

"Close Loop" Mechanistic Schemes for Hydrocarbon Polymer Oxidation

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SYNOPSIS

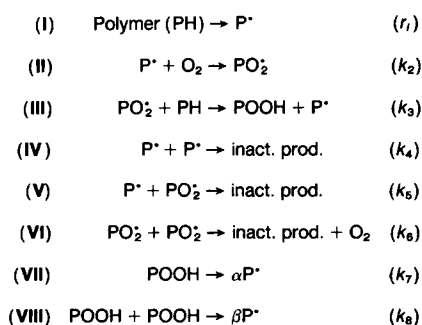
Mechanistic schemes of radical oxidation of hydrocarbon polymers in which initiation is only due to unimolecular or bimolecular hydroperoxide decomposition have been studied. The results of their kinetic analysis have been compared with literature data relative to the thermal oxidation of polypropylene in solid state (60–160°C). These data are in remarkably good agreement with the "unimolecular" scheme whose main characteristics are: (1) the quasi-independence of the kinetic behavior with initial conditions (for low initial content of thermolabile structures), and (2) the fact that an arbitrarily defined induction period depends only on the rate constant of unimolecular hydroperoxide decomposition.

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INTRODUCTION

There is an abundant literature on mechanisms and kinetics of low-temperature thermal oxidation of unstabilized hydrocarbon polymers. Most of the authors agree implicitly or explicitly with the hypothesis that, from a qualitative point of view, the whole trend of the process can be predicted from the following mechanistic scheme:^{1,2}



The mode of writing of reactions (VII) and (VIII) will be justified in the following.

In conditions where oxidation is nondiffusion controlled, reactions (IV) and (V) can be neglected. This case can be schematized by following expression:³

$$L \leq 2 \left(\frac{D}{k} \right)^{1/2}$$

where *L* is the sample thickness, *D* the coefficient of diffusion of O₂ in the polymer, and *k* a pseudo-first-order constant which could be: *k* = *r*/[O₂], *r* being the maximum rate of oxygen consumption and [O₂] the oxygen equilibrium concentration.

The case of "extrinsic" initiation by ionizing radiation or radical initiators such as AIBN at low temperature [where branching by reactions (VII) and (VIII) can be neglected] has been widely studied. It is well known that rate of hydroperoxide build-up is given by:

$$\frac{d[\text{POOH}]}{dt} = k_3[\text{PH}] \left(\frac{r_i}{k_6} \right)^{1/2} \quad (1)$$

However, in the general case of reasonably pure samples thermal oxidation, branching cannot be neglected. Billingham and George⁴ have suggested a transposition of eq. (1) to the case of unimolecular branching:

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$$\frac{d[\text{POOH}]}{dt} = k_3[\text{PH}]\left(\frac{\alpha k_7[\text{POOH}]}{k_6}\right)^{1/2} \quad (2)$$

It seems, however, that no detailed kinetic study of this case has been reported in the literature. The case of predominating bimolecular branching has been studied, for instance, by Tobolsky and co-workers⁵ and reviewed by Reich and Stivala⁶ and Zlatkevich.⁷

It is well known that the thermal oxidation of polymers such as polyethylene displays an induction period, but what is not very clear is the cause of the induction phenomenon. At least three types of interpretation can be proposed:

1. At low conversions, unimolecular branching predominates, POOH groups accumulate slowly until a critical concentration $(\text{POOH})_c$ at which bimolecular branching becomes important and leads to a strong acceleration of the reaction.⁸ From IR measurements on solutions of low molecular weight hydroperoxides, it appears that the critical concentration (at which hydrogen-bonded POOH groups begin to appear) would be close to 0.05 mol L⁻¹.⁹
2. There is no change of kinetic regime but only an autoacceleration resulting only from the fact that the initiation rate increases with the POOH concentration, as described for example, by eq. (2).
3. Autoacceleration is linked to the heterogeneous character of the oxidation process.^{10,11} In this case, it would not be licit to use average concentrations of reactive species and oxidation products in a kinetic study derived from the above mechanistic scheme or any other.

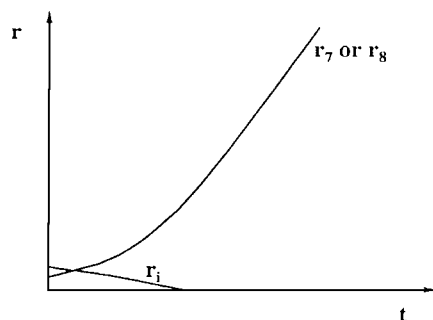
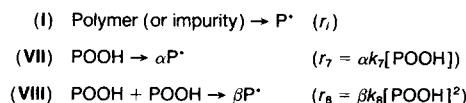


Figure 1. Schematic representation of time variations of radical production rate from hydroperoxides (r_7 or r_8) and other species (r_i).

