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Review: Auto-oxidation of aliphatic polyamides

Emmanuel Richaud [a,*], Octavie Okamba Diogo [a,b], Bruno Fayolle [a], Jacques Verdu [a],
Jean Guilment [b], François Fernagut [b]

[a] *Arts et Metiers ParisTech, CNRS, PIMM URM 8006, 151 bd de l'Hôpital, 75013 Paris, France*
[b] *ARKEMA, CERDATO, LEM, Route du Rilsan, 27470 Serquigny, France*

ABSTRACT

The literature on oxidation kinetics of polyamides and model compounds has been reviewed in order to try to extract suitable information for non-empirical kinetic modeling. Polyamide characteristics are systematically compared to polyolefin ones, these latter being more extensively studied. From kinetic analysis point of view, it is shown that oxidation attacks predominantly α amino methylenes of which C—H bond is considerably weaker than the other methylenes. As a result, propagation by H abstraction is considerably faster in polyamides than in polyethylene for instance. Termination by radical combination is also very fast. Another cause of PA oxidizability is the instability of α amino hydroperoxides linked to the inductive effect of nitrogen. This instability is responsible for many key features of oxidation kinetics especially the absence of induction period.

The main stable oxidation products are imides resulting from disproportionation processes meanwhile chain scissions resulting from rearrangements of α amino alkyls by β-scission are also significant process although their yield appears lower than in polyolefins.

Keywords:
Aliphatic polyamides
Oxidation
Mechanisms
Kinetics
Oxidation products

1. Introduction

Aliphatic polyamides are significant engineering polymers used as well in textiles (Nylon 6, Nylon 66) as in metal coatings (polyamide 11), flexible pipes for automotive or offshore applications (polyamides 11 and 12), etc…. Some of these applications are highly demanding from the durability point of view but polyamides are not intrinsically stable in the presence of oxygen, therefore an appropriate stabilization is necessary. These characteristics explain the relatively abundant literature published on polyamide oxidation in the past half century which was compiled recently [1–6].

It seemed interesting to us to revisit the literature through the prism of kinetic analysis trying to extract suitable information on elementary rate constants from available data and to compare systematically polyamides with polyolefins especially with polyethylene which could be considered as 'PA∞' i.e. the polyamide with an infinite distance between amide groups.

The review will be divided into two parts: the first one is devoted to kinetic analysis using classical mechanistic scheme as a frame to the literature interpretation. The second part is devoted to the nature of oxidation products in polyamides but also in model compounds.

2. Kinetic analysis

2.1. Mechanistic scheme

In a first approach, the interpretation of experimental data in the frame of a "close-loop scheme" will be tried [7,8]. In this scheme radical oxidation generates its own initiator, i.e. hydroperoxide groups (POOH). The decomposition of the latter can be uni or bimolecular.

$$\text{(1u)}\quad \mathrm{POOH} \rightarrow 2\mathrm{P}^\circ + \gamma_1 \mathrm{P{=}O} + \gamma_2 \mathrm{s} \quad k_{1u}$$

$$\text{(1b)}\quad \mathrm{POOH} + \mathrm{POOH} \rightarrow \mathrm{P}^\circ + \mathrm{POO}^\circ + \gamma_1 \mathrm{P{=}O} + \gamma_2 \mathrm{s} \quad k_{1b}$$

$$\text{(2)}\quad \mathrm{P}^\circ + \mathrm{O}_2 \rightarrow \mathrm{POO}^\circ \quad k_2$$

$$\text{(3)}\quad \mathrm{POO}^\circ + \mathrm{PH} \rightarrow \mathrm{POOH} + \mathrm{P}^\circ \quad k_3$$

$$\text{(6)}\quad \mathrm{POO}^\circ + \mathrm{POO}^\circ \rightarrow \text{inactive product} + \mathrm{O}_2 \quad k_6$$

P=O and s define respectively a carbonyl compound and a chain scission, and γ_1 and γ_2 the associated yields of formation.

This scheme involves several classical hypotheses:

- there is a single reactive site (PH) in the monomer unit.
- oxygen is in excess so that termination involving P° radicals is negligible.

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* Corresponding author.
E-mail address: emmanuel.richaud@ensam.eu (E. Richaud).

- HO° and PO° radicals formed in POOH decomposition events react fast to give P° radicals.
- there is initially a small quantity of POOH groups responsible for the first initiation steps.

This set of hypotheses was first used by Tobolsky et al. [9]. In the kinetic analysis, one considers generally that a steady state is reached at a low conversion ratio, in other words that substrate consumption is negligible. It will also be supposed here that oxidation is not diffusion controlled in the samples under investigation (thin films). The possible consequences of such a hypothesis will be discussed at the end of this section.

2.2. Propagation and termination

Propagation and termination rate constants are relatively difficult to obtain separately. In contrast, the ratio $k_3[PH]/k_6{}^{1/2}$ which represents the intrinsic oxidizability of the substrate can be more or less easily determined from oxidation kinetic curves. This determination is especially easy when oxygen is in excess i.e. when termination results almost exclusively from peroxyl bimolecular radicals combination (reaction (6), rate constant k_6). In this case, it can be demonstrated that when a steady state is reached at relatively low conversion, the maximum oxygen consumption rate is given (in unimolecular mode, see later) by:

$$(r_{OX})_{MAX} = -\frac{d[O_2]}{dt} = 2\frac{k_3^2}{k_6}[PH]^2 \qquad (1)$$

In the oxygen deficit regime, P° radicals participate to termination by two reactions:

(4) $P^\circ + P^\circ \rightarrow$ inactive product $\quad k_4$

(5) $P^\circ + POO^\circ \rightarrow$ inactive product $\quad k_5$

The best way to determine $(r_{Ox})_{MAX}$ and k_5 consists in studying the effect of oxygen pressure P_{O_2} on the maximum oxidation rate r_{Ox}. The equilibrium oxygen concentration $[O_2]$ in polymer is given by:

$$[O_2] = S_{O_2} \times P_{O_2} \qquad (2)$$

where S_{O_2} is the oxygen solubility in PA amorphous phase and P_{O_2} is the partial O_2 pressure.

In polyamides, $S_{O_2} = 1.5 \times 10^{-8}$ mol l^{-1} Pa^{-1} [10] so that: $[O_2] = 3 \times 10^{-4}$ mol l^{-1} under air at atmospheric pressure. S_{O_2} changes with temperature are expected to be negligible in agreement with some published data on PA6 [6] and PE [11].

At constant initiation rate, i.e. here in steady state, one can demonstrate that [12]:

$$r_{OX} = (r_{OX})_{MAX} \bullet \frac{\beta[O_2]}{1+\beta[O_2]} \qquad (3)$$

$$\text{where}: \beta = \frac{k_2 k_6}{k_3 k_5 [PH]} \qquad (4)$$

The curve $r_{Ox} = f([O_2])$ is a hyperbole having a horizontal asymptote at $r_{Ox} = (r_{Ox})_{MAX}$. $(r_{Ox})_{MAX}$ and β can be determined graphically from a graph "$1/r_{Ox}$ vs $1/[O_2]$":

$$\frac{1}{r_{OX}} = \frac{1}{(r_{OX})_{MAX}} + \frac{1}{\beta \bullet (r_{OX})_{MAX} \bullet [O_2]} \qquad (5)$$

Literature [13–15] reports the effect of oxygen pressure on oxidation kinetics of PA. In the case of thermal oxidation, some results at 155 and 200 °C [13] are plotted in Fig. 1.

