Thermooxidative Ageing of Polyoxymethylene, Part 1: Chemical Aspects

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ABSTRACT: The thermal oxidation of unstabilised POM homopolymer has been studied at 90, 110, and 130°C under various oxygen pressures ranging from 0 to 2.0 MPa by gravimetry and IR spectrometry. This latter reveals essentially the formation of formate (F) groups and alcohols in smaller quantities. The formate growth and mass loss rates increase pseudo hyperbolically with oxygen pressure, the asymptotic level being reached at pressures up to 0.5 MPa. These results lead to propose a mechanistic scheme of radical chain oxidation in which depolymerization is initiated by hydroperoxide unimolecular decomposition, one formate and one chain scission being formed per decomposition event whereas the kinetic chain length of the depolymerization zip is of the order of 100. A kinetic model derived from the mechanistic scheme, taking into account substrate consumption, simulates correctly the shape of kinetic curves and the effect of temperature and oxygen pressure. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1783–1792, 2008

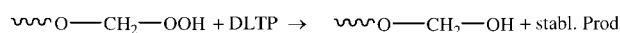**Key words:** polyoxymethylene; thermooxidation; mechanisms; kinetics

INTRODUCTION

Polyoxymethylene (POM) is often cited as an example of polymer undergoing predominant depolymerization during thermal aging at processing temperatures, typically above 150°C.[1] POM became an industrial polymer, at the end of 50s, when the problem of its short-term instability was solved by chain end capping or by introduction of randomly distributed ethylenic groups in the chains. POM depolymerization is characterized by relatively high apparent activation energy so that its rate tends to be negligible in the domain of use temperatures. Furthermore, POM crystallizes easily owing to its high structural symmetry, and since most of the low temperature aging processes (oxidation, hydrolysis, etc.) involve the transport of low molar weight species (oxygen, water) into the polymer. These processes are expected to be prevented in the crystalline phase owing to its impermeability to these reagents. As the amorphous phase is permeable to O_2, its degradation can affect certain use properties, for instance mechanical ones. Hydrolysis is expected only in the presence of acids,[2] e.g., in very peculiar used conditions. In contrast, oxidation is expected to be relatively easy, owing to the high reactivity of etheric methylenes to hydrogen abstractions by radicals.[3] It was shown very soon that POM thermal ageing is noticeable accelerated in the presence of oxygen.[1] Most of the fundamental published works on POM oxidation mechanisms, originated from two research groups from the former USSR, one was directed by Yenikolopyan and coworkers,[2,4–8] the other by Neiman and coworkers.[9–11] Both groups took distinct points of view: the former one considered that the predominant process is depolymerization and that oxygen can play an accelerating role transforming the monomer: formaldehyde, into formic acid, of which the catalytic role on depolymerization is well established. The Neiman's group considered rather the role of hydroperoxides resulting from the radical chain oxidation. Sukhov et al. tried to make a synthesis of both works in 1969.[2] What was clearly established is that, thermal ageing of POM at moderate temperatures (typically below 150°C) results essentially from radical chain processes. Indeed, this mechanism has been put in evidence by the accelerating role of radical initiators such as peroxides[12] and by the stabilizing role of well known radical scavengers such as hindered phenols or nitroxy radicals.[11] It is reasonable to assume that oxidation radical chains, which produce hydroperoxides are initiated by decomposition of these latter that explains the autoaccelerated character of the kinetics. An attempt was made to check the initiating roles of hydroperoxides, using a well known hydroperoxide decomposer: the dilaurylthio-
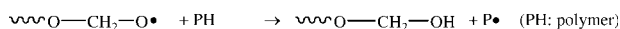
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dipropionate (DLTP) as stabilizer. The results were somewhat ambiguous: DLTP slows down oxygen uptake but accelerates mass loss (due to depolymerization). The explanation given by the authors[2] can be summarized as follows:

$$\text{wwwO—CH}_2\text{—OOH} + \text{DLTP} \rightarrow \text{wwwO—CH}_2\text{—OH} + \text{stabl. Prod}$$

$$\text{wwwO—CH}_2\text{—OH} \rightarrow \text{zip depolymerization}$$

Thermal hydroperoxides are converted into terminal alcohols, which are well known to be initiating sites for nonradical depolymerization.

Indeed, hydroperoxides can also be transformed into alcohols trough radical reactions:

$$\text{wwwO—CH}_2\text{—OOH} \rightarrow \text{wwwO—CH}_2\text{—O}\bullet + \text{OH}\bullet$$

$$\text{wwwO—CH}_2\text{—O}\bullet + \text{PH} \rightarrow \text{wwwO—CH}_2\text{—OH} + \text{P}\bullet \quad \text{(PH: polymer)}$$

In other words, we can expect "secondary" depolymerization processes induced by oxidation.

After the end of the 60's, the amount of published work on POM thermooxidation decreased drastically and no decisive novelty appeared, to our knowledge, in the domain of thermooxidation mechanisms and kinetics.

The aim of our research work is to to apply chemical kinetic concepts to predict polymer embrittlement. The main originality consisting to use numerical methods to solve complex kinetic schemes without simplifying hypotheses.[13,14] This first part is devoted to chemical aspects, the main objective being to build a kinetic model able to predict oxidation induced changes of the molecular weight distribution (MWD). The second part will focus on the relationships between MWD changes and the embrittlement process.

Concerning the first part of this program, a noticeable difficulty comes up against the main kinetic parameters, which have to be determined from experiments performed on the unstabilized polymer. Indeed, unstabilized POM is too instable to allow molecular weight measurements with the chosen methods. MWD measurements are feasible with stabilized (industrial) POM samples, but the nature of stabilizers and thus of stabilizing mechanisms are confidential. We have chosen to do complementary experiments on both unstabilized and stabilized samples, and to make a reasonable assumption for the relationship between oxidation rate and chain scission rate.

EXPERIMENTAL

The experiments were conducted with 60 μm films, obtained by compression molding of an industrial

homo-polyoxymethylene (Delrin100 NC010) are supplied by Dupont. To obtain the films, injected sheet was melted for 3 min at 190°C between two metal plates, recovered of silicone sheet, under the pressure of 10 MPa. Average molecular weights of the polymer determined by rheometric measurements (see below) were: $M_n = 70$ kg mol^{-1} and $M_W = 140$ kg mol^{-1}. The crystallinity ratio after annealing estimated by using DSC is close to 0.73. For unstabilized samples, films were purified by extraction in an ethanol, chloroform and hexane mixture (with 1/1/4 proportions) in a soxhlet apparatus for 50 h.

