



Review article

Review: Auto-oxidation of aliphatic polyamides



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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.

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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].

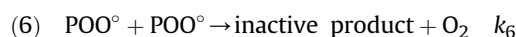
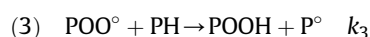
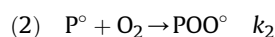
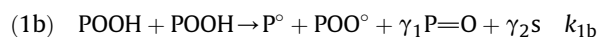
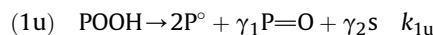
It seemed interesting to us to revisit the literature through the prism of kinetic analysis trying to extract suitable information on elementary rate constants from available data and to compare systematically polyamides with polyolefins especially with polyethylene which could be considered as 'PA ∞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



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 $^\circ$ radicals is negligible.

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- 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.

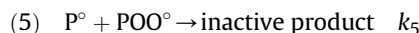
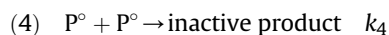
This set of hypotheses was first used by Tobolsky et al. [9]. In the kinetic analysis, one considers generally that a steady state is reached at a low conversion ratio, in other words that substrate consumption is negligible. It will also be supposed here that oxidation is not diffusion controlled in 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 $k_3[\text{PH}]/k_6^{1/2}$ 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 peroxy 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:

$$(r_{\text{OX}})_{\text{MAX}} = -\frac{d[\text{O}_2]}{dt} = 2 \frac{k_3^2 [\text{PH}]^2}{k_6} \quad (1)$$

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



The best way to determine $(r_{\text{OX}})_{\text{MAX}}$ 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 $[\text{O}_2]$ in polymer is given by:

$$[\text{O}_2] = S_{\text{O}_2} \times P_{\text{O}_2} \quad (2)$$

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

In polyamides, $S_{\text{O}_2} = 1.5 \times 10^{-8} \text{ mol l}^{-1} \text{ Pa}^{-1}$ [10] so that: $[\text{O}_2] = 3 \times 10^{-4} \text{ mol l}^{-1}$ 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]:

$$r_{\text{OX}} = (r_{\text{OX}})_{\text{MAX}} \cdot \frac{\beta [\text{O}_2]}{1 + \beta [\text{O}_2]} \quad (3)$$

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

The curve $r_{\text{OX}} = f([\text{O}_2])$ is a hyperbole having a horizontal asymptote at $r_{\text{OX}} = (r_{\text{OX}})_{\text{MAX}}$. $(r_{\text{OX}})_{\text{MAX}}$ and β can be determined graphically from a graph “ $1/r_{\text{OX}}$ vs $1/[\text{O}_2]$ ”:

$$\frac{1}{r_{\text{OX}}} = \frac{1}{(r_{\text{OX}})_{\text{MAX}}} + \frac{1}{\beta \cdot (r_{\text{OX}})_{\text{MAX}} \cdot [\text{O}_2]} \quad (5)$$

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.

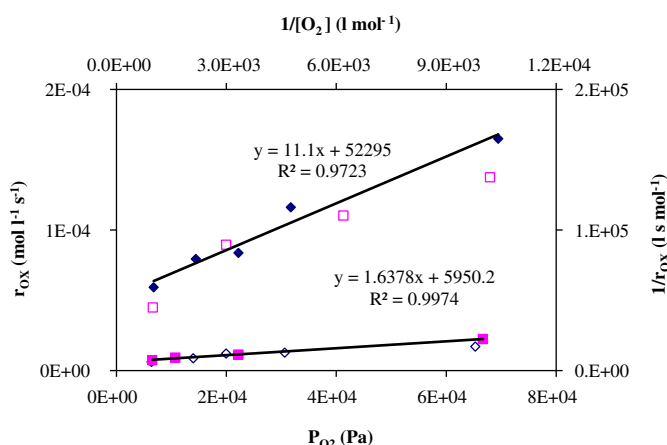


Fig. 1. Effect of oxygen pressure on oxidation rate of PA6 at 155 (◆, ◇) and 200 °C (■, □). Close symbols correspond to $1/r_{\text{O}_2}$ vs $1/[\text{O}_2]$ and open ones to r_{O_2} vs P_{O_2} .

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

A critical oxygen pressure ($[\text{O}_2]_{\text{C}}$) can be defined as follows:

- $[\text{O}_2] > [\text{O}_2]_{\text{C}}$, oxidation is considered as in excess oxygen regime i.e. that all P° are scavenged into POO° and termination kinetics mainly occur by the $\text{POO}^\circ + \text{POO}^\circ$ coupling and oxidation rate reaches a maximal value $(r_{\text{O}_2})_{\text{MAX}}$.
- $[\text{O}_2] < [\text{O}_2]_{\text{C}}$, termination kinetics occur by the three reactions of radical coupling and termination rate is given by Achimsky [16]:

$$[\text{O}_2]_{\text{C}} = 1.2/\beta^{-1} \quad (6)$$

Using $P_{\text{atm}} = 0.02 \text{ MPa}$, and $S_{\text{O}_2} = 1.5 \times 10^{-8} \text{ mol l}^{-1} \text{ Pa}^{-1}$, it is found: $[\text{O}_2]_{\text{atm}} = 3 \times 10^{-4} \text{ mol l}^{-1}$ so that: $[\text{O}_2]_{\text{C}} > [\text{O}_2]_{\text{atm}}$ ($[\text{O}_2]_{\text{atm}}$ 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 $(r_{\text{OX}})_{\text{MAX}}$:

$$\beta = \frac{k_2}{k_5} \cdot \sqrt{\frac{2k_6}{(r_{\text{OX}})_{\text{MAX}}}} \quad (7)$$

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

where $\beta^2 \cdot r_{\text{OX}} \sim 420 \text{ mol l}^{-1} \text{ s}^{-1}$ 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)	$1/(r_{\text{OX}})_{\text{MAX}}$	$(r_{\text{OX}})_{\text{MAX}}$	$1/(r_{\text{OX}})_{\text{MAX}} \cdot \beta$	β (l mol ⁻¹)	$\beta^2 \cdot (r_{\text{OX}})_{\text{MAX}}$ (l mol ⁻¹ s ⁻¹)	$[\text{O}_2]_{\text{C}}$ (mol l ⁻¹)
155	52,295	1.91E-05	11.1	4711	424.4	1.1E-03
200	5950.2	1.68E-04	1.6	3634	2219.1	1.4E-03

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