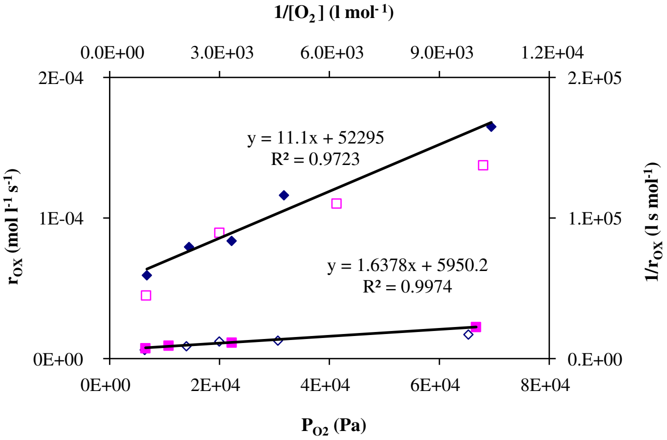


Fig. 1. Effect of oxygen pressure on oxidation rate of PA6 at 155 (◆, ◇) and 200 °C (■, □). Close symbols correspond to $1/r_{O_2}$ vs $1/[O_2]$ and open ones to r_{O_2} vs P_{O_2}.

The dependence is actually linear and the parameters values are reported in Table 1.

A critical oxygen pressure ($[O_2]_C$) can be defined as follows:

- $[O_2] > [O_2]_C$, oxidation is considered as in excess oxygen regime i.e. that all P° are scavenged into POO° and termination kinetics mainly occur by the $POO^\circ + POO^\circ$ coupling and oxidation rate reaches a maximal value $(r_{O_2})_{MAX}$.
- $[O_2] < [O_2]_C$, termination kinetics occur by the three reactions of radical coupling and termination rate is given by Achimsky [16]:

$$[O_2]_C = 1.2/\beta^{-1} \qquad (6)$$

Using $P_{atm} = 0.02$ MPa, and $S_{O_2} = 1.5 \times 10^{-8}$ mol l^{-1} Pa^{-1}, it is found: $[O_2]_{atm} = 3 \times 10^{-4}$ mol l^{-1} so that: $[O_2]_C > [O_2]_{atm}$ ($[O_2]_{atm}$ being the oxygen concentration which is dissolved into polyamide amorphous phase in air under atmospheric pressure). Hence, PA is far from the oxygen excess in air under atmospheric pressure i.e. that termination process involves P° radicals.

(Eqs. (4) and (5)) can be rewritten to obtain a relation between k_6 and $(r_{Ox})_{MAX}$:

$$\beta = \frac{k_2}{k_5} \bullet \sqrt{\frac{2k_6}{(r_{OX})_{MAX}}} \qquad (7)$$

$$\text{so that}: \quad k_6 = \frac{1}{2} \bullet \left(\frac{k_5}{k_2}\beta\right)^2 \bullet (r_{OX})_{MAX} \qquad (8)$$

where $\beta^2 \cdot r_{Ox} \sim 420$ mol l^{-1} s^{-1} at 155 °C and 2200 mol l^{-1} at 200 °C. The ratio k_5/k_2 is unknown. One can notice that both reactions (2) and (5) are radical combinations involving P° radical. Typical free enthalpy values ΔG_f are [12]:

Table 1
Kinetic parameters determined from Fig. 1, Eqs. (5) and (6).

T (°C)	$1/(r_{Ox})_{MAX}$	$(r_{Ox})_{MAX}$	$1/(r_{Ox})_{MAX} \cdot \beta$	β (l mol^{-1})	$\beta^2 \cdot (r_{Ox})_{MAX}$ (l mol^{-1} s^{-1})	$[O_2]_C$ (mol l^{-1})
155	52,295	1.91E-05	11.1	4711	424.4	1.1.E-03
200	5950.2	1.68E-04	1.6	3634	2219.1	1.4.E-03

$$\text{for}: (2)\mathrm{P}^{\circ} + \mathrm{O}_2 \rightarrow \mathrm{POO}^{\circ} \quad \Delta G_{\mathrm{f}} \sim -64\ \mathrm{kJ\ mol^{-1}}$$

$$\text{for}: (5)\mathrm{P}^{\circ} + \mathrm{POO}^{\circ} \rightarrow \mathrm{POOP} \quad \Delta G_{\mathrm{f}} \sim -235\ \mathrm{kJ\ mol^{-1}}$$

Both reactions are exothermal but POO° radicals are clearly more reactive than O_2. In other words, $k_5 >> k_2$.

$$\text{We know that}: \quad k_3 = \sqrt{\frac{(r_{OX})_{MAX} \cdot k_6}{2[PH]^2}} \tag{9}$$

Substituting k_6 by its value in (Eq. (9)):

$$k_3 = \frac{1}{2} \cdot \frac{k_5}{k_2} \cdot \frac{\beta \cdot (r_{\mathrm{OX}})_{\mathrm{MAX}}}{[\mathrm{PH}]} \tag{10}$$

so that: $k_3 = 3.7 \times 10^{-3} \cdot k_5/k_2$ at 155 °C and $2.5 \times 10^{-2} \cdot k_5/k_2$ at 200 °C. This equality will be discussed in the following of this article.

There is another way for determining indirectly k_3 from dissociation energy values for the scission of C—H bonds in α-position of the amino group (denoted by BDE in the following). In the second approach, we will use semi-empirical relationships linking BDE and Arrhenius parameters for k_3 i.e. the preexponential factor (denoted by k_{30}) and its activation energy E_3. According to Korcek et al. [17]:

$$\log k_3(30\ ^{\circ}\mathrm{C}) = 16.4 - 0.048 \times \mathrm{BDE(C-H)} \tag{11}$$

for secondary POO° radicals

$$E_3 = 0.55 \times (\mathrm{BDE(C-H)} - 261.5) \tag{12}$$

When only one rate constant value $k_3(T)$ at $T \neq 30$ °C is available, BDE can be calculated or obtained using Eqs. (11) and (12) by solving the following equation:

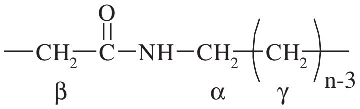
$$k_3(30\ ^{\circ}\mathrm{C}) = k_3(T) \cdot \exp\left[-\frac{550 \times (\mathrm{BDE} - 261.5)}{R} \times \left(\frac{1}{303} - \frac{1}{T}\right)\right] \tag{13}$$

Some literature data about $k_3(T)$ or E_3 and subsequent estimation of BDE using Eqs. (11) and (12) are given in Table 2.

