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Polypropylene stabilization by hindered phenols — Kinetic aspects

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ABSTRACT

This article deals with polypropylene stabilization by hindered 2,6-di-tert-butylphenols. Two aspects are mainly considered: the influence of stabilizer structure, of its concentration and temperature on induction period duration through a literature compilation completed by results obtained on PP samples stabilized by Irganox 1010 in conditions in which physical loss was negligible. Results show that the induction period duration is almost proportional to the phenol concentration and that the proportionality ratio is almost independent of the stabilizer structure in the investigated phenol family. A unique set of kinetic parameters can be therefore used to model the kinetic behaviour of all the family members. The kinetic approach can be more or less complex depending on the number of secondary processes taken into account. The results of simulations indicate that a two steps process allows generation of a kinetic behaviour in good agreement with experimental trends regarding effects of both stabilizer concentration and temperature on induction time.

1. Introduction

The framework of this study is the development of a reliable lifetime prediction methods for polymer ageing by a non-empirical way, which requires the resolution of a system of differential equations derived from a mechanistic scheme. However, schemes for radical chain oxidation reach complexity level for which there is no analytical solution. Numerical methods are indeed the way in such cases but except in rare attempts [1,2], they were not used in this filed before the beginning of 2000's. Nevertheless, their efficiency was demonstrated in the case of unstabilised hydrocarbon polymers such as polyethylene [3,4], polypropylene [5,6] or unsaturated elastomers [7–9]. It remains now to incorporate stabilization effects in the model but there are at least two reasons to envisage the failure of this attempt:

- The well-known important role of transport phenomena in stabilizer performance [10,11].
- The high complexity of stabilization mechanisms.

The difficulties linked to stabilizers physical loss can be solved by incorporating transport or loss terms in differential equations for stabilizers consumption [12,13], and literature values taken from literature for diffusion or volatility [14,15].

The increased complexity of mechanistic schemes involving stabilizer reactions is not a problem from a numerical point of view. Indeed, schemes with 15–20 equations have been successfully solved for unstabilised unsaturated elastomers [7–9]. Hence, the main difficulty is not the ignorance of stabilization mechanisms but rather the wide variety of mechanisms reported in the literature and the lack of consensus on their relative importance.

We have schematically the following alternative:

① If all the proposed mechanisms are of comparable importance, the complexity of stabilization mechanism cannot be easily reduced in the kinetic analysis. The probability, for two distinct stabilizing mechanisms, to have a common set of kinetic parameters values, is low and each polymer-stabilizer couple is a particular case which requires a separate study.
② If a relatively wide stabilizer family displays common kinetic features, then it becomes possible to envisage a reduction of the complexity of mechanistic schemes and the elaboration of a unique kinetic model valid for all the members of the considered stabilizer family.

This work aimed to determine if 2,6-di-tert-butylphenols constitute a homogeneous family from a kinetic point of view, which needs first to find a set of criteria defining a stabilizer family which could be:

① Induction time duration: This is the most interesting quantity because it is under the direct influence of stabilizer action and it

is not very sensitive to experimental parameters such as sample thickness, sensitivity of characterization method (FTIR, oxygen absorption, chemiluminescence, etc...). A given kinetic model of stabilization must simulate at least the existence of an induction period and the changes of this latter with stabilizer concentration.

② Stabilizer depletion kinetics: the stabilizer is consumed during induction period. The model must therefore simulate stabilizer depletion curves.

③ Temperature effect: using physically reasonable activation energies for the elementary reactions, the model must simulate the global temperature effect on the induction period and stabilizer consumption rate even if the global behaviour does not obey Arrhenius law.

Using these hypotheses, it is now possible to check mechanistic schemes involving stabilizer, starting from the simplest one and adding complexity step by step. For this purpose, 2,6-di-tert-butylphenols constitute the most common stabilizer family. There is a wide consensus on the nature on the primary stabilization event consisting in scavenging peroxy radicals:

$$POO^\circ + AH \rightarrow POOH + A^\circ \quad k_{S1}$$
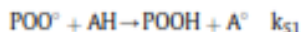
The simplest approach here consists in assuming that the resulting radical A° is unable to propagate oxidation, which is true, and is stable [16,17], which is questionable.

It has been soon established that phenoxy radicals isomerise into cyclohexadienyl radicals able to participate to a wide variety of reactions among which are dimerisation or polymerization, reactions with phenoxy radicals, with oxygen, or scavenging another peroxy radical [18–21].

The relative importance of these processes depends on the nature, the polarity and the steric hindrance of para-substituent groups. Among these secondary processes, many have no influence on stabilization. In contrast, scavenging of peroxy radicals could significantly contribute to the stabilization effect and cannot be ignored. What is their real importance? The answer to this question will be the aim of the second step of our approach.

2. Experimental

2.1. Materials

The stabilizer used was Irganox 1010 (denoted by AO1 in Fig. 1 and AH in the kinetic analysis) supplied by Ciba SC. Samples were prepared by a two-step procedure adapted from previous work [22,23]:

① A commercial PP sample (of which the characteristics are detailed elsewhere [24]) was purified by dissolution (polymer weight ~2 g) into refluxing 1,2-dicholorobenzene (200 ml). After 2 min at refluxing temperature (c.a 180 °C), solution was hot filtered to eliminate impurities. Methanol was dripped to selectively precipitate PP. The PP pellets were washed with ethanol and dried.

② Antioxidant was incorporated into PP by pouring a solution of Irganox 1010 in THF on the purified PP beads under N_2 flow to quickly evaporate the solvent (m_{AH} being the mass of added antioxidant). The stabilized PP was pressed under 15 MPa at 180 °C during 20 s. Thickness of obtained films was of the order of 70 μm, and can be considered as low enough to neglect oxidation thickness gradients due to the kinetic control by oxygen diffusion.