Isothermal aging tests are performed under ambient air (0.02 MPa) and various oxygen pressure (up to 2 MPa). The autoclaves were thermally equilibrated for 24 h prior to exposure. The pressure of 0.02 MPa corresponds to an exposure in air.

A Bruker IFS 28 spectrophotometer with a resolution of 4 cm^{-1} was used for infrared measurements. Homogeneity of degradation in the sample thickness is checked by using mapping IR measurements with the help of an optical microscope coupled with a motorized X-Y scale, with distance increments of 10 μm. Gravimetric measurements were made on a Mettler Toledo balance, model AT261 delta range, with a precision of 0.1 mg.

Rheological measurements were performed in dynamic oscillatory mode with a Rheometric Scientific ARES rheometer using parallel plates geometry (plate diameter 25 mm and gap 0.5 mm), at atmospheric pressure. Ten films have been used to obtain one measurement for an exposure condition given. The pulsation range is between 0.1 and 100 rad s^{-1} and the maximum strain amplitude is optimized to measure reliable torque values in the Newtonian domain (10%). Viscosity measurements were performed at 190°C under nitrogen to avoid oxidation during measurements. The molar mass distribution was determined from the viscoelastic spectrum, using the Mead's model.[15]

RESULTS

Mass loss in unstabilized samples

The gravimetric curves obtained in air at atmospheric pressure, and high oxygen pressure (2.0 MPa) at 90, 110, and 130°C are shown in Figures 1 and 2.

As it shown in Figure 1, the curves display an induction period (1 h at 130°C, ~ 500 h at 110°C, ~ 1000 h at 90°C) during which mass loss is slightly autoaccelerated. Induction period is roughly estimated from the intersection between extrapolation of linear part corresponding to a pseudo steady state and time axis. Then, when pseudo steady state is reached, the corresponding mass loss rates are of the order of 5 × 10^{-3}% h^{-1} at 90°C, 20 × 10^{-3}% h^{-1} at
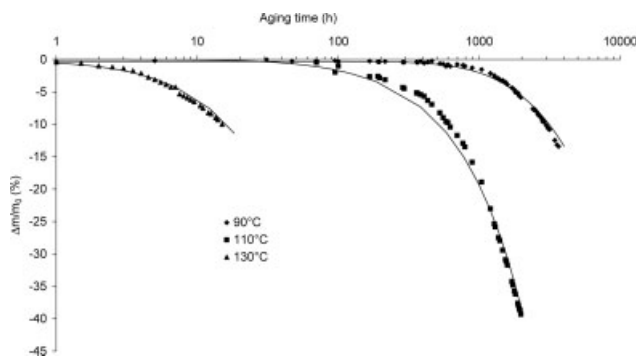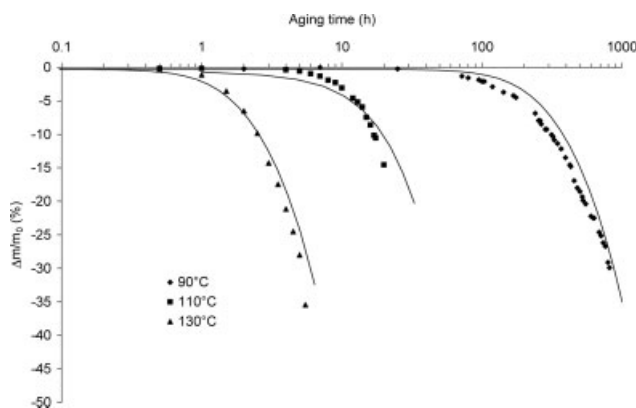
Figure 1 Kinetic curves of mass loss at 90, 110, and 130°C in air at atmospheric pressure. Points correspond to experimental data, curves are generated by the kinetic model.

110°C, and $\sim 300 \times 10^{-3}\%$ h^{-1} at 130°C. At 110°C, mass losses close to 40% have been reached whereas no significant slowing down was observed. As one can observe in Figure 2, the gravimetric curves obtained at high oxygen pressure (2.0 MPa) exhibit the same shape but the mass loss rate is considerably higher for a given temperature of exposure.

Gravimetric curves obtained at 130°C under various oxygen pressures are presented in Figure 3. It can be first observed that no significant degradation is observed under vacuum in the timescale of one day that indicates that depolymerization is almost totally induced by oxidation at the temperature under study. Moreover, an increasing oxygen pressure induces a faster mass loss process. Figure 4 shows the dependence of the mass loss rate on oxygen pressure: Mass loss rate is an increasing function of oxygen pressure but tends towards an asymptotic value ($\sim 7\%$ h^{-1}) at high pressures, above 0.5 MPa (see Fig. 4).

Changes of IR spectrum for unstabilized samples

Even at high mass losses, up to 10% for instance, the IR spectrum of POM undergoes only small changes.

Figure 2 Kinetic curves of mass loss at 90, 110, and 130°C under pure oxygen at 2.0 MPa pressure. Points correspond to experimental data; curves are generated by the kinetic model.
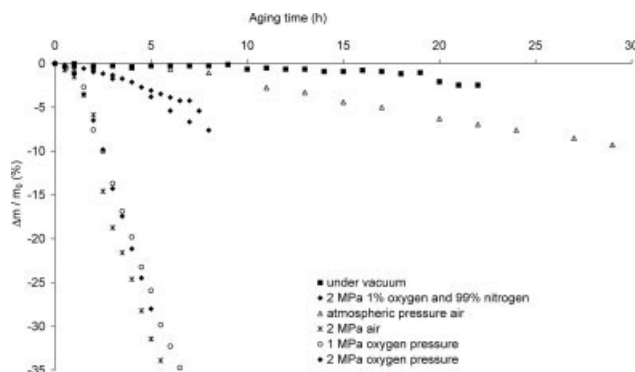

**Figure 3** Mass loss at 130°C at different oxygen pressure.

Two bands appear a wide band of low intensity around 3400 cm^{-1}, which can be attributed classically to hydrogen bonded hydroxyl groups, and a relatively narrow band at 1736 cm^{-1}, which can be attributed to formate (F) groups (Fig. 5). The concentrations of both species have been estimated taking molar absorptivities of 70 L mol^{-1} cm^{-1} for hydroxyls and 500 L mol^{-1} cm^{-1} for formates. Hydroxyls remain always in small concentration (<0.1 mol L^{-1}) and grow almost proportionally to formates of which the concentrations can be about four times higher. Mechanism of generation for the formates will be discussed below.