BDE value is extracted and compared with the only value we found for BDE in polyglycine. BDE and thus E_3 values display relatively little scatter. The most probable values are:

$$\mathrm{BDE} \sim 355 - 360\ \mathrm{kJ\ mol^{-1}}$$

$$E_3 \sim 53 \pm 3\ \mathrm{kJ\ mol^{-1}}$$



$$-\mathrm{CH_2}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{NH}-\mathrm{CH_2}\left(\mathrm{CH_2}\right)_{n-3}$$

Fig. 2. Kinds of methylene units in PA.

E_3 was found significantly lower than in PE (73 kJ mol^{-1}) [20] explaining why aliphatic PA is more reactive than PE. However, three kinds of C—H bonds can be distinguished in PA (Fig. 2).

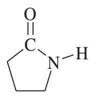
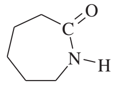
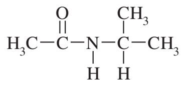
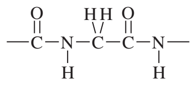
γ Methylenes (in the core of polymethylenic sequences) are expected to have a reactivity close to PE ones because inductive effects in saturated chains cannot propagate beyond one carbon as this is not through (e.g. shown in NMR). The feature of PA reactivity is therefore due to α or β carbons. As it will be shown below (see part 4 of 'Oxidation products' section), α carbons are the most reactive. In a first approach, it will be considered that oxidation occurs selectively on these carbons (their concentration is about 10.5 mol l^{-1} in PA6 and 5.5 mol l^{-1} in PA11). The relative ease of propagation in polyamides is linked to the destabilizing role of nitrogen atom on the neighboring methylene. The Arrhenius diagram of k_3 is given in Fig. 3.

α amino methylenes are almost as reactive as allylic methylenes in polybutadiene and much more reactive than tertiary C—H so that k_3 is rather high compared for example with PP as noted by George [21].

Using k_3 values from Fig. 3 and Eq. (9), it is now possible to assess k_3 and then k_6 from the experimental values of $(r_{\mathrm{OX}})_{\mathrm{MAX}}$. The resulting estimations are given in Table 3.

The termination reactions between POO° radicals appear very fast that is presumably due to the existence of an efficient disproportionation process (see section 1 of the 'Oxidation products'). Activation energy E_6 would be also very low. Let us recognize that the above results are to be considered with caution because they result from a unique set of measurements. However, the relatively low value found above can be tentatively checked from a series of papers by Gijsman et al. [22–25] in which several values of the oxygen absorption rate are reported. Those values lead to the Arrhenius plot of k_3^2/k_6 (Fig. 4).

Table 2
Estimation of BDE (αC—H) from kinetic parameters values reported by Denisov and Afanas'ev [18] and measured for polyglycine by Rauk et al. [19].

Molecule	T (K)	k_3 (l mol^{-1} s^{-1})	E_3 (kJ mol^{-1})	Ref.	BDE (C—H) (kJ mol^{-1})
	364	11.8		[18]	351.5
			55.5		362.9
 $\mathrm{H_3C}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\underset{\mathrm{H}}{\mathrm{N}}-\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_3}$	353	0.98		[18]	376.6
			54.4		360.9
 $-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\underset{\mathrm{H}}{\mathrm{N}}-\overset{\mathrm{H\,H}}{\mathrm{C}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\underset{\mathrm{H}}{\mathrm{N}}-$				[19]	350

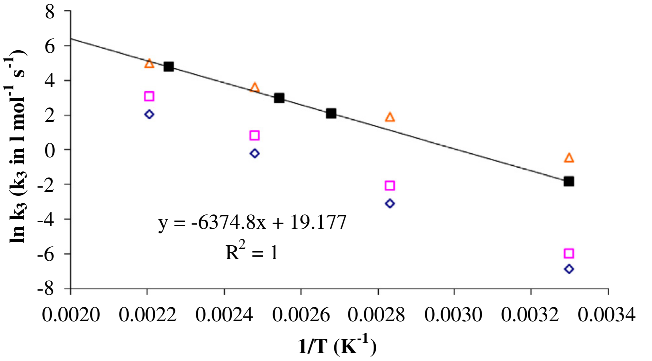


Fig. 3. Arrhenius diagram for k_3 in PA (■) with values PE (□, BDE = 395 kJ mol^{-1}), PP (◇, BDE = 385 kJ mol^{-1}) and BR (△, BDE = 345 kJ mol^{-1}) determined from Korcek's law.

From Arrhenius plot of k_3^2/k_6 (Fig. 4), it can be deduced that:

$$E_{OX} = 2E_3 - E_6 \sim 90 - 115 \text{ kJ mol}^{-1}$$

The upper limit is close to the value reported by Bernstein et al. [26]. Comparables values (73 kJ mol^{-1} [27] and 110 kJ mol^{-1} [28]) were observed considering the maximal chemiluminescence emission i.e. on the assumption that activation energy on $(I_{CL})_{MAX}$ is: $E_S = 2E_3 - E_6$ [29]. However, all data converge towards the fact that $2E_3 - E_6 \sim 90$ kJ mol^{-1} so that E_6 is relatively low. The exact value of E_6 and the coexistence of termination processes involving alkyl and peroxy radicals remains however open and requires studies under a wide range of oxygen pressures [12].

2.3. *Hydroperoxides decomposition*

The most striking feature of PA oxidation kinetics is the absence of induction period even at low temperature (60 °C) for samples having initially a low (eventually non measurable) hydroperoxides content. In the frame of the chosen mechanistic scheme, this behavior can be attributed to an especially low stability of PA hydroperoxides. If hydroperoxides decompose as soon as they are formed, they cannot accumulate and they cannot eventually reach the critical concentration necessary for bimolecular decomposition reaction to begin. Then, the POOH decomposition remains unimolecular in the whole course of oxidation. It will be assumed in the following that it is effectively the case for polyamides.

In the chosen mechanistic scheme, hydroperoxide concentration is expected to increase and to tend towards an asymptotic value $[\text{POOH}]_\infty$ corresponding to the steady state where POOH destruction by reaction (1u) is equilibrated by POOH formation by reaction (3). In oxygen excess regime, for unimolecular initiation, the steady state POOH concentration $[\text{POOH}]_S$ is theoretically given by:

$$[\text{POOH}]_\infty = \frac{k_3^2}{k_{1u}k_6} \cdot [\text{PH}]^2 \tag{14}$$

In fact, the substrate consumption induces a decrease of oxidation rate at high conversion and the matter that [POOH] passes through a maximum $[\text{POOH}]_{MAX}$ and then decreases more or less slowly [30]. In a first approximation, $[\text{POOH}]_{MAX}$ will be assumed close to $[\text{POOH}]_\infty$ and, for exposures in air under atmospheric pressure, the asymptote will be assumed close to the infinite value under oxygen excess $[\text{POOH}]_\infty$.

Table 3
Estimated k_3 and k_6 values from the results in Fig. 1.