Irganox 1010 weight ratios were converted into antioxidant group concentration (denoted by [AH]) in amorphous phase by the formula:

$$[AH] = f_{AH} \frac{1}{1 - x_C} \cdot \frac{m_{AH}/M_{AH}}{m_{PP}/d_{PP}} \qquad (1)$$

- f_{AH} being the antioxidant functionality, i.e. the number of phenol groups per molecule.
- x_C being the crystallinity ratio of films on the order of 0.5.
- m_{AH} and m_{PP} being the respective masses of antioxidant and PP.
- M_{AH} being the molar mass of antioxidant.
- d_{PP} being the density of PP (0.95 kg l^{-1}).
- x_{AH} being the antioxidant weight ratio ranging from 0 to 0.5%, which means that melting transition divides the stabilizer concentration in amorphous phase by 2.

Some comparisons will be done with published data for PP stabilized with various other hindered phenols (see Results section).

2.2. Exposure conditions

Samples were exposed in air under atmospheric pressure at 80, 100 and 130 °C.

2.3. Samples characterization

FTIR spectrophotometry was performed using a Nicolet Impact 410 spectrophotometer driven by Omnic 3.1 software. 32 scans were averaged to obtain a 4 cm^{-1} resolution. The IR carbonyl absorbances were converted to concentrations using Beer–Lambert's law with a molar absorptivity of 300 l mol^{-1} cm^{-1} at the peak maximum (1712 cm^{-1}).
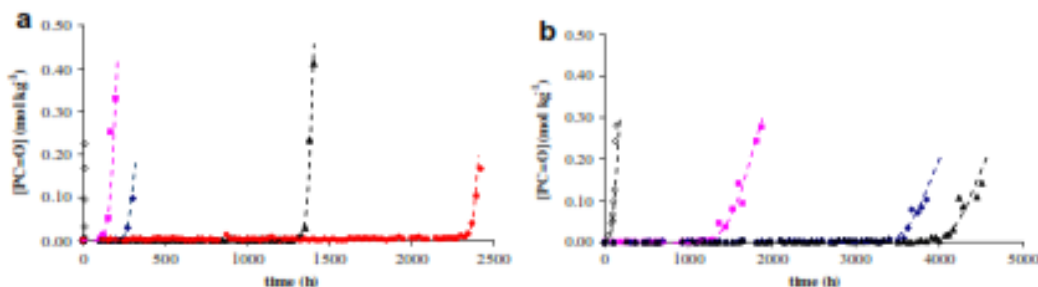

Fig. 1. Oxidation kinetics at 130 (a) et 100 °C (b) for pure PP (○), PP + 0.05% (■), PP + 0.1% (◆), PP + 0.2% (▲) and PP + 0.5% Irganox 1010 (●).

3. Results

Kinetic curves at 130 °C and 100 °C are presented in Fig. 1. Results obtained at 80 °C were presented elsewhere [25]. It is well known that kinetics of thermal oxidation of hydrocarbon at moderate temperature are characterized by an induction period after which one observes hydroperoxides, alcohols and carbonyl build-up, oxygen uptake and mass variation, chemiluminescence emission and exothermal heat flow. Induction period durations are of the same order of magnitude whatever the measured quantity [26,27]. Starting from this observation, we have gathered data of various mixtures PP + phenolic antioxidant (see Table 1) all belonging to the 2,6-di-tert-butylphenol family [28 36] for sample of comparable thickness.

The induction period durations have been plotted against concentration of phenolic group (given by Eq. (1)) for the eight

Table 1
Chemical structure of the stabilizers.

Molecule	Structure	MAH (g mol^{-1})	f_{AH}
AO1		1176	4
AO2		530	1
AO3	R = CH$_2$	783	3
AO4	R = CH$_2$	774	3
AO5		220	1
AO6		636	2
AO7		638	2
AO8		568	2

temperatures at which data were available for distinct stabilizers (see Fig. 2). The observed scatter is not surprising for such a compilation since results differ by the sensitivity of measurement technique, mode of sample preparation, structure and composition of polypropylene (crystallinity, catalyst used for polymerization…).

We have then calculated the "Stabilizer Efficiency factor" (denoted by SE) defined by:

$$SE = \frac{t_{ind} - t_{ind0}}{[AH_0]} \qquad (2)$$

where:

- t_{ind} and t_{ind0} are respectively the induction periods values for stabilized polymer and unstabilised one.
- $[AH]_0$ is the initial stabilizer concentration of a sample of which induction period value is t_{ind}.

The average values and the corresponding standard deviations are reported in Table 2. These results call for the following comments:

① Available standard deviation values are significantly lower than SE average values. Considering the diversity of the possible sources of dispersion (initial stabilizer purity, loss during sample preparation, effect of PP impurities or pre-oxidation), it seems that SE is a common characteristic of all the antioxidants under
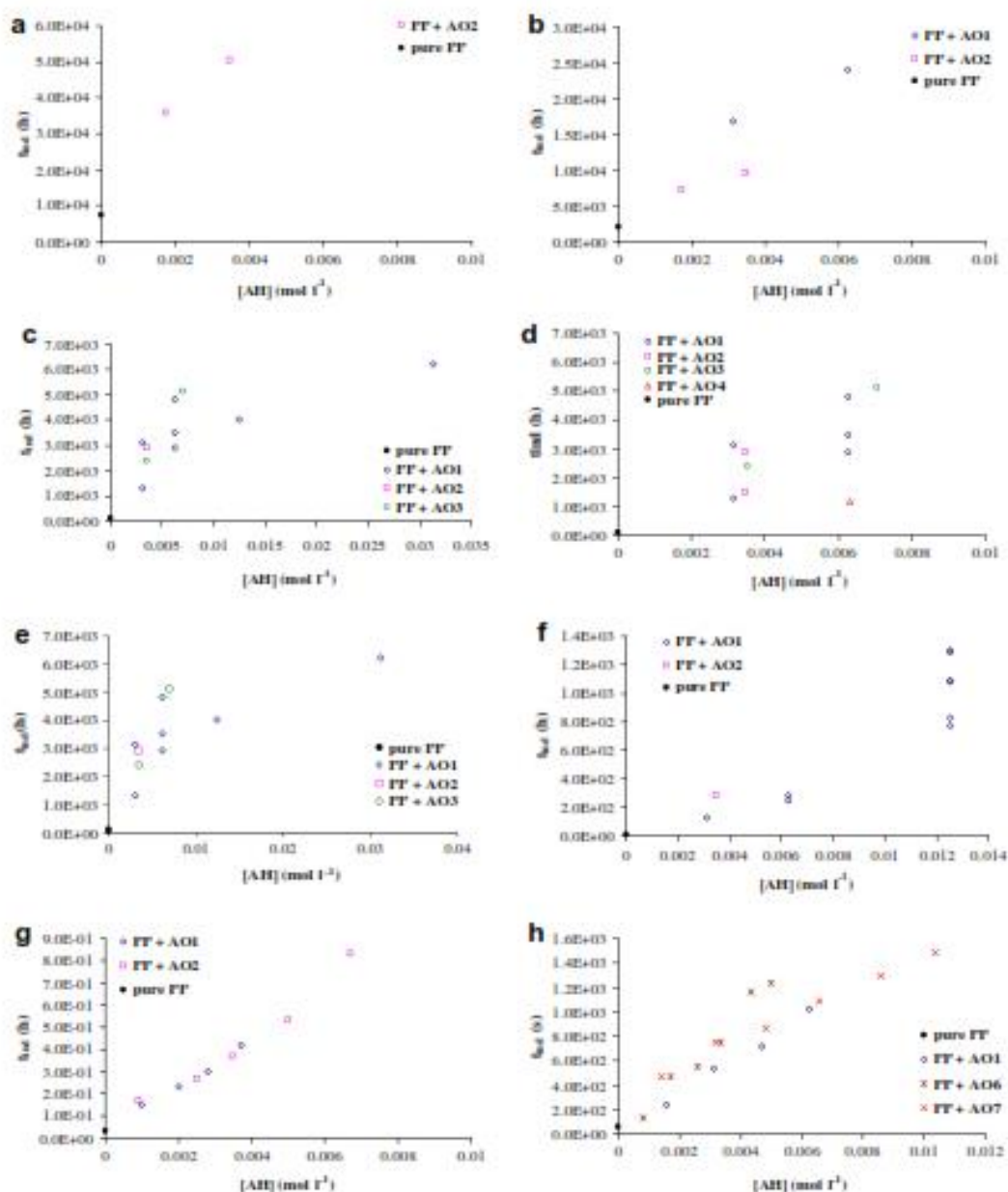

Fig. 2. Compilation of induction time duration against stabilizer concentration at 40 °C (a) 60 °C (b), 80 °C (c), 100 °C (d), 120 °C (e), 130 °C (f) 190 °C (g), 200 °C (h).

Table 2
SE parameter for PP films (or model hydrocarbon) stabilised AO1 ... AO8 at various temperatures. * corresponds to squalene oxidation.

T (°C)	t_{indB} (h)	AO1	AO2	AO3	AO4	AO5	AO6	AO7	AO8
200	0.015	3.5 ± 0.4							
190 (*)	0.002	10.2 ± 1.6				9.4 ± 1.2	11.8 ± 2.6	21.0 ± 7.2	
190	0.003	9.3 ± 1.0	9.9 ± 2.1						4.8
130	5	$(6.0 \pm 2.6) \times 10^5$	7.9×10^5						
120	15	$(5.3 \pm 1.1) \times 10^5$	$(2.4 \pm 0.5) \times 10^5$	6.8×10^5	9.8×10^5				
100	100	$(5.1 \pm 2.7) \times 10^5$	$(6.1 \pm 2.9) \times 10^5$	6.8×10^5	1.7×10^5				
80	500	$(9.0 \pm 4.0) \times 10^5$	$(2.4 \pm 0.3) \times 10^5$	1.8×10^6					
60	2400	$(5.0 \pm 1.0) \times 10^6$	$(3.1 \pm 0.7) \times 10^6$						
40	6000		$(1.2 \pm 0.2) \times 10$						

study and then presumably of all the 2,6-di-tert-butylphenol family at least in the concentration range under consideration, i.e., $[AH]_0 \leq 10^{-2}$ mol l^{-1}.

② When SE = $f(T)$ curves are available, they display clearly a maximum in the 120   130 °C interval as illustrated in Fig. 3 by plotting the average induction period duration for PP + 0.001 mol l^{-1} phenol.

③ If differences of SE values exist from one antioxidant to another, they remain on the same order than uncertainties. For instance SE (AO1) appears to be lower than SE(AO2) at 60, 80 and 120 °C, but the reverse is true at 100 °C and 190 °C.

④ The stabilizers under study differ in molar mass and molecular architecture and consequently in their rate of physical loss. The existence of a quasi-linear induction time   phenolic group concentration dependence indicates that physical phenomena play a secondary role otherwise this linearity would result from a very surprising coincidence [16].

⑤ Some theories predict the existence of a critical antioxidant concentration below which the antioxidant is practically inefficient [37 39]. The above results confirm rather that there is no critical concentration.

4. Discussion

4.1. Kinetic modelling

4.1.1. First step in kinetic modelling: Model M_1

The first step in kinetic modelling consists in adding a single stabilization event to the unstabilised polymer mechanistic scheme which gives:

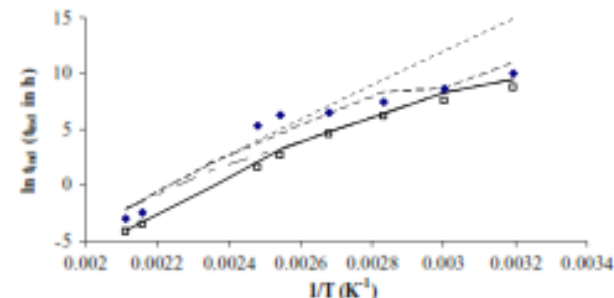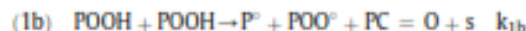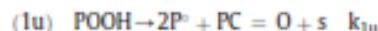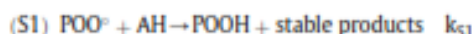(1u) $POOH \rightarrow 2P° + PC = O + s$ k_{1u}

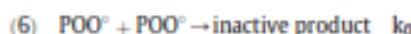(1b) $POOH + POOH \rightarrow P° + POO° + PC = O + s$ k_{1b}
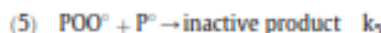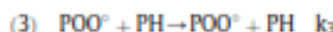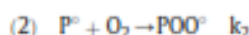

Fig. 3. Arrhenius plot of experimental induction period durations for unstabilised (□), or stabilized with 0.001 mol l^{-1} phenolic antioxidant PP (♦). Lines correspond to kinetic modelling for pure PP ( ) or stabilized one using $k_{S1} = 4.10^5$ l mol^{-1} s^{-1} at 200 °C and various activation energy values (: 50 kJ mol^{-1},   : 85 kJ mol^{-1}, - : 150 kJ mol^{-1}).