The kinetic curves of formate growth in air at atmospheric pressure and high oxygen pressure (2.0 MPa) are presented in Figures 6 and 7, respectively. Formate (and alcohol) buildup is strongly accelerated (more than 10 times) by the increase of oxygen pressure. Since mass loss is essentially due to monomer evolution, it can be expressed in terms of formaldehyde moles evolved par mass unit. It seemed to us interesting to determine the ratio λ:

$$\lambda = \frac{\text{Number of formaldehyde moles evolved}}{\text{Number of formate moles formed}}$$
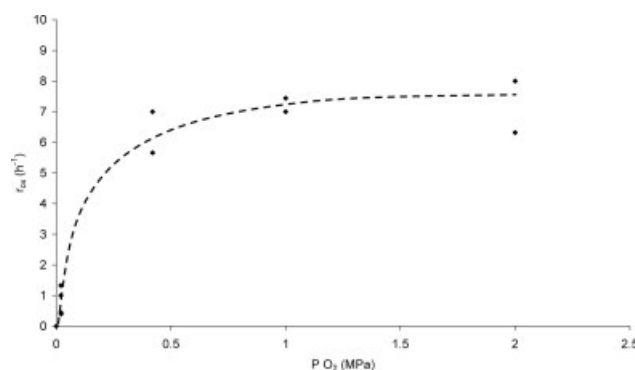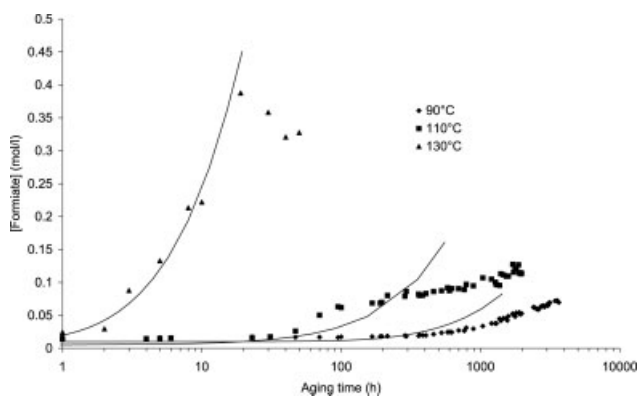

Figure 4 Oxidation rate determined from asymptotic mass loss in function of oxygen pressure at 130°C.
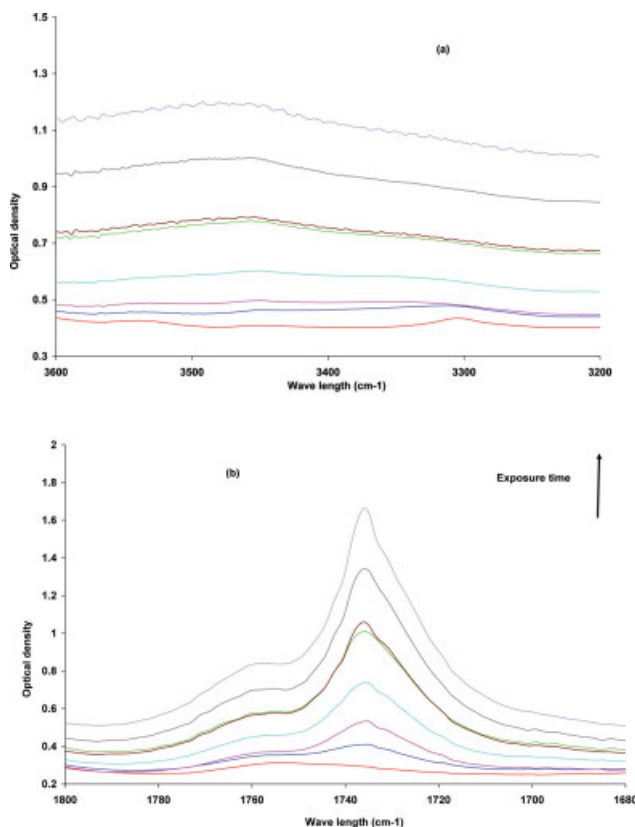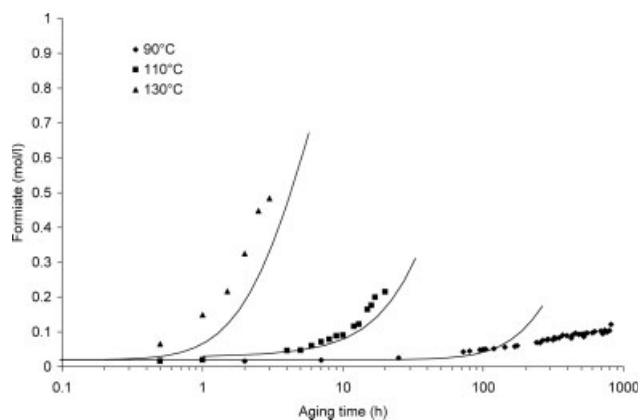
Figure 5 IR spectral changes up to 1900 h of exposure at 110°C under air: (a) hydroxyl absorption region centered at 3400 cm^{-1} and (b) formate absorption region centered at 1736 cm^{-1}. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
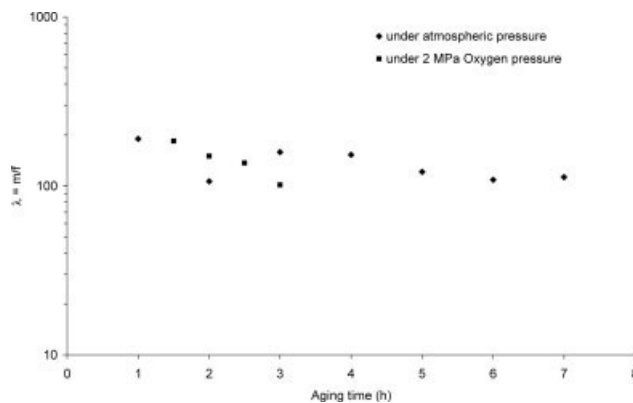
Figure 7 Formate buildup at 90, 110, and 130°C under pure oxygen at 2.0 MPa pressure. Points correspond to experimental data; curves are generated by the kinetic model in which kinetic constant values have been determined from mass loss simulations (see Fig. 2).
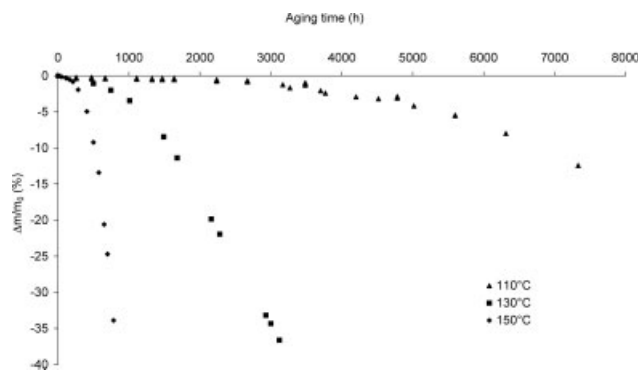
Stabilized POM