	155 °C	200 °C	E (kJ mol^{-1})
k_3 (l mol^{-1} s^{-1})	102	421	53
k_6 (l mol^{-1} s^{-1})	3.1.E+10	5.9.E+10	25

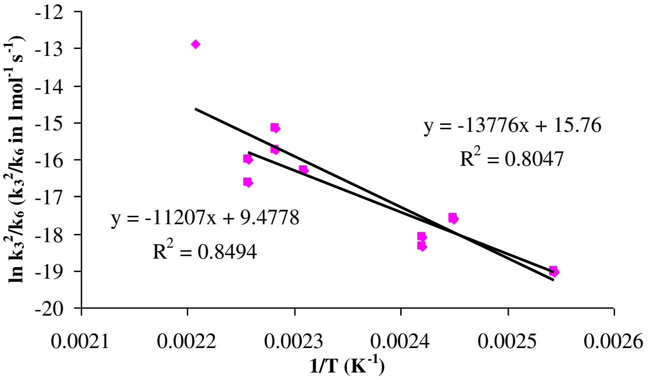


Fig. 4. Compilation of k_3^2/k_6 ratio for several polyamides from oxygen absorption measurements (two regression attempts were made the first one takes into account the data obtained at 180 °C, the corresponding activation energy is 115 kJ mol^{-1}, meanwhile the second attempt neglects this data to improve the correlation. The corresponding value of the activation energy is 93 kJ mol^{-1}). Symbols correspond to data extracted from Refs. [22–25].

It seemed to us interesting to compare available data on $[\text{POOH}]_{MAX}$ for polyolefins [30,31] and polyamide 6 [22] (Table 4).

The hydroperoxides concentrations at steady state appear noticeably lower for polyamides than for polyolefins. It can be linked to the especially low hydroperoxides stability in polyamides i.e. k_{1u} high values leading to low values for $[\text{POOH}]_\infty$ according to Eq. (14). One can notice these k_{1u} high values are consistent with a unimolecular decomposition mechanism.

It is noteworthy that $[\text{POOH}]_{MAX}$ is an increasing function of temperature for polyamides whereas it is a decreasing function of temperature for PE and PP. If $[\text{POOH}]_{MAX}$ is close to $[\text{POOH}]_\infty$ as hypothesized above, Eq. (14) leads to:

$$E_{POOH} = 2E_3 - E_{1u} - E_6 \tag{15}$$

E_{POOH} expressing the thermal stability of POOH: for example, when it is positive, it means that POOH becomes more stable at high temperature. Since $E_3 \sim 53$ kJ mol^{-1} for PA and 73 kJ mol^{-1} for PE, one can see that:

$$E_{1u} + E_6 < 106 \text{ kJ mol}^{-1} \text{for PA} \quad \text{where } E_{POOH} > 0 \tag{16}$$

$$E_{1u} + E_6 > 146 \text{ kJ mol}^{-1} \text{for PE} \quad \text{where } E_{POOH} < 0 \tag{17}$$

As discussed in 'Propagation and termination', E_6 is small (0–10 kJ mol^{-1}). This set of inequality also indicates that the activation energy of unimolecular hydroperoxide decomposition (E_{1u}) is considerably lower for polyamides ($E_{1u} < 106$ kJ mol^{-1}) than for PE ($E_{1u} = 140$ kJ mol^{-1}). As a confirmation $E_{1u} = 65$ kJ mol^{-1} was reported by George [21].

Table 4
Maximum hydroperoxide concentrations for some polyolefins and for polyamide 6.

Substrate	T (°C)	$[\text{POOH}]_{MAX}$ (mmol l^{-1})	Ref.
PE	160	228	[31]
PE	160	326	[31]
PP	120	800	[30]
PP	100	1000	[30]
PP	80	1200	[30]
PP	60	1500	[30]
PA6	140	20	[22]
PA6	120	7	[22]

Let us now consider the initiation rate constant k_{1u} values for unimolecular decomposition. We have two available sets of data:

- the first one for PA11 and PA12 hydroperoxides by Lemaire et al. [32,33] at 60 °C.
- the second one on model amide hydroperoxides by Sagar [34] at 131 and 77 °C.

In the case of PA11 and PA12, rate constants were not reported. We tried to determine them from the experimental curves of [POOH] decay at 60 °C (Fig. 5).

Two attempts were made:

- one with the unimolecular model:

$$[\mathrm{POOH}] = [\mathrm{POOH}]_0 \cdot \exp(-k_{1u} \cdot t) \tag{18}$$

- the other with the bimolecular model:

$$1/[\mathrm{POOH}] - 1/[\mathrm{POOH}]_0 = k_{1b} \cdot t \tag{19}$$

Both models are almost undistinguishable owing the data scatter. The results do not permit to demonstrate the unimolecular character of POOH but bimolecular reaction does not fit other observations as written above. Thus, we supposed that initiation occurred only by unimolecular POOH decomposition and the corresponding k_{1u} values are listed in Table 5.

In the case of model compounds (Table 5), it is possible to assess the activation energy E_{1u} at ca 90 kJ mol^{-1} consistently with the inequality (Eq. (17)). Activation energy E_{1u} for polyamides can also be assessed from the results of Table 5. We know that for a true first order process, the preexponential factor k_{1u0} is sharply linked to the frequency of the corresponding molecular vibration i.e. $k_{1u0} \sim 10^{13}$ s^{-1}. Activation energy would be thus 115 kJ mol^{-1} i.e. slightly higher than the value previously found for model compounds (90 kJ mol^{-1}) but of the same order of magnitude and anyhow, significantly lower than for polyolefin ones. The low value of E_6 (Fig. 4) is thus confirmed.

Since inductive effects cannot propagate beyond one carbon atom in a saturated chain, it can be assumed that methylenes in the core of polyethylene sequences in aliphatic polyamides do not differ significantly from polyethylene sequences. It can be deduced that the high instability of PA hydroperoxides is linked to their placement in α-position of amide groups, more precisely to nitrogen atoms of which the destabilizing role on adjacent hydroperoxide is well known [6,33].

2.4. To summarize literature data on rate constants

Literature data are too scarce and too scattered to allow precise assessments of elementary rate constants but their analysis leads to relatively clear conclusions:

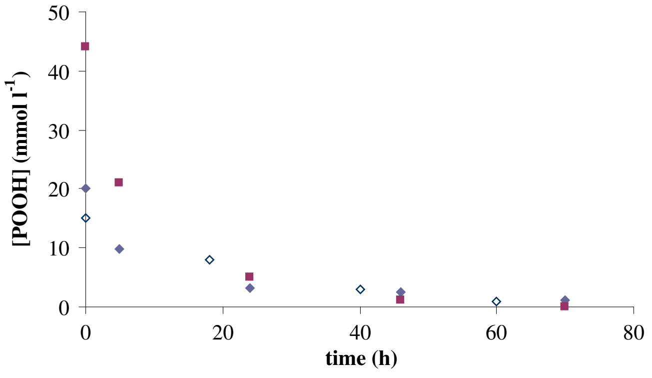
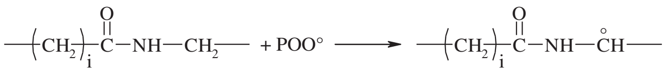


Fig. 5. Kinetics of POOH thermolysis in PA11 (◆, ◇) and PA12 (■) at 60 °C [32,33].