(2) $P° + O_2 \rightarrow POO°$ k_2

(3) $POO° + PH \rightarrow POO° + PH$ k_3

(4) $P° + P° \rightarrow$ inactive product k_4

(5) $POO° + P° \rightarrow$ inactive product k_5

(6) $POO° + POO° \rightarrow$ inactive product k_6

(S1) $POO° + AH \rightarrow POOH +$ stable products k_{S1}

- Initiation and termination processes are balanced reactions. This mode of writing has been justified in previous publications [40,41].
- It is clear that P° react quickly with O_2. However, termination reactions involving P° (i.e. reactions (4) and (5)) were shown to play a major role under atmospheric pressure [5].
- The Arrhenius parameters of the rate constants (except k_{S1} which will eventually be estimated in this work) have been previously determined [5,6]. They are listed in Table 3.

The following system of differential equations can be derived:

$$\frac{d[P°]}{dt} = 2k_{1u}[POOH] + k_{1b}[POOH]^2 - k_2[P°][O_2] + k_3[POO°][PH] - 2k_4[P°]^2 - k_5[P°][POO°] \quad (4)$$

$$\frac{d[POO°]}{dt} = k_{1b}[POOH]^2 + k_2[P°][O_2] - k_3[POO°][PH] - k_5[P°][POO°] - 2k_6[POO°]^2 - k_{S1}[POO°][AH] \quad (5)$$

$$\frac{d[POOH]}{dt} = -k_{1u}[POOH] - k_{1b}[POOH]^2 + k_3[POO°][PH] + k_{S1}[POO°][AH] \quad (6)$$

$$\frac{\partial[O_2]}{\partial t} = -k_2[P°][O_2] + k_6[POO°]^2 + D_{O_2}\frac{\partial^2[O_2]}{\partial x^2} \quad (7)$$

$$\frac{d[PH]}{dt} = -\gamma_{1u}k_{1u}[POOH] - \gamma_{1b}k_{1b}[POOH]^2 - k_3[POO°][PH] \quad (8)$$

$$\frac{\partial[AH]}{\partial t} = -k_{S1}[POO°][AH] + D_{AH}\frac{\partial^2[AH]}{\partial x^2} \quad (9)$$

where:

- γ_{1u} and γ_{1b} are the number of PH units consumed per respectively unimolecular and bimolecular POOH decomposition event [5].

Table 3
Rate constant values (at 80 °C) and activation energy values.

k_{1u} (s^{-1})	k_{1b} (l mol^{-1} s^{-1})	k_2 (l mol^{-1} s^{-1})	k_3 (l mol^{-1} s^{-1})	k_4 (l mol^{-1} s^{-1})	k_5 (l mol^{-1} s^{-1})	k_6 (l mol^{-1} s^{-1})
1.3×10^{-8}	0.5×10^{-5}	1.0×10^{7}	6.3×10^{-2}	5.0×10^{30}	4.0×10^{9}	1.2×10^{4}
E1u (kJ mol^{-1})	E1b (kJ mol^{-1})	E_2 (kJ mol^{-1})	E_3 (kJ mol^{-1})	E_4 (kJ mol^{-1})	E_5 (kJ mol^{-1})	E_6 (kJ mol^{-1})
135	105	10	60	0	0	60

- D_{O_2} and D_{AH} are the respective diffusion coefficients of oxygen and stabilizer in the polymer. For the sample thickness under study (200 μm or lower), oxidation gradients can be neglected and the diffusion term relative to oxygen can be suppressed in Eqs. (7) and (9).

The system is solved using a commercial solver ODE23s by Matlab® using the following boundaries conditions [42] at $t = 0$:

- $[O_2] = S_{O_2} \times P_{O_2}$, S_{O_2} being the solubility of oxygen in PP amorphous phase, taken equal to 1.4×10^{-8} mol l^{-1} Pa^{-1} and assumed to be temperature independent.
- $[P^\circ]_0 = [POO^\circ]_0 = 0$
- $[PH]_0 = 24$ mol l^{-1}
- $[POOH] = [POOH]_0$ depending on polymer pre-oxidation state (see later).

In the thermal oxidation at moderate temperatures, typically $T \leq 120$ °C for PP, the existence of an induction period indicates a very low initiation rate, typically less than 10^{-12} mol l^{-1} s^{-1}, at the beginning of exposure. Among the various possible explanations of such values [42], it is convenient to consider a virtual POOH concentration ($[POOH]_0 \neq 0$) kinetically equivalent to all the initially present radical sources. It is also often convenient to take $[POOH]_0 = 10^{-4}$ mol l^{-1} event though one can envisage a two decades variation corresponding to data scatter.

The above kinetic model with these boundary conditions will be called M_1. Kinetic curves for carbonyl build-up are generated from the following equation:

$$\frac{d[PC=O]}{dt} = (1 - x_C) \cdot \left(\gamma_{COu} k_{1u}[POOH] + \gamma_{COb} k_{1b}[POOH]^2 \right) \quad (10)$$

γ_{COu} and γ_{COb} being the carbonyl yields of respectively uni- and bimolecular POOH decomposition taken equal to 1 from previous study [43]. $(1 - x_C)$ term is included to take into account the fact that oxidation possibly occurs only in amorphous phase.