Mass loss curves obtained in air at atmospheric pressure are shown in Figure 9. The curves display a more marked induction period (t_i induction period value is determined from the intersection between extrapolation of linear part corresponding to a pseudo steady state and time axis). Compare to unstabilized samples, induction period for stabilized samples is slightly longer than for unstabilized samples: $t_i = 100$ h at 150°C; $\sim$ 1000 h at 130°C, and $\sim$ 5000 h at 110°C. No measurable mass loss was observed at 70°C after 5000 h exposure. Formate growth is also observed in IR spectra.

From rheometric measurements, the shape of MWD curves established show tendency towards a bimodal distribution, which would be indicative of heterogeneous degradation was observed. The corresponding average molar masses are given in Table I:

λ has been plotted against exposure time at 130°C, for 0.02 and 2.0 MPa oxygen pressure (Fig. 8). λ displays a slight tendency to decrease but keeps a value of the order of 100–200 whatever the oxygen pressure.

Figure 6 Formate buildup at 90, 110, and 130°C in air at atmospheric pressure. Points correspond to experimental data; curves are generated by the kinetic model in which kinetic constant values have been determined from mass loss simulations (see Fig. 1).

Figure 8 Ratio (λ) between the number evolved formaldehyde molecules per mass unit (m) and formate concentration (F) in function of exposure time in air at atmospheric pressure and under 2 MPa oxygen pressure at 130°C. The straight line is a guide for eye.

Figure 9 Kinetic curves of mass loss at 90, 110, and 130°C in air at atmospheric pressure in the case of stabilized POM.

Figure 10 Number average molar mass M_n against exposure time in air at atmospheric pressure, for the three temperatures under study: 110, 130, and 150°C in the case of stabilized POM.

The molar mass decreases continuously and the polydispersity index remains close to 2, that indicates the existence of a random chain scission process.

The number average molar mass M_n has been plotted against exposure time in air at atmospheric pressure, for the three temperatures under study: 110, 130, and 150°C (Fig. 10). The curve displays a sigmoid shape, with pseudo induction period times lower than for mass loss but of the same order.

From M_n, it is possible to determine the number s of chain scissions per mass unit:

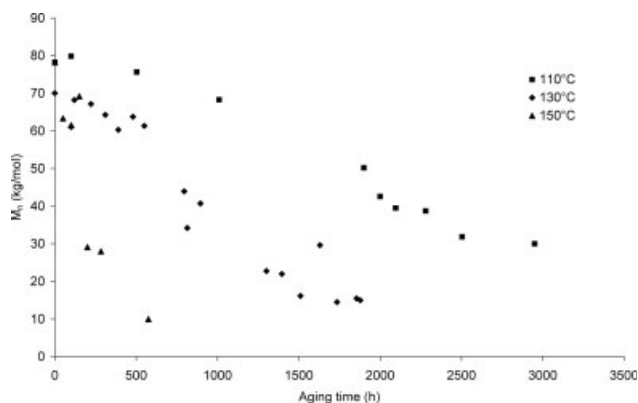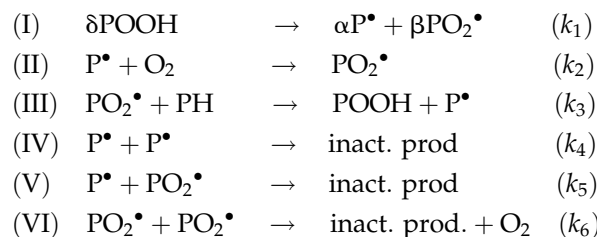$$s = \frac{1}{M_n} - \frac{1}{M_{n0}}$$

It is then interesting to consider the parameter λ' defined by

$$\lambda' = \frac{\text{Number of formaldehyde moles evolved}}{\text{Number of chain scissions}}$$

λ' has been plotted against exposure time in Figure 11 for the results obtained at 130°C. It appears that λ' values display a noticeable scatter but remain of the order of ~ 100 in the whole time interval under consideration. In other words: $\lambda' \sim \lambda$.
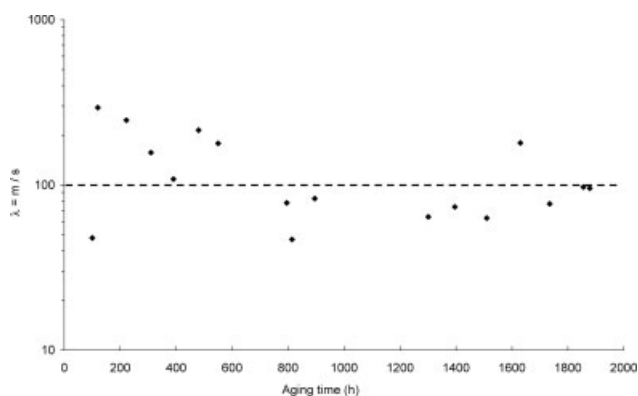
DISCUSSION

A mechanistic scheme for POM oxidation

The standard mechanistic scheme for radical chain oxidation of hydrocarbon substrates can be used, in a first approach, as a basis for discussion. This scheme can be ascribed:

(I)	$\delta POOH$	$\rightarrow$	$\alpha P^\bullet + \beta PO_2^\bullet$	(k_1)
(II)	$P^\bullet + O_2$	$\rightarrow$	$PO_2^\bullet$	(k_2)
(III)	$PO_2^\bullet + PH$	$\rightarrow$	$POOH + P^\bullet$	(k_3)
(IV)	$P^\bullet + P^\bullet$	$\rightarrow$	inact. prod	(k_4)
(V)	$P^\bullet + PO_2^\bullet$	$\rightarrow$	inact. prod	(k_5)
(VI)	$PO_2^\bullet + PO_2^\bullet$	$\rightarrow$	inact. prod. $+ O_2$	(k_6)

where two modes of hydroperoxyde decomposition are to be distinguished: unimolecular decomposition with $\delta = 1$, $\alpha = 2$, and $\beta = 0$ and bimolecular decomposition with $\delta = 2$, $\alpha = 1$ and, $\beta = 1$. PH is the methylene unit of POM.