① Polyamides are more reactive towards oxygen than polyolefins. This is due to the high reactivity of the α amino methylene. The oxidative attack displays a relatively high selectivity on this group:



$$-\!\left(CH_2\right)_i\!-\overset{\displaystyle O}{\overset{\|}{C}}-NH-CH_2- \;+ POO^\circ \longrightarrow -\!\left(CH_2\right)_i\!-\overset{\displaystyle O}{\overset{\|}{C}}-NH-\overset{\circ}{C}H-$$

② As far as auto-oxidation is concerned, another factor contributes strongly to the PA oxidizability: the hydroperoxide instability which is responsible for:
- The absence of induction period,
- The fact that POOH decomposition occurs in unimolecular mode,
- The relatively low maximum POOH concentration.

③ In air at atmospheric pressure, oxygen is not in excess, which means that termination reactions occur partly by P° + POO° combination [12]. Its rate constant k_5 is significantly higher than the rate constant k_2 of oxygen addition on alkyl radicals.

④ Termination P° + POO° but also POO° + POO° are very fast compared to those of polyethylene. One can suspect that it is due to the existence of an efficient disproportionation process.

2.5. Simulation of kinetic curves

Gijsman et al. [16] published kinetic curves of oxygen uptake and carbonyl build-up at several temperatures ranging between 120 and 170 °C under 1 bar oxygen pressure for PA6. The curves are reproduced in Figs. 6 and 7 together with a first kinetic modeling (see below).

Let us first note that oxygen consumption rate at 120 °C (Fig. 6) would be in the order of 10^{-7} mol l^{-1} s^{-1}. A simplified approach for diffusion coupling [35] leads to:

$$\mathrm{TOL}^2 = \frac{D_{O_2} \cdot [O_2]}{r_{OX}} \tag{20}$$

Using $[O_2] \sim 3.10^{-4}$ mol^{-1} (see above) and $D_{O_2} \sim 5 \times 10^{-11}$ m^2 s^{-1} [6], one finds: TOL $\sim 10^{-4}$ m. In other words, oxidation would not be diffusion controlled in those samples. In the following of such a comprehensive study, we will keep the hypothesis of a homogeneous oxidation.

These results are especially interesting because, for the chosen oxygen pressure, PA oxidation is not too far from the oxygen excess regime that allows suppressing reactions (4) and (5) in the mechanistic scheme. The kinetic scheme is thus composed of the following equations:

$$\frac{d[P^\circ]}{dt} = 2k_{1u}[\mathrm{POOH}] - k_2[P^\circ][O_2] + k_3[\mathrm{POO}^\circ][\mathrm{PH}] \tag{21}$$

$$\frac{d[\mathrm{POO}^\circ]}{dt} = k_2[P^\circ][O_2] - k_3[\mathrm{POO}^\circ][\mathrm{PH}] - 2k_6[\mathrm{POO}^\circ]^2 \tag{22}$$

$$\frac{d[\mathrm{POOH}]}{dt} = -k_{1u}[\mathrm{POOH}] + k_3[\mathrm{POO}^\circ][\mathrm{PH}] \tag{23}$$

$$\frac{d[\mathrm{PH}]}{dt} = -\gamma_{1u}k_{1u}[\mathrm{POOH}] - k_3[\mathrm{POO}^\circ][\mathrm{PH}] \tag{24}$$

where γ_1 is the yield in PH consumed per initiation event.

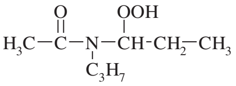
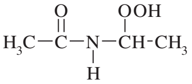
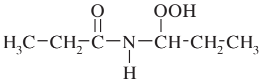
It was shown that the following initial condition can be used [36]:

At $t = 0, [P^\circ] = [\mathrm{POO}^\circ] = 0$

$[\mathrm{POOH}]_0 = 10^{-3}$mol l^{-1}

$[\mathrm{PH}]_0 = 12$ mol l^{-1}for PA6

Table 5
Literature data on the first order rate constant of POOH decomposition in several model compounds, PA11 and PA12, PE and PP.

Molecule	131 °C		77 °C		60 °C		Ref.
	c_0 (mol l^{-1})	k_u (s^{-1})	c_0 (mol l^{-1})	k_u (s^{-1})	c_0 (mol l^{-1})	k_u (s^{-1})	
 $H_3C-C(=O)-N(C_3H_7)-CH(OOH)-CH_2-CH_3$	0.725	4.78×10^{-4}					[34]
 $H_3C-C(=O)-N(H)-CH(OOH)-CH_3$	0.491	8.28×10^{-4}					[34]
 $H_3C-CH_2-C(=O)-N(H)-CH(OOH)-CH_2CH_3$	0.525	8.22×10^{-4}					[34]
	0.2	6.90×10^{-4}	0.548	4.35×10^{-6}			
	0.185	6.38×10^{-4}					
	0.065	5.50×10^{-4}	0.222	1.35×10^{-5}			
PA11					0.015–0.020	1.35×10^{-5}	[32,34]
PA12					0.044	2.1×10^{-5}	[32,33]
PE		6.4×10^{-6}		1.0×10^{-8}		8.7×10^{-10}	[20]
PP		5.9×10^{-6}		1.2×10^{-8}		1.1×10^{-9}	[12]

The oxygen consumption rate is given, in non-diffusion controlled conditions by:

$$\frac{d[O_2]}{dt} = -k_2[P^\circ][O_2] + k_6[POO^\circ]^2 \tag{25}$$

For carbonyl groups, it is supposed that, in the whole oxidation course, the kinetic regime is close to the steady state so that initiation and termination rates are almost equal. In these conditions, it is licit to consider that carbonyls are formed only in initiation step but including in γ_{CO} the contribution of termination events:

$$\frac{d[P{=}O]}{dt} = \gamma_{CO} k_{1u}[POOH] \tag{26}$$

k_2 was fixed equal to 10^8 l mol^{-1} and k_3 was taken from Fig. 3 and the oxygen solubility $S_{O_2} = 1.5 \times 10^{-8}$ mol l^{-1} Pa^{-1}, we determined the rate constants values giving the best fit of experimental data using a try and error procedure. The resulting rate constants are listed in Table 6. It is found: $E_{1u} \sim 82$ kJ mol^{-1} and $E_6 = 0$ so that the inequality (16) is fulfilled.

These results (Figs. 6 and 7) call for the following comments:

① Globally, the model composed of the above differential equations simulates relatively well the curves of carbonyl build-up but not oxygen uptake. This is not surprising if we consider the number of parameters and the simplicity of the curves, which could be described by functions having one or two parameters.

② k_6 appears relatively high. In fact, as written above, termination involving P° radicals certainly have an influence (and especially if oxidation process is diffusion limited which was not taken into account here). It was shown that $k_3 = \delta \cdot k_5 / k_2$ (δ being equal to 3.7×10^{-3} at 155 and 2.5×10^{-2} respectively at 155 and 200 °C). Even if there is of course some uncertainty on the δ value, this conclusion militates in favor of k_5 being at least 100 or 1000 times higher than k_2 as observed for instance in PE. In other words, the model employed here neglects the termination between P° and POO° that is compensated by an anomalously high k_6 value. A kinetic model taking into account terminations involving P° radicals in PA is under investigation in our laboratory.