Simulations of carbonyl build-up curves are presented in Fig. 4. The stabilizing effect of phenols is an increasing function of their reactivity, this latter being expressed by the rate constant k_{S1}. The dependence of induction period with k_{S1} and $[AH]_0$ in model M_1 is shown in Fig. 5a. For the highest initial hydroperoxide concentration (10^{-2} mol l^{-1}), the stabilizer is almost inefficient because it is almost totally consumed by radicals generated by the decomposition of initially present hydroperoxides of which the concentration is on the same order or higher than the phenol concentration. Taking $[POOH]_0$ equal to 10^{-3} mol l^{-1}, convenient induction time durations are obtained using $k_{S1} = 30 \pm 20$ l mol^{-1} s^{-1}.

The characteristics of M_1 model can be summarized as follows:

① It is able to generate kinetic curves with the same shape as experimental ones.
② However, the curves induction time duration versus initial stabilizer concentration display a negative concavity (Fig. 5b), which is not observed in experimental ones.

Neglecting this curvature, it could be concluded that the model M_1 is able to describe the experimental results. However, the

existence of secondary processes involving phenoxy radicals and their by-products cannot be ignored. We were thus interested in estimating the influence of these processes on the stabilizing effect and to refine eventually the M_1 model to obtain better predictions of induction times at every stabilizer concentrations.

4.1.2. Kinetic model M_2: influence of POO° termination by cyclohexadienonyl radicals

Phenoxy radicals A° can rearrange into cyclohexadienonyl radicals B° which participate to a wide variety of reactions among which combinations with peroxy radicals appear especially important because they contribute to stabilization. The simplified scheme could be:

(S1) POO° + AH → POO + A° k_{S1}

(Iso) A° → B° k_{Iso}

(S2) POO° + B° → POO B k_{S2}

(B) B° → other reactions k_B
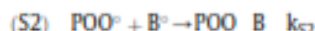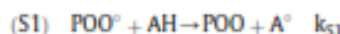
Taking into account all these processes requires new differential equations relative to A° and B° in the scheme:

$$\frac{d[A^\circ]}{dt} = k_{S1}[POO^\circ][AH] - k_{Iso}[A^\circ] \quad (11)$$

$$\frac{d[B^\circ]}{dt} = k_{Is}[A^\circ] - k_{S2}[POO^\circ][B^\circ] - k_B[B^\circ] \quad (12)$$

Nevertheless, model M_1 is not too far to give a good prediction, and addition of two functions [A°] and [B°] and three parameters k_{Iso}, k_{S2} and k_B would lead to a situation where the inverse problem would have an infinite number of solutions. We need thus to determine independently some parameters (k_{Iso} and k_B for instance) or to simplify the scheme.

A relatively reasonable way of simplification consists in adding two hypotheses:
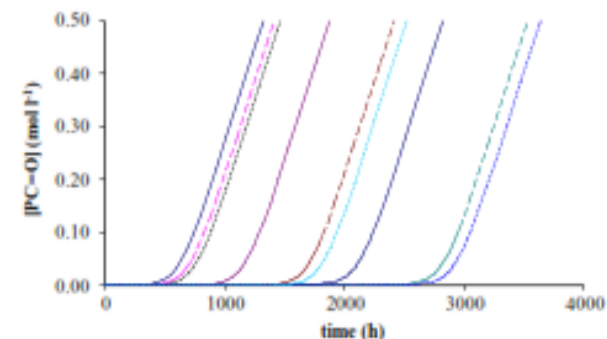

Fig. 4. Simulation of carbonyl build up curves at 80 °C using model M_1 with parameters given in Table 3. $[POOH]_0 = 10^{-3}$ mol l^{-1} (——), $[POOH]_0 = 10^{-4}$ mol l^{-1} (— —), $[POOH]_0 = 10^{-5}$ mol l^{-1} (·····).
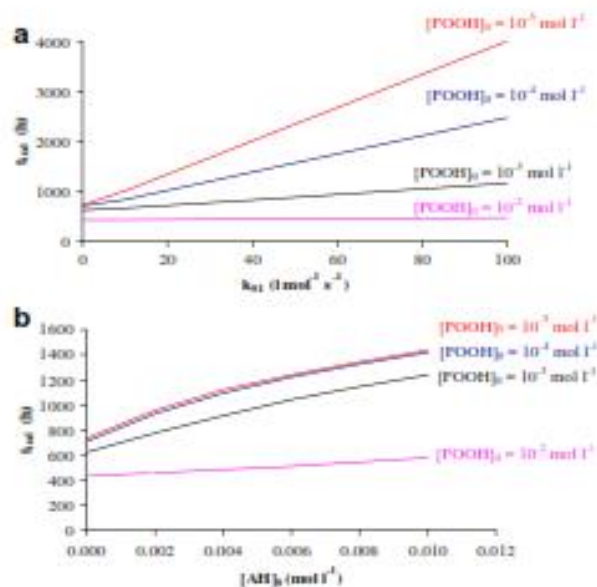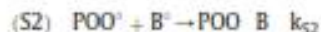
Fig. 5. Simulations of induction period durations at 80 °C using model M_1 (a): Changes with k_{S1} using $[AH]_0 = 0.005$ mol l^{-1} (b): Changes with $[AH]_0$ using $k_{S1} = 20$ l mol^{-1} s^{-1}.

Fig. 6. Simulations of induction periods durations at 80 °C for PP + phenols with $[AH]_0 = 10^{-3}$ mol l^{-1}.

① The A° isomerisation into B° is almost instantaneous so that the stationary concentration of A° is very low and A° can be ignored in the kinetic analysis.

② The termination B° + POO° predominates overall the other reactions involving B°. Indeed, this hypothesis tends to overestimate the stabilizing power of phenols under study. In model M_1, each phenol scavenges POO° radical meanwhile in model M_2, each phenol would scavenge two POO° radicals. The reality is probably in between.