TABLE I
Average Molar Masses and Polydispersity Index During Exposure at 150°C Under Air

Time of exposure (h)	M_W (kg mol^{-1})	M_n (kg mol^{-1})	IP
0	142	70	2.02
50	132	65	2.02
113	107	55	1.97
161	96	46	2.06
210	76	37	2.07
283	61	31	1.95

Figure 11 Ratio (λ') against exposure time for the results obtained at 130°C under air in the case of stabilized POM (see text). The straight line is a guide for eye.

POM hydroperoxides are expected to be unstable, owing to the destabilizing effect of the ether groups in α. In other words, POOH stationary concentrations are expected to be low, as confirmed by the low intensity of the OH infrared band. Low POOH concentrations are favorable to unimolecular rather than bimolecular decomposition, which is consistent with the progressive autoacceleration observed during induction period. As a matter of fact, bimolecular initiation leads to more abrupt rate changes at the end of the induction period.[14] It will be assumed, thus, $\delta = 1$, $\alpha = 2$, and $\beta = 0$ in our kinetic modeling.

Since oxygen addition to radicals is very fast ($k_2 = 10^8 - 10^9$ L mol^{-1} s^{-1}), the pressure dependence of oxidation rate is expected to have the hyperbolic shape obtained here[16] (Fig. 4). As a matter of fact, the oxidation rate, directly linked to the concentration of PO$_2^\bullet$ radicals, is expected to increase with the oxygen concentration (which is proportional to oxygen pressure through Henry's law [O$_2$] = S_p), until the state where all the P$^\bullet$ radicals resulting from initiation are transformed into PO$_2^\bullet$ ones. In this kinetic regime, which will be named regime of oxygen excess, terminations IV and V, involving P$^\bullet$ radicals tend to negligible and the oxidation rate tends to become independent of oxygen pressure, as observed.

In all the radical oxidation processes, the concentration ratio [PO$_2^\bullet$]/[P$^\bullet$] can vary from zero (in the absence of oxygen) to infinity (in a large oxygen excess), since P$^\bullet$ radicals react very fastly with oxygen. There is necessarily oxygen concentration ranges where:

$$k_6[PO_2^\bullet]^2 > k_5[P^\bullet][PO_2^\bullet] > k_4[P^\bullet]^2$$

at high oxygen concentration

$$k_5[P^\bullet][PO_2^\bullet] > k_6[PO_2^\bullet]^2 \text{ and } k_4[P^\bullet]^2$$

at medium oxygen concentration

$$k_6[PO_2^\bullet]^2 < k_5[P^\circ][PO_2^\bullet] < k_4[P^\bullet]^2$$

at low oxygen concentration

Furthermore, where initiation is due to POOH decomposition e.g. when initiation results from the decomposition of an oxidation product, the whole termination rate is expected to be an increasing function of the oxygen concentration.

Finally, the variation of termination rates with oxygen pressure is expected to have the shape of Figure 12 whatever the substrate structure, provided that the above mechanistic scheme is obeyed. The whole oxidation rate is expected to increase with oxygen concentration in the domain where terminations with P$^\bullet$ radicals are nonnegligible and then to tend towards an asymptotic value in oxygen excess
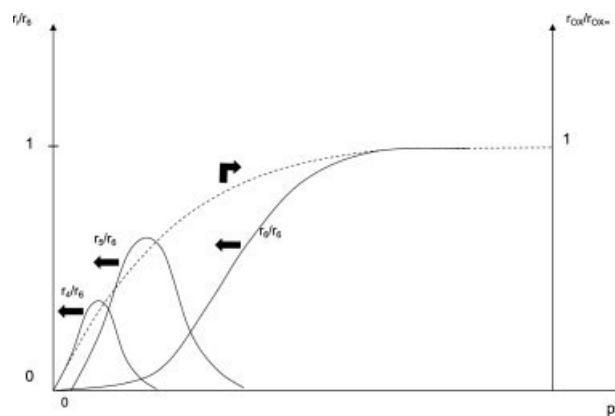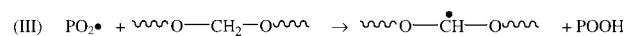
Figure 12 Shape of the curves of pressure dependence of the relative oxidation rate $r_{OX}/r_{OX\infty}$ and relative termination rates r_4 (P$^\bullet$ + P$^\bullet$), r_5 (P$^\bullet$ + PO$_2^\bullet$) and r_6 (PO$_2^\bullet$ + PO$_2^\bullet$).
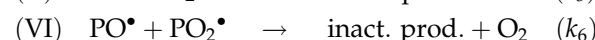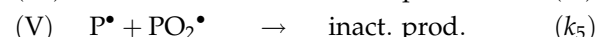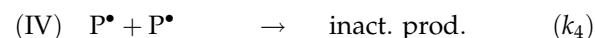
regime. Since experimental results showed that POM oxidation rate is sharply oxygen pressure dependant, this means that, presumably oxidation is far from oxygen excess regime, in other words P$^\bullet$ + PO$_2^\bullet$ terminations are presumably more important than PO$_2^\bullet$ + PO$_2^\bullet$ ones.

Interesting information can be obtained from these results. It has been seen that the depolymerization rate increases "continuously" with oxygen pressure (Fig. 3). It can be concluded that depolymerization does not originate from P$^\bullet$ radicals since these latter tend to disappear when oxygen pressure increases.