③ The simulation has been obtained with a set of parameters values confirming the trends deduced from the preceding analysis of literature data i.e. the need for high values of initiation and propagation rate constants but also of termination one. The combination of such features is not obvious. The fact that the temperature effect is well simulated with such a complex combination of physically valid activation energies is also a positive effect in favor of this model.

④ There is however an apparent discrepancy in the early period of exposure especially in oxygen uptake curves where

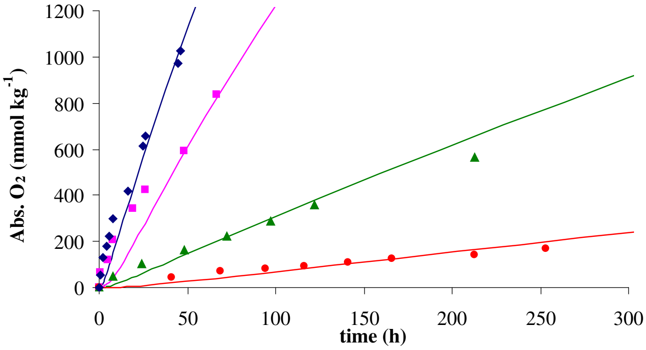


Fig. 6. Simulation of oxygen uptake (full lines) compared with experimental results at 120 (●), 140 (▲), 160 (■) and 170 °C (◆).

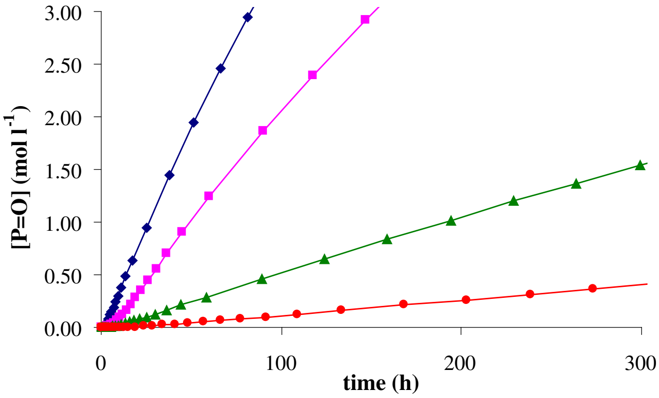


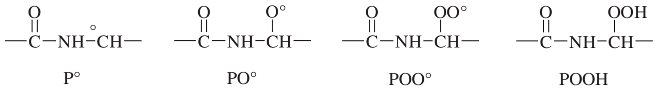
Fig. 7. Simulation of carbonyl build-up results under 1 bar oxygen at 120 (●), 140 (▲), 160 (■) and 170 °C (◆).

experimental oxidation rates are higher than predicted ones. Experimental curves display an inflexion point which is impossible to simulate with the above kinetic scheme. Among the possible explanations of this behavior, one can mention the hypothesis of radical generation by polymer thermolysis, as shown for instance in the case of PA12 by chemiluminescence measurements [28]. These results can be summarized as follows: the sample is maintained under nitrogen for a time t_1 at a chosen temperature. Then oxygen is admitted in the cell and a light burst of intensity I_{MAx} is immediately emitted by the sample. I_{MAx} is an increasing function of t_1. There is apparently no other explanation of this phenomenon than the existence of a process of radical generation by polymer thermolysis. It remains to check its rate is low at the temperature under consideration so that it dominates in the early stage of exposure but becomes rapidly negligible relatively to hydroperoxides decomposition.

3. Oxidation products

3.1. Imides

Since it is widely recognized that α amino methylenes are the most reactive groups in radical oxidation, most of the stable products must result from reactions of the corresponding radicals and hydroperoxides i.e.:



Imides (P=O) appear practically always as a major stable product [3,37]. They result obviously from attacks of α amino methylenes through disproportionation processes. Various mechanisms can be imagined:

(Ia) $\mathrm{POOH} \rightarrow [\mathrm{PO}^{\circ}\ {}^{\circ}\mathrm{OH}]_{cage} \rightarrow \mathrm{P{=}O} + \mathrm{H_2O}$

(Ib) $\mathrm{POOH} + \mathrm{POOH} \rightarrow \mathrm{H_2O} + [\mathrm{POO}^{\circ}\,{}^{\circ}\mathrm{OP}]_{cage} \rightarrow \mathrm{POOH} + \mathrm{P{=}O} + \mathrm{H_2O}$

(Ic) $\mathrm{POO}^{\circ} + \mathrm{POOH} \rightarrow \mathrm{POOH} + \mathrm{P{=}O} + \mathrm{HO}^{\circ}$

(Id) $\mathrm{POO}^{\circ} + \mathrm{POO}^{\circ}[\mathrm{PO}^{\circ}\ {}^{\circ}\mathrm{OP}]_{cage} + \mathrm{O_2} \rightarrow \mathrm{P{=}O} + \mathrm{POH}$

- Processes Ia and Ib would contribute to lower the efficiency of initiation. If they were the predominant source of imides, it would be difficult to explain the high efficiency of initiation by POOH decomposition.
- Process Ic is an induced POOH decomposition. It replaces a relatively selective POO° radical by a highly reactive (and non selective) HO° radical. Here, it would be difficult to explain the high selectivity of oxidative attack on polyamides.
- Process Id is probably the predominant termination mode in oxygen excess but it carries also an inconvenient linked to the formation of an apparently unstable alcohol (see below).

Table 6
Rate constants values for best fit of Figs. 6 and 7.

T (°C)	k_{1u} (s^{-1})	k_2 (l mol^{-1} s^{-1})	k_3 (l mol^{-1} s^{-1})	k_6 (l mol^{-1} s^{-1})	[POOH]$_{inf}$ (mol l^{-1})
170	$5*10^{-4}$	10^8	170	$5*10^{11}$	0.017
160	$3*10^{-4}$	10^8	121	$5*10^{11}$	0.014
140	$1*10^{-4}$	10^8	60	$5*10^{11}$	0.010
120	$3*10^{-5}$	10^8	27	$5*10^{11}$	0.007

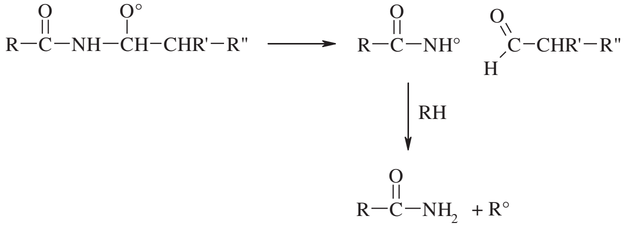
Many authors [34,38–40] have studied the decomposition of α amino hydroperoxides. Their results are summarized in Table 7.