M_2 would thus involve two (balanced) reactions:

(S1) POO° + AH → POOH + B° k_{S1}

(S2) POO° + B° → POO B k_{S2}

Reaction (S2) is a termination probably slower than termination (5) because radicals B° are resonance stabilized but is considerably faster than H abstraction by POO° (reaction S1):

$$k_5 > k_{S2} \gg k_{S1} \qquad (13)$$

The model M_2 has been operated with various k_{S1} and k_{S2} values (Fig. 6). It calls for the following comments:

① Two regimes can be clearly distinguished:
- for $k_{S2} < 10^3$ l mol^{-1} s^{-1}, reaction (S2) has practically no effect on stabilization.
- for $k_{S2} > 10^5$ l mol^{-1} s^{-1}, the stabilization effect of (S2) reaches an asymptotic value which increases slowly with k_{S1}.

It seems reasonable to suppose that $k_{S2} \geq 10^5$ l mol^{-1} s^{-1}. Hence (S2) plays a significant stabilizing role provided that B° is not consumed by competitive processes and that its reaction products do not interfere with the oxidation chain process (see below).

② The model M_2 improves the linearity of t_{ind} $[AH]_0$ curves (Fig. 7). A negative concavity remains but it is less marked than in Model M_1.
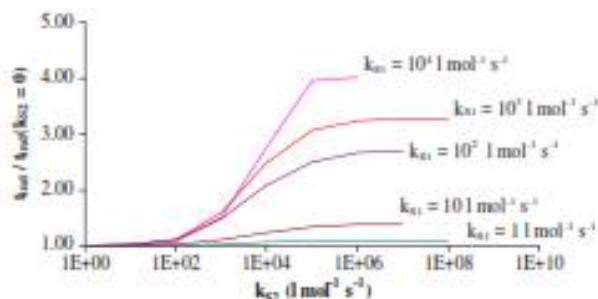
4.1.3. Kinetic model M_3: influence of coupling or polymerization of cyclohexadienonyl radicals

Cyclohexadienonyl radicals B° can react by coupling, disproportionation or polymerization reactions [44,45] which have an indirect influence on the stabilization since they compete with termination (S2). These processes can be tentatively represented by a single (virtual) bimolecular process [46]:

(S3) B° + B° → inactive products k_{S3}

A first estimation can be made as follows: the induction time is calculated from two runs of the kinetic model:

- the first one with $k_{S2} = 0$
- the second one with $k_{S2} = 10^6$ l mol^{-1} s^{-1} and $k_{S3} = 0$.

If the resulting induction time values are t_{ind1} for the first run (i.e., from model M_1) and t_{ind2} for the second one (i.e., from model M_2), it is sure that whatever the k_{S3} value:

$$t_{ind1} \leq t_{ind} \leq t_{ind2} \qquad (14)$$

If t_{ind2} and t_{ind} are on the same order of magnitude, incorporating the S3 reaction into the mechanism would be an useless complication, except maybe at high stabilizer concentrations.

4.1.4. Kinetic model M_4: reinitiation from by products

Termination S2 by coupling gives a peroxide which is certainly unstable at high temperature. Its decomposition generates two alkyl radicals able to initiate new oxidation chains:
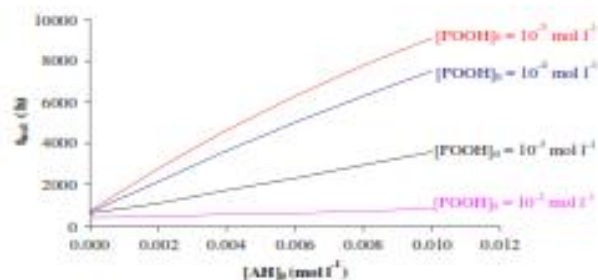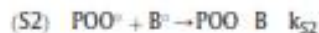
(S1) POO° + AH → POOH + B° k_{S1}

Fig. 7. Simulations of induction period durations at 80 °C using model M_2 with $[AH]_0$ using $k_{S1} = 20$ l mol^{-1} s^{-1} and $k_{S2} = 10^6$ l mol^{-1} s^{-1}.

(S2) $POO^* + B^* \rightarrow POO\text{-}B$ k_{S2}

(S3) $B^* + B^* \rightarrow$ inactive products k_{S3}

(S4) $POO\text{-}B \rightarrow 2P^*$ k_{S4}

Peroxides are generally more thermally stable than corresponding hydroperoxides. A value of the decomposition rate constant k_{S4} was reported [43]: $(k_{S3})_0 \sim 10^{14}$ l mol^{-1} s^{-1} and $E_{S3} \sim 125$-150 kJ mol^{-1} so that it ranges between 10^{-9} and 10^{-7} l mol^{-1} s^{-1} at 80 °C. Some data presented in Fig. 2, were tentatively simulated with various sets of kinetic parameters (Table 4). Indeed, k_{S4} increase can be compensated by k_{S1} increase. Incorporation of reaction (S4) in the model would be useful only to adjust k_{S1} value if this latter was considered too low compared with data obtained for model compounds.

4.1.5. To conclude about simulation runs

Our investigation is not exhaustive but it suggests that the stabilizing effect could be relatively well represented by a combination of two reactions:

(S1) $AH + POO^* \rightarrow POOH + B^*$ k_{S1}

(S2) $B^* + POO^* \rightarrow POO\text{-}B$ k_{S2}
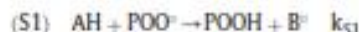
All the other reactions have only secondary effects on polymer stability. Their role could be taken into account by slight modifications of k_{S1} and k_{S2} values. The same conclusion was drawn when trying to model the stabilization by quinone methide generated as phenols by-products [47,48]. Let us note that the direct reaction between O_2 and phenol surely occurs [32] but it was shown to be negligible under atmospheric pressure for PP.

It will be assumed that reaction (S2) is fully efficient i.e. that $k_{S2} \geq 10^5$ l mol^{-1} s^{-1}. We have chosen arbitrarily $k_{S2} = 10^6$ l mol^{-1} s^{-1}. We will now try to calculate the k_{S1} parameter from an inverse approach [6].