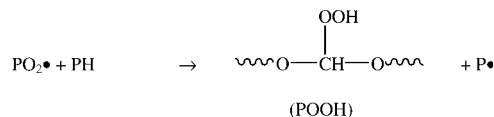Let us now consider the possible mechanisms of elementary steps: Propagation is assumed to occur on randomly distributed monomer units:
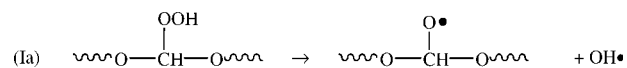
(III)   PO$_2^\bullet$ + $\sim\!\!\sim$O—CH$_2$—O$\sim\!\!\sim$ → $\sim\!\!\sim$O—$\overset{\bullet}{C}$H—O$\sim\!\!\sim$ + POOH

P$^\bullet$ radicals can react with oxygen or terminate:

(IV)   P$^\bullet$ + P$^\bullet$ →   inact. prod.   (k_4)
(V)   P$^\bullet$ + PO$_2^\bullet$ →   inact. prod.   (k_5)
(VI)   PO$^\bullet$ + PO$_2^\bullet$ →   inact. prod. + O$_2$ (k_6)

PO$_2^\bullet$ radicals can abstract hydrogens or terminate

$$\text{PO}_2\bullet + \text{PH} \quad \rightarrow \quad \sim\!\!\sim\text{O}-\underset{|}{\overset{\overset{\displaystyle OOH}{|}}{C}}\text{H}-\text{O}\sim\!\!\sim \quad + \text{P}\bullet$$

(POOH)

The resulting hydroperoxide is expected to decompose easily to give alkoxyl and hydroxyl radicals[9–11]:

(Ia) $\sim\!\!\sim$O—$\overset{\overset{OOH}{|}}{C}$H—O$\sim\!\!\sim$ → $\sim\!\!\sim$O—$\overset{\overset{O\bullet}{|}}{C}$H—O$\sim\!\!\sim$ + OH$\bullet$

OH$^\bullet$ radicals abstract hydrogens and initiate new oxidation chains:

(Ib) $OH^\bullet + PH \rightarrow H_2O + P^\bullet$

$PO^\bullet$ radicals can also abstract hydrogen to give a very instable secondary alcohol (A2):

(Ic)   (A2)
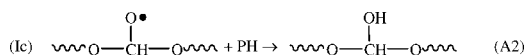
This secondary alcohol can decompose though a molecular mechanism, giving a formate (F), a monomer molecule and a primary alcohol (A1):

(Id)   (F)   (A1)
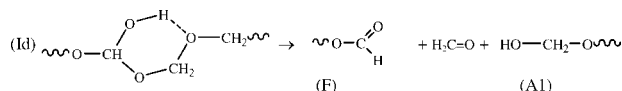
A1 is well known to be an efficient initiator of depolymerization.

The predominance of the sequence of reactions starting from H abstractions by $PO^\bullet$ radicals would give however alcohols and formates in same quantity, whereas it is experimentally found that formates largely predominate.

$PO^\bullet$ radicals are however well known to give also β scissions, favored in the case of POM by the relative weakness of the C—O bond.


(Id)   (PO•)   (F)   (P₁O•)
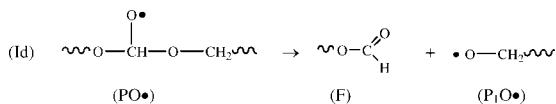
If β scission is thermodynamically favored, then the resulting primary alkoxyl $P_1O^\bullet$ is expected to initiate a depolymerization zip. Indeed, it could also abstract an hydrogen and then give a primary alcohol also able to initiate depolymerization.

Two important remarks can be thus done as it has been proposed by Gardette et al.:[17]

i. Each hydroperoxide decomposition event creates one alkoxyl radical $PO^\bullet$. This latter can react through various pathways but leads always to a species ($P_1O^\bullet$ or P_1OH) able to initiate depolymerization.

ii. Each hydroperoxide decomposition event, whatever mechanisms of secondary processes are, creates a formate group and induces one chain scission.

Concerning termination mechanisms, the following hypotheses or remarks can be made:

a. Alkyl + Alkyl terminations as expected to be favored only at extremely low oxygen pressure.[18] In the case of POM, coupling seems to be the only possible way (IVa):

(IVa)   (k_4)
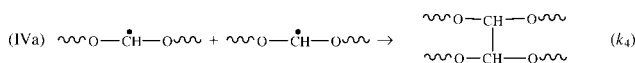
Coupling is expected to give branching and crosslinking. Unfortunately, OH—CH bonds would be very difficult to observe by FTIR at such low concentrations. The gel point which is not reached here, would correspond to a bridge concentration of the order of ½ M_W. Branching or crosslinking were never observed, to our knowledge in POM thermoxidation studies.

Cross terminations alkyl + alkoxyl can occur by disproportionation (IVb):

(IVb)

$P^\bullet$ + $P_1O^\bullet$ → PH +   F
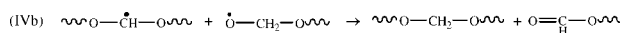
In the usual formalism for the presentation of mechanisms, it is considered that $PO^\bullet$ radicals are fast transformed into $P^\bullet$ ones so that they can be ignored in kinetic analyses. In the case of POM, however, $PO^\bullet$ radicals could play an important role in terminations. In a first approach, however, $PO^\bullet$ radicals will be assimilated to $P^\bullet$ ones.

b. Alkyl + peroxyl terminations: As it has been shown, this type of termination largely predominates in cases of exposure in air at atmospheric pressure.

Coupling would lead to very instable peroxide crosslinks of which the decomposition would give $PO^\bullet$ radicals able to disproportionate in the cage (Va):

(Va)   (C)   (A2)
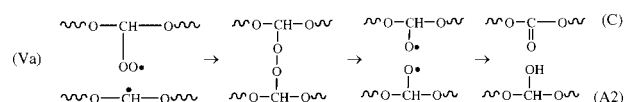
As for $P^\bullet$ radicals, $PO_2^\bullet$ ones can terminate by disproportionation with $P_1O^\bullet$ radicals (Vb):

(Vb)

$PO_2^\bullet$ + $P_1O^\bullet$ → $POOH$ +   F
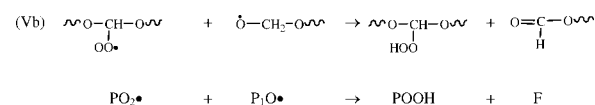
c. Peroxyl + peroxyl terminations: this termination is expected to predominate only at high oxygen pressures, typically above 0.5 MPa (see Fig. 4). Since coupling is disfavored (as crosslinking), Russel's mechanism seems to be the most probable as in alkyl + peroxyl reactions (VI):

(VI)   (C)   (A2)
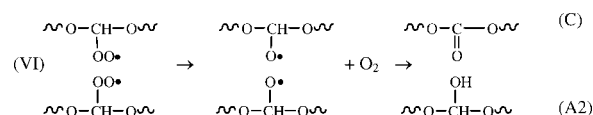
Indeed, since alkoxy radicals are also formed in oxygen excess, termination V could also occur at high oxygen pressure. In a first approach, it will be neglected.The existen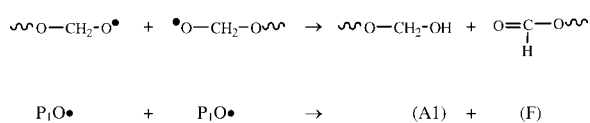ce of nonterminating $P^{\bullet} + PO_2$ and $PO_2^{\bullet} + PO_2^{\bullet}$ reactions is not excluded but, in a first approach, it is considered that, in this case, k_5 and k_6 are apparent termination rate constants, taking into account the fact that the yield of termination is lower than unity.

