evidence for the efficiency of the protective action of chromium[2,6], nickel, and cobalt[184] salts, sodium and potassium halides[185], and phosphorus-containing compounds[3]. In recent years much attention has been devoted to manganese and phosphorus compounds[186–190], which prevent the photosensitising action of titanium dioxide, as well as copper and iodine compounds[191–195].

One should note that many of the compounds indicated also function as thermostabilisers of polyamides. For example, sodium bromide is effective both in thermal oxidation and in the photochemical oxidation of polyamides[196]. A qualitative correlation has been observed between the thermal and photochemical efficiencies of a number of copper-containing complexes of cyclo-1,3-phenylenethioisoindolenines used as stabilisers of PA-6.[197,198] There is also the opposite evidence: copper naphthenate, which is a powerful inhibitor of thermal oxidation of polyamides[199], does not influence the photochemical oxidation of *N*-alkylamides in an oxygen atmosphere[107], which is probably associated with the absence of oxidation chains in this instance.

Attempts have been made in a number of studies to elucidate the mechanism of the reaction of the most effective light stabilisers for polyamides—copper compounds. The changes in the supermolecular structure of PA-6 as a function of the introduction of copper-containing stabilisers (stabilines) have been studied[200]. It has been found that the introduction of stabilines tends to strengthen cord fibres, which can reduce the diffusion of oxygen into polyamides. This effect in the diffusion region of the photochemical oxidation leads to retardation of the oxidation process. However, in natural photoageing of polyamides, which lasts for months, one can hardly expect limiting by diffusion-dependent processes. Furthermore, the stabilising action of copper salts with respect to light has been observed also in the photochemical oxidation of PA-6 in the kinetic region[112].

The study of the gas evolution on irradiation of PA-6 by the total light of a moderate-pressure mercury lamp *in vacuo* has shown[201] that copper, chromium, zinc, and cadmium chlorides do not affect the gas evolution and that, on irradiation by light at $\lambda > 300$ nm, copper chloride accelerates the evolution of H_2. Under these conditions, the above stabilisers retard the decrease of the mechanical strength characteristics of PA-6. It has been suggested[201] that the action of the test compounds is due to their shielding properties. This explanation is apparently inadequate, because the shielding effect should lead solely to a decrease of the rate of gas evolution. It was shown subsequently, taking into account the shielding effects, that the protective action of copper and certain other metal salts cannot be reduced wholly to the shielding effect[112].

When PA-6 films are irradiated *in vacuo*, the addition of copper acetylacetonate (0.001–0.01 mol kg^{-1}) does not affect the evolution of CO and increase slightly the rate of evolution of H_2, which has been explained by the absence of an effect by copper acetylacetonate and the primary photochemical processes in polyamides[202]. However, at the same concentrations copper acetylacetonate reduces severalfold the quantum yields of the degradation processes, of the absorption of oxygen, and other PA-6 photochemical oxidation processes. Copper acetylacetonate retarded the benzophenone-sensitised photochemical oxidation of polyamides but did not influence the luminescence and kinetics of the consumption of benzophenone. This permits the conclusion that copper compounds are capable of inhibiting dark polyamide photoageing processes.

Since hydroperoxides were not detected in PA-6 fibres stabilised by copper salts, it was suggested that the additives suppress oxidation as a result of the formation of an inactive complex with the peroxy-radicals or as a result of the decomposition or binding of hydroperoxides with formation of inactive compounds[197,200]. An analogous effect—the absence of hydroperoxides—had been observed earlier in a study[65] of the photochemical oxidation of model amides with the addition of manganese salts, which enabled the authors to reach the same conclusion concerning manganese salts. Strictly speaking, the decreased content of peroxy-compounds may be a consequence also of other processes preventing the formation of peroxides.

A qualitative analogy between the action of copper salts and an acceptor of alkyl radicals (the 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxy-radical) has been observed[120,202]; the efficiency of the alkyl radical acceptor increases, like that of copper acetylacetonate, with decrease of the partial pressure of oxygen in accordance with the increase of the relative role of the alkyl radical participating in the photochemical oxidation of polyamides. Thus copper compounds can compete with oxygen in the alkyl radical oxidation reaction. The ability of copper(II) compounds to oxidise alkyl radicals has been demonstrated[203,204]. We believe that the protective action of copper(II) salts as a result of their interaction with alkyl radicals is most likely, although other protective mechanisms cannot be ruled out.