4.2. Identification of kinetic parameters

k_{S1} was calculated from fitting lifetime values from all above presented data by comparing:

- Experimental induction periods values from chemiluminescence with simulated values for POOH build-up curves. It can be recalled that POOH decomposition is considered as the source of chemiluminescence [49,50].
- Experimental times to embrittlement with simulated time to reach $M_W = 200$ kg mol^{-1}, which is the criterion for ductile brittle transition in PP [51].
- Experimental and simulated induction periods for oxygen absorption or carbonyl build-up.

The initial hydroperoxide concentration $[POOH]_0$ being a key quantity in our modelling approach, the determination of its value calls for the following comments. In unstabilised polymers, it can be in principle determined from induction time values using the kinetic model through an inverse approach [52]. For relatively clean samples, t_{ind} was shown to be not very sensitive to $[POOH]_0$ variations [42]. A value of $[POOH]_0 = 10^{4 \pm 2}$ mol l^{-1} gives generally good results. It seemed to us interesting to choose a value of 10^{-3} mol l^{-1} here with a possible risk of slight underestimation of the polymer stability. This value is close to the sensitivity limit of common titration methods. We don't exclude cases where $[POOH]_0$ would be measurable but, according to our experience, it is out of reach in relatively "clean" samples. Anyhow, it can be recalled that in the model, $[POOH]_0$ is a "composite value" aimed to take into account all the possible sources of radicals: hydroperoxides, dialkylperoxides, oxygen polymer complexes, and more generally all the impurities or structural irregularities able to decompose into radicals in a very short time scale compared to induction period duration. There are thus at least two reasons to consider $[POOH]_0$ as the unique adjustable parameter of the model.

The crystallinity ratio x_C was arbitrarily taken equal to 0 in molten state and 0.5 in solid one considering that small variations of x_C induce only small variations of the kinetic parameters (see later).

Determined k_{S1} values are presented in Fig. 8. They call for the following comments:

① At 400 K and below k_{S1} values display a limited scatter (less than one decade). The apparent activation energy could be on the order of 80 ± 20 kJ mol^{-1}.
② In the melting temperature interval (400 K < T < 450 K), k_{S1} value displays relatively high scatter (2-3 decades) and appears almost temperature independent.
③ In liquid state at $T \geq 450$ K, the number of available data is too low to appreciate the trends of variation.

The scatter can be discussed as follows:

① Stabilizer consumption during samples processing is not taken into account. The antioxidant concentration at the beginning of exposure is probably lower than its nominal value.
② Scatter increases when approaching to the melting temperature region, in agreement with the observation of some already observed discontinuities [38,39]. A possible explanation would be that the crystallinity ratio increase caused by annealing at temperatures just below T_m provokes an underestimation of "true" stabilizer concentration compared to theoretical one (Eq. (1)). The fact that t_{ind} is proportional to $k_{S1}[AH]_0$ (Figs. 5 and

Table 4
Simulations of experimental value of induction period of PP + 0.005 mol l^{-1} phenol at 80 °C with various sets of kinetic parameters. $[AH]_0$ and $[POOH]_0$ in mol l^{-1}, k_{S1} k_{S2} and k_{S3} in l mol^{-1} s^{-1}, k_{S4} in s^{-1} and t_{ind} in h.

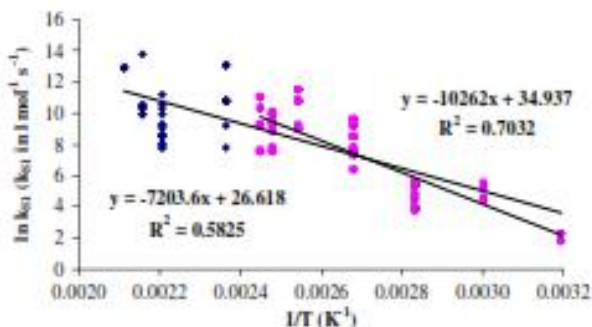| $[POOH]_0$	$[AH]_0$	k_{S1}	k_{S2}	k_{S3}	k_{S4}	t_{ind}
10^{-2}	0.005	40	10^8	0	0	3426
10^{-3}	0.005	40	10^6	0	10^{-9}	3405
10^{-3}	0.005	40	10^6	0	10^{-8}	3240
10^{-3}	0.005	43	10^6	0	10^{-8}	3418
10^{-3}	0.005	40	10^8	0	10^{-7}	2506
10^{-3}	0.005	75	10^6	0	10^{-7}	3434

Fig. 8. Arrhenius plot of k_{S1} values determined from inverse method.

7) implies that $[AH]_0$ underestimation is compensated by k_{S1} overestimation in this temperature range.

② At elevated temperatures, k_{S1} could be underestimated in case of stabilizer loss by evaporation [13]. The linearity of induction period-stabilizer concentration is a pertinent criterion to determine if volatile loss can be neglected [13], which is surely the case for high molar mass stabilizers (for example AO1). Data at 180 °C were available for only one stabilizer weight ratio, which prevented us from applying this simple reasoning. However, it is clear that a great part of stabilizers was lost during processing or exposure given their low molar mass (c.a. $\leq$300 g mol^{-1}). A more rigorous way for calculating stabilization kinetic parameters bases on the simultaneous simulation of both PC=O and POOH build up curves together with residual stabilizer concentration curve [13] which is unfortunately generally not present in the compiled papers.

④ Last, the peroxy cyclohexanedienone thermal decomposition, neglected here (see above) could accelerate ageing at elevated temperatures. In other words, k_{S1} could be underestimated at temperatures c.a. 180 200 °C.

Despite these uncertainties, the results presented in Fig. 8 can be considered as an original method for estimating k_{S1} and its activation energy. Two linear regressions were made:

- A first one including all available data: it gives a pre-exponential factor higher than 10^{11} l mol^{-1} s^{-1} with an activation energy close to 60 kJ mol^{-1}.
- A second one excluding some questionable data (in molten state) has a pre-exponential factor of 10^{13} l mol^{-1} s^{-1} with an activation energy of about 85 kJ mol^{-1}.