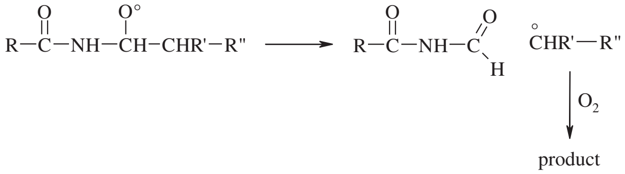
These results call for the following comments:

① α Amino hydroperoxides are effectively unstable since their decomposition can be studied even at low temperatures.
② Imides are effectively the major oxidation products.
③ Their yield appears as a decreasing function of temperature. In other words, there is a competitive process having a higher activation energy.
④ The imide yield is considerably higher in heterocycles than in aliphatic amides. The simplest interpretation is that there is a conformation favored in aliphatic amides and forbidden in heterocyclic ones, favoring the above mentioned competitive processes.
⑤ α Amino alcohols are not observed in other words if they are formed, they decompose fast into more stable products.

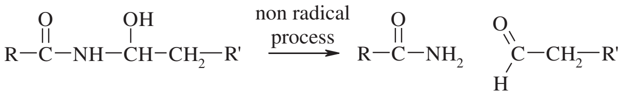
3.2. Aldehydes, acids

According to the data of Table 7, all the other stable products of the α amino hydroperoxides would result from β scissions of the corresponding alkoxy radicals. Two modes of β scission could be imagined:

IIa


IIb


But, as it has been previously shown, some disproportionation events responsible for the formation of imides can also give secondary α amino alcohols. These latter are unstable and could decompose into primary amide and aldehyde:

IIc


$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}NH{-}\overset{OH}{\overset{|}{C}H}{-}CH_2{-}R'} \xrightarrow[\text{process}]{\text{non radical}} \mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}NH_2} \quad \mathrm{\overset{O}{\underset{H}{C}}{-}CH_2{-}R'}$$

In the presence of oxygen, aldehydes can be rapidly converted into acids.

When, in case I2 (see Table 7), ethanol is formed, one can suppose that it is a product of the oxidation of the primary alkyl radical resulting from the β scission IIb. It can be reasonably supposed that the competition β scission IIa leading to an aminyl radical is thermochemically disfavored so that, if pairs of primary amide and aldehyde are formed, they result from the decomposition of α amino alcohols (reaction IIc).

Table 7
Literature data about oxidation products of amide model compounds.

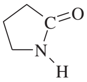
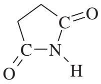
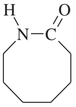
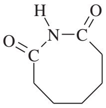
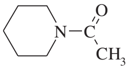
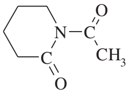
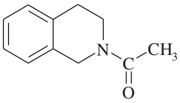
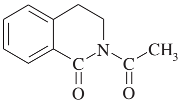
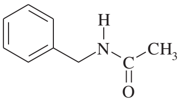
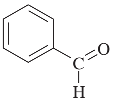
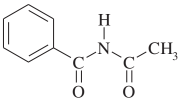
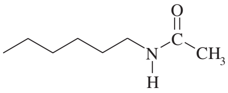
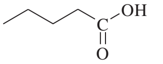
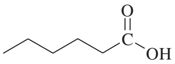
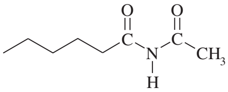
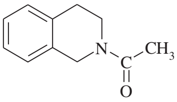
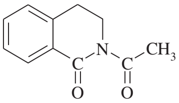
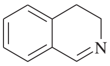
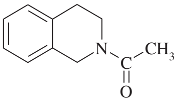
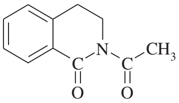
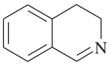
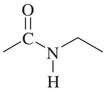
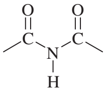
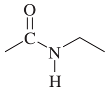
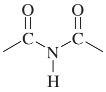
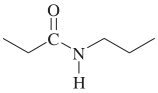
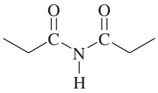
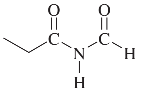
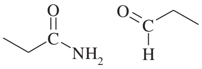
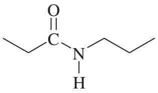
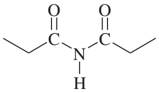
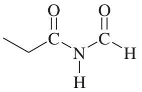
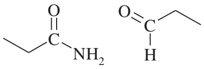
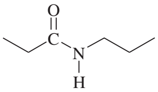
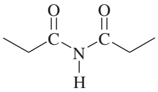
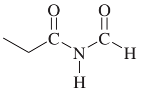
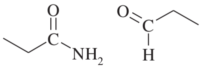
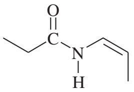
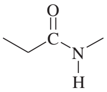
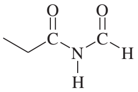
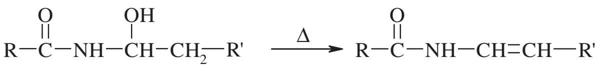
Amide	*T* (°C)	Code	Products	Presumed process of formation	Yield (%)	γ_S/γ_{CO}	Ref.
	80	A		I	90–93		[38,39]
	80	B		I	98		[39]
	80	C		I	42–94		[38,39]
	20	D		I	87		[38]
	20	E1 E2	 	IIc I	19 69	0.22	[38]
	80	F1 F2 F3	  	? IIc I	14 13 37	0.42	[38]
	20	G1 G2	 	I III	91 7	0.07	[39]
	80	G1 G2	 	I III	87 10	0.10	[39]
	0	H		I	73		[40]

Table 7 (*continued*)

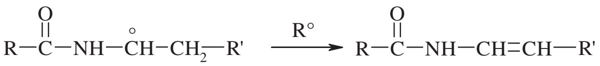
Amide	*T* (°C)	Code	Products	Presumed process of formation	Yield (%)	γ_S/γ_{CO}	Ref.
	75	H		I	38		[40]
	0	I1 I2 13	  + EtOH 	I IIb IIa	48 3 14	0.26	[40]
	75	I1 I2 I3	  + EtOH 	I IIb IIa	19 26 3	0.60	[40]
	131	I1 I2 I3 I4	  + EtOH  	I IIb IIa III	40 30 15 15	0.45	[40]
	75	J		IIb	39	–	[40]

The formation of unsaturated amides (I4) seems to occur only at high temperature (131 °C) since these products are not observed, for the same substrate at 75 and 0 °C. One can imagine a dehydration of secondary alcohols:

IIIa 

$$\mathrm{R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NH{-}\overset{\displaystyle OH}{\overset{|}{C}H}{-}CH_2{-}R'} \xrightarrow{\Delta} \mathrm{R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NH{-}CH{=}CH{-}R'}$$

or a disproportionation involving a P° radical:

IIIb 

$$\mathrm{R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NH{-}\overset{\circ}{C}H{-}CH_2{-}R'} \xrightarrow{R^\circ} \mathrm{R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NH{-}CH{=}CH{-}R'}$$

where R° can be another alkyl radical, an alkoxy radical or peroxy radical.

3.3. *Chain scissions*

Chain scission is a very important process in practice because it is the main cause of embrittlement of polymers undergoing aging [41]. Almost all the reactions competing with imide formation, except IIIa and IIIb are chain scissions. Assuming that Table 7 gives an exhaustive view of reaction products, one can estimate the yield of chain scissions per POOH decomposition event. It varies from 0 to 0.6. These results are however to be taken with cautions. For instance, in the case of n propyl amide (I), the yield of chain scission seems to vary non-monotonously with temperature, which seems surprising.