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In conclusion we may note that the mechanism of the photoageing of polyamides continues to be the subject of numerous investigations.

A number of recent studies[205–214] are of interest for the elucidation of the mechanisms of the primary photochemical processes responsible for the initiation of the photoageing of polyamides. The nature of the luminescence in polyamides continues to be controversial[205,213]. Additional data[216], showing that the main primary reaction in the direct photolysis of amides is the breakdown of the amide linkage, have been obtained. It has been shown[214,215] that, in the sensitisation of the photoageing of polyamides by compounds of different classes, the principal primary initiation reaction involves the abstraction of a hydrogen atom with formation of the macroradical $RCONH\dot{C}HCH_2R'$ (P_1). Therefore the possibility of the involvement of singlet oxygen $^1O_2$ in initiation steps appear unlikely. An analogous conclusion was reached in other investigations[209,210] of the photochemical oxidation of

PA-6,6 and in a study[217] of the photochemical oxidation of low-molecular-weight amides.

A number of studies have been made on the mechanism of the photochemical oxidation of polyamides[218,219]. It has been shown experimentally for the first time[218] that the photochemical oxidation of PA-6 and PA-548 proceeds with participation of peroxy-radicals P_1O_2; measurements have been made of the rate of destruction of peroxy-macroradicals and of the corresponding rate constants [$k_d = 2.4\times10^{15}\exp(-16000/RT)$] kg mol^{-1} s^{-1} in both PA-6 and PA-548. $k_p/k_d^{1/2} = 1.4\times10^{-4}$ kg$^{1/2}$ (mol s)$^{-1/2}$ for the photochemical oxidation of PA-548 at 25 °C has been measured[219]. It was shown in the same study[219] that the chain oxidation becomes significant at extremely low rates of oxidation, comparable to the rates of photochemical oxidation of PA-6 under natural conditions.

The ideas concerning the role of secondary photolytic reactions in polyamides, discussed above, have found further confirmation in a number of investigations[212,218,220]. The possibility of the photochemical reaction of the amino-radicals has been demonstrated[212] and the photorecombination of PA peroxy-radicals, which proceeds at extremely high rates, has been observed[218].

New studies have been made on the mechanism of the stabilisation of polyamides with respect to the action of light[207,221,222]. It has been shown[221] that the grafting of an inhibitor of radical processes (vinylhydroquinone) to PA-6 protects the polyamide against the action of light. It has been shown by EPR [222] that copper salts react with the macroradicals $\dot{P}_1$ and the rate constant for this reaction has been measured.

It can be regarded as established that the photoageing of polyamides is a radical-chain process with quadratic oxidation chain termination and that the oxidative degradation processes make the main contribution to the photochemical decomposition. Thus the photoageing of polyamides resembles the photoageing of certain carbochain polymers (for example, polyolefins, in relation to which an analogous conclusion has been reached[8]).

Whereas the photochemical oxidation of carbochain polymers is known to be initiated by hydroperoxy- and carbonyl groups, the nature of the photoinitiating groups in polyamides on irradiation by long-wavelength light continues to be controversial. The mechanism of the photoinitiated oxidation of polyamides can differ from the mechanism of the photoinitiated oxidation of other polymers. The cause of this difference may be related to the greater number of nitrogen-containing products (pyrroles, imides, and imines) which exhibit an intense ultraviolet absorption.

Although the nature of the chromophoric group responsible for the initiation of the photoageing of polyamides remains controversial, studies have shown that effective stabilisation of polyamides (as well as other polymers) with respect to the action of light can be achieved by introducing radical process inhibitors into the polyamide.

The photoageing of polyamides is characterised by a complex composition of products and a large number of reactions, the relative rates of which depend on experimental conditions. Secondary photolytic processes make a significant contribution to the photoageing process and studies of the photochemical reactions of polyamide macroradicals merit particular attention.

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