All the above terminations V and VI, involving $PO_2^{\bullet}$ radicals, have in common an important feature: they lead to instable species able to initiate a depolymerization zip (A2) or an oxidation chain (POOH). Termination Va and VI lead to the formation of a carbonate (C). This latter is in principle easily observable in IR, above 1755 cm^{-1}, but it was never clearly observed (see Fig. 5). Concerning termination of the depolymerization process, we have the following alternative:

i. Depolymerization is initiated by primary alkoxyl radicals. In this case, it can be terminated by disproportionation:

$$\text{\textasciitilde\textasciitilde}O-CH_2-O^{\bullet} + {}^{\bullet}O-CH_2-O\text{\textasciitilde\textasciitilde} \rightarrow \text{\textasciitilde\textasciitilde}O-CH_2-OH + O=\overset{|}{\underset{H}{C}}-O\text{\textasciitilde\textasciitilde}$$

$$P_1O\bullet \quad + \quad P_1O\bullet \quad \rightarrow \quad (A1) \quad + \quad (F)$$

It is noteworthy that this process leads to the formation of a new depolymerization precursor (A1).

ii. Depolymerization is initiated by primary alcohols and occurs through a molecular mechanism. Grassie and Roche have postulated an unimolecular termination process[19] but no mechanism was proposed, to our knowledge, in this case.

To summarize on termination processes, it appears that most of the easily imaginable mechanisms can be disproved because they lead to structures (crosslinks, carbonates) that are not experimentally found or appear to have a low efficiency because they lead to unstable species, especially terminal alcohols. Primary alkoxyl radicals could play an important role because they can react by disproportionation. Finally, little is known on termination mechanisms in POM oxidation and, at this state of our knowledge, kinetic modeling is only possible using virtual termination events: $P^{\bullet} + P^{\bullet}$, $P^{\bullet} + PO_2^{\bullet}$, and $PO_2^{\bullet} + PO_2^{\bullet}$ that are supposed kinetically equivalent to true ones.
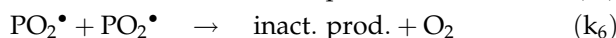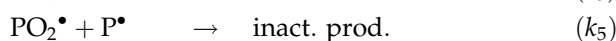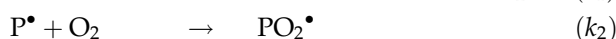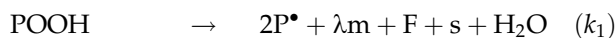
Concerning random chain scissions, two main pathways can be imagined: a radical pathway initiated by secondary alkoxyl radicals, e.g. directly

linked to hydroperoxide decomposition, and a molecular pathway linked to the decomposition of secondary alcohols. It is noteworthy that each chain scission gives a formate and a precursor of depolymerization. Thus, the number of evolved formaldehyde molecules par formate unit (λ) or per chain scission (λ') can be assimilated, at least in a first approach, to the kinetic chain length of depolymerization, this latter being assumed to be independent of the presence or not of stabilizers. In other words, the fact that $\lambda - \lambda'$ is not a coincidence.

Kinetic modeling for POM oxidation

According to the previous mechanistic considerations, the following mechanistic scheme could be tentatively proposed:

Initiation :

POOH	$\rightarrow$	$2P^{\bullet} + \lambda m + F + s + H_2O$	(k_1)
$P^{\bullet} + O_2$	$\rightarrow$	$PO_2^{\bullet}$	(k_2)
$PO_2^{\bullet} + PH$	$\rightarrow$	$POOH + P^{\bullet}$	(k_3)
$PO_2^{\bullet} + P^{\bullet}$	$\rightarrow$	inact. prod.	(k_5)
$PO_2^{\bullet} + PO_2^{\bullet}$	$\rightarrow$	inact. prod. $+ O_2$	(k_6)

where m is a monomer molecule, s is a chain scission. Termination IV has been neglected that restricts the model validity to relatively high oxygen pressures, presumably $P \geq 0.02$ MPa.

The kinetic scheme derived from the above mechanism is composed of four differential equations:

$$\frac{d[P^{\bullet}]}{dt} = 2k_1[POOH] - k_2[P^{\bullet}][O_2] + k_3[POO^{\bullet}][PH]$$
$$- 2k_4[P^{\bullet}]^2 - k_5[P^{\bullet}][POO^{\bullet}]$$

$$\frac{d[POO^{\bullet}]}{dt} = k_2[P^{\bullet}][O_2] - k_3[POO^{\bullet}][PH]$$
$$- k_5[P^{\bullet}][POO^{\bullet}] - 2k_6[POO^{\bullet}]^2$$

$$\frac{d[POOH]}{dt} = -k_1[POOH] - 2k_{1b}[POOH]^2$$
$$+ k_3[POO^{\bullet}][PH]$$

$$\frac{d[PH]}{dt} = -k_3[PH][POO^{\bullet}] - k_{1u}[POOH]$$
$$- k_{1b}[POOH]^2$$

with the following initial conditions: initial values for alkyl concentration $[P^{\bullet}]_0 = 0$, for alkoxyl concentration $[PO_2^{\bullet}]_0 = 0$, for methylene group concentration $[PH]_0 = 42$ mol L^{-1}. Initial value of hydroperoxide $[POOH]_0$ has to be determined by inverse method and will be discussed below.

	k_1 (s^{-1})	k_2 (L mol^{-1} s^{-1})	k_3 (L mol^{-1} s^{-1})	k_5 (L mol^{-1} s^{-1})	k_6 (L mol^{-1} s^{-1})
90°C	5×10^{-6}	10^7	0.04	5×10^{11}	2×10^5
110°C	4×10^{-5}	10^7	0.12	5×10^{11}	6×10^5
130°C	8×10^{-4}	10^7	0.3	5×10^{11}	1.5×10^6
E_a (kJ mol^{-1})	153	0	60	0	38