Concerning the pre-exponential factor, one can observe that its value is high compared to the diffusion rate constant of particle encounter in the liquid state (10^9 l mol^{-1} s^{-1}), which seems difficult to justify. There are two distinct explanations:

- In our case, many adjustments would be possible due to the existing data scatter. The uncertainty in A factors is hence high.
- More fundamentally, one cannot totally exclude the possibility of a non Arrhenius behaviour in the whole temperature range, as theorized by Waite [53] and Emanuel and Buchachenko [54] for the case of diffusion controlled reaction. Such a behaviour is expected for a reaction between a macroradical and a molecule in relatively low concentration.

However, let us mention that pre-exponential factors for many fast reactions are many decades higher than the 10^9 l mol^{-1} s^{-1} limit (see [55]). Assuming in the frame of this work the k_{S1} is a genuine constant, E_{S1} ranges undoubtedly between 60 and 85 kJ mol^{-1}. This value will be tentatively justified in the following so as to validate the model.

5. Physical sense of kinetic parameters

5.1. Stabilizer yield k_{S1}/k_3

Identically to other substrates [46,56,57], the condition $k_{S1} \gg k_3$ is verified. However, k_{S1} value is lower than in numerous articles [58 60] no doubt depending on hypothesis made for kinetic model. Let us consider the ratio expressing stabilization efficiency:

$$\frac{r_{S1}}{r_3} = \frac{k_{S1}[POO^\circ][AH]_0}{k_3[POO^\circ][PH]_0} = \frac{k_{S1}[AH]_0}{k_3[PH]_0} \qquad (15)$$

This ratio remains lower than unity but of the same order. The fact that a significant stabilization is observed while r_{S1} is not strictly higher than r_3 could be explained by the positive role of (S2). Furthermore, relatively low values for k_{S1} in PP are expected compared to PE ones (a set is available in [43]) since secondary peroxy radicals are more reactive than tertiary ones for a given substrate [61].

5.2. Rate constant for POO$^\circ$ + A$^\circ$

For the termination reaction between A$^\circ$ and a secondary (PE type) POO$^\circ$ radical, a rate constant close to 10^8 l mol^{-1} s^{-1} was reported [43] with zero activation energy. Here, PP value is 2 3 decades lower in good agreement with precedent considerations. Let us recall that the k_{S2} value is not decisive and its precise determination by our approach is not easy given the low model sensitivity to k_{S2}.

5.3. Dependence of temperature and (S1) activation energy

Fig. 3 illustrates the temperature effect on the kinetic of oxidation of a stabilized PP and shows that:

- if E_{S1} is lower than 50 kJ mol^{-1}, model overestimates induction periods durations at low temperatures.
- if E_{S1} is higher than 150 kJ mol^{-1}, model underestimates the lifetime at moderate temperature.

Korcek [61] proposed a correlation between Bond Dissociation Energy (BDE) and activation energy:

$$E = 0.55 \times BDE(A - H) - 143.9 \qquad (16)$$

E and BDE being expressed in kJ mol^{-1}.

Using BDE values ranging from 320 to 360 kJ mol^{-1} [45,62 65], E_{S1} would be close to 45 kJ mol^{-1}, which is not acceptable given the results presented in Fig. 3. Given that the linear correlation between $\log_{10}$ k and BDE differs for the reaction between POO$^\circ$ and phenol hydroxyl group, and between POO$^\circ$ with hydrocarbons [62], a good agreement between Eq. (16) and our experimental results is illusory.

We have then used the Intersecting Parabolas Method extensively studied by Denisov [66]. The activation energy can be estimated from:

$$E_e = \frac{b \cdot r_e}{1 - \alpha^2} \cdot \left[1 - \alpha \cdot \sqrt{1 - \frac{1 - \alpha^2}{(b \cdot r_e)^2} \cdot \Delta H_e} \right] \qquad (17)$$

where:

- E_e is the activation energy (kJ mol^{-1})
- $2b^2$ is the bond force constant of the broken bond
- r_e characterizes the displacement of abstracted atom
- $br_e = 14.4$ kJ mol^{-1}. Let us precise that the calculation is not very sensitive to this parameter.
- α is the ratio b/b_f, b_f being the strength of the formed bond. Here, $\alpha = 1.014$.
- ΔH_e is the reaction enthalpy (kJ mol^{-1}) of the reaction POO$^\circ$ + AH → POOH + A$^\circ$ reaction.

Since:

- for a tertiary hydroperoxide: BDE(POO-H) = 358.6 kJ mol^{-1}
- for a phenol: BDE(Ar OH) is close to 330 kJ mol^{-1}

then : $\quad \Delta H_e = -30 \text{ kJ mol}^{-1}$.

ΔH_e being in any case between -10 and -30 kJ mol^{-1}. Activation energy ranges between 62 and 86 kJ mol^{-1}. In other words, values calculated from exploitation of our compilation are justified by this theoretical assessment.

6. Conclusions

This paper was dedicated to the PP stabilization by various hindered phenol derivatives. The phenols "quasi-universal character" was shown. It means that independently of their structural complexity, the driving force of phenols chemical efficiency is the reaction:

$POO^{\circ} + AH \rightarrow POO + A^{\circ} \quad k_{S1}$
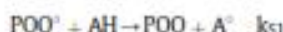
Its activation energy for (S1) reaction is close to 70 ± 10 kJ mol^{-1} was calculated and discussed.

The polymer pre-oxidation (due to severe processing or use of recycled materials) was shown to drastically decrease the stabilizer efficiency.

The influence of further secondary reactions was then discussed. There is whether stabilization process: the termination of peroxy radicals by B$^{\circ}$ ones, or many non stabilizing processes involving B$^{\circ}$ and phenoxy (A$^{\circ}$) radicals. It appeared that all these processes can be included in a single step provided that its rate constant value k_{S2} is adjusted in order to take into account all the competitive processes:

$POO^{\circ} + A^{\circ} \rightarrow POO \quad A \quad k_{S2}$

The influence of destabilizing steps, for example: POO A $\rightarrow$ 2P$^{\circ}$ was shown to be negligible especially in the low temperature range.

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