In the case of aliphatic polyamides, there is relatively few information. In the case of photooxidation, Margolin [42] observed that there is about one chain scission per 6 oxygen molecules reacted, a ratio 3 times lower than for PP [43]. Another interesting comparison can be made: in polyolefins, embrittlement (due to chain scission), occurs at very low conversion eventually before the carbonyl groups can be detected by IRTF [44,45]. In polyamides in contrast, embrittlement occurs when CO build up is reaching a plateau [22,46,47]. For these polymers, as for polyolefin's, chain scission induces chemicrystallization [41]. The difference between polyamides and polyolefins could thus be due to the lower yield of chain scission (per carbonyl group) in polyamides. The only way to reconcile this trend (if it is comforted in the future) with the available analytical data is to suppose that imides are formed in reactions Ia, Ib or Ic but not in Id because, in this case, owing to the unstability of α amido alcohol resulting from the disproportionation, there would be equality of imides and chain scission yields. But reactions Ia, Ib and Ic are not devoid of inconvenient:

- reaction Ia is disfavored by the small size of hydroxyl radicals which can easily escape from the cage.
- reactions Ib and Ic are disfavored by the low POOH concentrations (see above).

If reaction Id is not frequent, we have to imagine another very efficient termination process, which is not obvious. For us, the key question of chain scission mechanism remains open.

3.4. *Other products*

It is now clear that oxidation products of polyamides result mainly from the attack of α amino methylenes but is this attack totally selective?

No doubt, the other methylenes are reactive, otherwise PE would be stable in the 120–170 °C temperature range, which is not the case.

Many authors have hypothesized that only α CH_2 is attacked [48–50]. However other authors have reached the opposite conclusion [51,52]. Polyamides undergo discoloration during their oxidation and the above mentioned products of a methylenes oxidation are not chromophores. Li et al. [53] supposed that CO groups reacting from the attack of the β methylenes could be the cause of discoloration. According to Allen et al. [54], the phosphorescence of oxidized polyamides would be due to α,β unsaturated ketones whereas for George [13], it would be due to unsaturated amides resulting from the exclusive attack of α methylenes. Levantovskaya [55] proposed an intramolecular reaction between α amino peroxyl and β CH_2 to explain the formation of formaldehyde in thermal oxidation of polyamide.

A simple calculation (see Appendix 1) shows that for a fully selective attack of α methylenes (they would be at least 100 times more reactive than β methylene), the difference of bond dissociation energy (BDE) must be higher than 56 kJ mol^{-1} which is too high. Finally, it seems that the attack of β methylenes cannot be neglected. Its modeling needs to use a co-oxidation scheme which is now possible [56].

Regarding discoloration, it must be noticed that if the presence of unsaturated species (I4 in Table 7) is confirmed, it indicates the existence of disproportionation processes involving P° radicals only possible in oxygen deficit regime. If these species were responsible for discoloration, they would disappear in oxygen excess which remains to demonstrate.

4. Conclusion

From this survey of literature data relative to mechanisms and kinetics of aliphatic amides oxidation, we reached the following conclusions:

① The data are too partial and too scattered to permit precise determination of elementary rate constants. However, it was possible to make interesting estimations and comparisons with polyolefins and especially polyethylene.
② There is a wide consensus on the fact that α amino methylenes are considerably most reactive than all the other methylenes. In a first approach, one can consider that oxidation attacks only α amino methylenes.
③ This attack leads first to α amino hydroperoxides (a POOH), which are strongly destabilized by the inductive effect of neighboring (electronegative) nitrogen atom. This instability carries important consequences: first, oxidation kinetics do not display induction period, even at relatively low temperatures (<100 °C). Secondly, POOH decomposition occurs mainly by unimolecular mode. Thirdly, POOH concentration remains low (compared to polyolefins). Fourthly, the activation energy of POOH decomposition (i.e. of radical initiation for chain oxidation) is relatively low (compared to polyolefins).
④ Propagation by hydrogen abstraction is faster than for polyolefins, that explains the selectivity of the attack on the α methylenes. Its activation energy E_3 ($\sim$50 kJ mol^{-1}) is lower than the one in polyethylene (i.e. the methylenes others than α methylene in polyamides for which $E_3 \sim 70$ kJ mol^{-1}).
⑤ Termination is also very fast probably thanks to very efficient disproportionation processes.
⑥ The oxidation of α methylenes leads mainly to imide groups. At least four elementary processes can be involved in imide formation.
⑦ Most of the other oxidation products of α methylenes result from rearrangements of α amino alkoxyls or α amino hydroxyls leading to chain scissions with terminal aldehydes or alcohols. The yield of chain scission seems to be lower than for polyolefins but the reason is not well understood.
⑧ It is difficult to imagine that methylenes other than α amino ones are totally unreactive. Their attack seems to be responsible for chromophore formation and the resulting polyamide discoloration. Many hypotheses have been emitted for this phenomenon but they need to be checked. Accounting for methylenes other than α methylenes ones will need to build a co-oxidation kinetic model.

Appendix A

For a polyamide *j*, the propagation steps would be then written:

$$3\alpha \quad POO^\circ + \alpha PH \rightarrow POOH + \alpha P^\circ \quad k_{3\alpha}$$

$$3\beta \quad POO^\circ + \beta PH \rightarrow POOH + \beta P^\circ \quad k_{3\beta}$$

The reaction rates are:

$$r_{3\alpha} = k_{3\alpha}[POO^\circ][\alpha PH]$$
$$r_{3\beta} = k_{3\beta}[POO^\circ][\beta PH] = (j-1)\cdot k_{3\beta}[POO^\circ][\alpha PH]$$

In other words : $r_{3\beta}/r_{3\alpha} = (j-1)\cdot k_{3\beta}/k_{3\alpha}$ where for instance $j = 5$ for PA6 and $j = 10$ for PA11. The condition for a total selectivity would be thus:

$$r_{3\alpha} \gg r_{3\beta}$$

$$\frac{k_{3\beta}}{k_{3\alpha}} \gg j-1$$

Let us consider that in practice, the rates must differ by at least more than two decades:

$$\frac{k_{3\beta}}{k_{3\alpha}} \gg 100 \cdot (j-1) \quad \text{or :} \quad \ln\left(\frac{k_{3\beta}}{k_{3\alpha}}\right) \gg \ln 100 \cdot (j-1)$$

According to Korcek et al. [17]:

$$\ln\left(\frac{k_{3\beta}}{k_{3\alpha}}\right) = 2.3 \times 0.048 \times \Delta \mathrm{BDE}$$

where ΔBDE is the difference of dissociation energies of αCH and βCH bonds. Combining both above relationships, one obtains the conditions:

$$\mathrm{DBDE} > \ln\left(100 \cdot \frac{j-1}{0.11}\right)$$

i.e. $\Delta \mathrm{BDE} > 56\ \mathrm{kJ\ mol^{-1}}$ for $j \geq 6$.

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