The rates of formate buildup and random chain scission are given by:

$$\frac{d[\mathrm{F}]}{dt} = \frac{ds}{dt} = k_1[\mathrm{POOH}]$$

The rate of monomer evolution is given by:

$$\frac{d[\mathrm{m}]}{dt} = \lambda k_1[\mathrm{POOH}]$$

The rate of oxygen absorption is:

$$\frac{d[\mathrm{O_2}]}{dt} = k_2[\mathrm{O_2}][\mathrm{P}^\bullet] - k_6[\mathrm{PO_2}^\bullet]^2$$

Mass changes are due to oxygen absorption, water loss (one water molecule per OH$^\bullet$ e.g., per decomposed hydroperoxide) and monomer loss (λ monomer molecules per POOH decomposition event). This leads to the following balance equation:

$$\frac{d\mathrm{m}}{dt} = \frac{(1 - X_C)}{\rho}\left[32\left(k_2[\mathrm{O_2}][\mathrm{P}^\bullet] - k_6[\mathrm{PO_2}^\bullet]^2\right)\right.$$
$$\left. - 18k_1[\mathrm{POOH}] - \lambda M_m k_1[\mathrm{POOH}]\right]$$

where X_C is the crystallinity ratio ($X_C = 0.73$), ρ the polymer density expressed in g L^{-1} ($\rho = 1450$ g L^{-1}), and M_m is the molar mass of formaldehyde ($M_m = 30$ g mol^{-1}).

For the sample under study, oxidation is almost homogeneously distributed into the sample thickness (see experimental part). This means that $[\mathrm{O_2}] = [\mathrm{O_2}]_S$ at every time and every location into the sample thickness. $[\mathrm{O_2}]_S$ is the equilibrium oxygen concentration in the polymer $[\mathrm{O_2}]_S = S_p$ with $S = 2.4 \times 10^{-8}$ mol L^{-1} Pa^{-1} according to Van Krevelen.[20] It is considered that S is temperature independent in the temperature interval under consideration.

Two kinetic parameters k_2 and k_3 were taken a priori equal to polypropylene ones what is known is that for satured compounds, k_2 and k_3 do not vary strongly from a methylene group to another with different neighbouring.[3] Furthermore a correct kinetic simulation depends in fact of rate constants combinations, especially k_3^2/k_6 and $k_2k_6/k_5k_3[\mathrm{PH}]$.

Thus the choice of k_2 and k_3 will determine the values of k_5 and k_6. However, the problem of determination of true values of k_2 and k_3 remains open in the case of POM.

All the other kinetics parameters: $[\mathrm{POOH}]_0$, k_1, k_5, and k_6 are determined from experimental mass loss changes, using the kinetic model though an inverse approach: The procedure for the resolution of the inverse problem using numerical methods has been previously described.[21,22]

The results concerning kinetic parameters found are summarized in Table II. Simulations of kinetic curves by the model using the parameters values of Table II are shown in Figures 1 and 2 for mass loss at two oxygen pressures: 0.02 MPa (corresponding air at atmospheric pressure) and 2 MPa (oxygen excess regime): the model fits well experimental data whatever exposure conditions. Concerning formate buildup (Figs. 5 and 6), the model predicts the good order of magnitude for the average growth rate, but the sigmoid character of kinetic curves is more marked for experimental curves than for model ones.

A possible explanation if this discrepancy could be that formats act as transfer agents in radical processes, for instance:
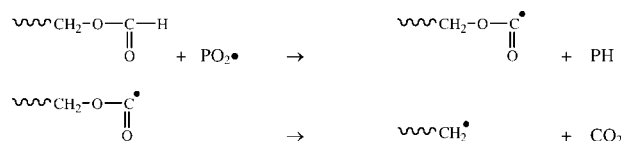
As predicted from analytical solutions of the kinetic scheme,[23] the model is not very sensitive to relatively large variations of the initial hydroperoxide concentration $[\mathrm{POOH}]_0$. Since such low concentrations are out of reach of common titration methods, $[\mathrm{POOH}]_0$ can be considered as an adjustable parameter. The value of 10^{-4} mol L^{-1} is equal to the chosen value in the case of PP.[21]

The rate constant values and their activation energies (see Table II) are physically realistic.[24] The choice for k_2 value is close to PP one. Literature values are generally somewhat higher (10^8 and 10^9 L mol^{-1} s^{-1} against 10^7 L mol s^{-1} here[18]), but increase of k_2, here, would lead to unrealistic high k_5 values. Unfortunately, little is known on structure-k_2 relationships.

The choice for k_3 is linked to the fact that k_3 depends mainly of the dissociation energy of the broken CH bond[3] and this latter is practically the same for tertiary and α etheric carbons (380–390 kJ mol^{-1}).

CONCLUSIONS

Mass loss and formate buildup have been used to monitor unstabilized POM thermal oxidation at several temperatures: 90, 110, and 130°C and several oxygen pressures ranging from 0 to 2.0 MPa. The whole kinetic behavior of the polymer can be simulated by a kinetic model derived from a mechanistic scheme of radical chain oxidation. This latter displays the following features: initiation results essentially from unimolecular hydroperoxide decomposition; propagation involves hydrogen abstractions to methylenes and hydroperoxide formation; termination results essentially from alkyl-peroxyl and peroxyl + peroxyl combinations, these latter being favored only at relatively high oxygen pressure, typically above 0.5 MPa. The hydroperoxides are relatively unstable and the alkoxyl radicals resulting from their decomposition react mainly by β scission to give a formate group and a primary alkoxyl radical able to initiate a depolymerization zip with a kinetic chain length of the order of 100.

Experiments performed on stabilized samples showed that kinetic of oxidation is considerably lower. On stabilized samples, the number of monomer molecules evolved par chain scission is also of the order of 100, e.g., that presumably, the number of chain scissions is equal to the number of formates, as expected from the chosen mechanistic scheme.

By using kinetic modeling, good simulations of mass loss are obtained whatever aging condition (oxygen pressure, temperature). Some discrepancies remain between the simulated and the experimental formate kinetic curves because the chosen mechanistic scheme is no doubt oversimplified at high conversion. As it has been suggested, formate consumption in secondary processes and the possible role of formaldehyde as transfer agent, owing to its high reactivity in hydrogen abstractions could complicate the kinetic analysis. However the proposed scheme seems to us a good point of departure for more detailed investigations.

The elementary rate constants and their activation energies have been determined using an inverse approach. Since application of Arrhenius equation to elementary rate constants is in principle licit, that is not the case for the whole oxidation process, this approach opens the way to nonempirical lifetime predictions at low temperature.

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