Despite that, it seemed interesting to make a kinetic study of two very simple systems governed by respectively unimolecular and bimolecular branching. Our aim is to show that, although their simplicity is not necessarily realistic, they can allow us to predict certain important trends of the oxidation process of polymers in solid state, even in cases such as PP, where the heterogeneity of the reaction is well demonstrated.

“CLOSE LOOP” MECHANISTIC SCHEMES: PRESENTATION AND JUSTIFICATION

Let us consider the case of a nonpre-oxidized, additive-free sample of polyolefin exposed at relatively low temperature, for instance $T \leq 100^\circ\text{C}$. There are three distinct ways of radical production in this case:

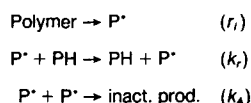


r_i corresponds to all the processes involving other groups than hydroperoxides. It is expected to be a decreasing function of time as a result of the consumption of reactive species. In contrast, r_7 and r_8 are increasing functions of time, at least in the case where $[\text{POOH}]$ is initially low and increases.

This article deals with the case illustrated in Figure 1, where, initially or after a short time of exposure, r_7 or r_8 becomes considerably higher than r_i so that latter can be neglected. This case is probably the most frequent in practice. As a matter of fact, for commercial polyolefins (PE, PP, copolymers), the regular parts of the chain and most of the irregular structures (branches, double bonds) are thermally stable (in the absence of O_2 or radicals) in the conditions under study. It is difficult to imagine species other than hydroperoxides but displaying comparable radical yields in the same conditions. If, however, they exist, they must be in very low concentration so that the condition $r_i \ll r_7$ or r_8 must be easy to satisfy. It is noteworthy that r_7 can be influenced by low concentrations of impurities displaying a catalytic effect on POOH decomposition, e.g., transition metals having a redox activity.

Experimental checking of the fact that $r_i \ll r_7$ or r_8 for the polymers and the conditions under study, is possible by various ways, e.g.:

1. Long-term ageing tests in inert atmosphere. For example, in PE, the following scheme can be applied:



Radiochemical ageing data¹² suggest that coupling of P^{\bullet} radicals is an important mode of termination at low or moderate temperature. Thus, in stationary state, the rate of crosslinking is expected to be of the same order of magnitude of as r_i . Sol-gel measurements offer a very sensitive detection of crosslinking since gelation occurs when one crosslinking event has occurred per weight average macromolecule. Despite that, no crosslinking has been reported (to our knowledge) in the case of anaerobic ageing at low temperature, which is consistent with very low values of r_i .

2. Chemiluminescence (CL) could offer another method. Recent results of studies of CL kinetics in polymers containing heteroatoms such as polyamides (PA12)¹³ and anhydride crosslinked epoxies (EP)^{14,15} can be summarized as follows: CL was studied in isothermal conditions. The sample is heated until the desired temperature under nitrogen. Then, oxygen is abruptly admitted in the test chamber. For the above-cited polymers studied at 150–220°C, the O_2 admission is accompanied by a CL intensity burst, the intensity of which depends of the duration of the preheating stage. Such a burst does not appear in the case of nonpre-oxidized, nonstabilized

PP tested in the same conditions. In this case, the intensity value, initially zero, increases in an autoaccelerated way (Fig. 2).

A simple explanation of the difference between EP and PP is the following: At 190°C, r_i is relatively high for EP and very low for PP. In the case of EP, radicals P^{\bullet} are formed and accumulate during the preheating stage. They are almost instantaneously transformed into PO_2^{\bullet} upon O_2 admission. PO_2^{\bullet} are responsible for chemiluminescence. In the case of PP, CL events can occur at an appreciable rate only when the rate of radical production has reached a certain value, considerably higher than the initial one (r_i).

Numerous other experimental evidences of the low value of r_i in polyolefins can be found in the available literature data. For instance the very high efficiency of chain breaking antioxidants would be difficult to understand in the case of high values of r_i . Indeed, even if $r_i \ll r_7$ or r_8 , reaction (I) can play a key role in the production of the first radicals. It seems, however, licit to neglect it provided that the following assumption is made: let us consider the real polymer PH. During its oxidation, it reaches, after a short time t_1 , a state where the hydroperoxide concentration $[\text{POOH}]_1$ is:

$$r_7 = \alpha k_7 [\text{POOH}]_1 \gg r_i$$

or

$$r_8 = \beta k_8 [\text{POOH}]_1^2 \gg r_i$$

Thus, for times longer than t_1 , r_i can be neglected. We can now consider an hypothetical polymer PH in which there is no radical production by reaction (I), but which initially contains hydroperoxides in such concentration $[\text{POOH}]_0$ as in an oxidation test:

$$[\text{POOH}] = [\text{POOH}]_1 \text{ for } t = t_1$$

In such a case, both polymers would differ at $t < t_1$ but would become indistinguishable at $t > t_1$. If t_i and $[\text{POOH}]_1$ are sufficiently low, the elimination of reaction (I) from the mechanistic scheme would be justified and "close loop" mechanistic schemes, in which the reaction produces its proper initiator at the exclusion of any other initiating species, could be used for a mechanistic study. Both cases of unimolecular (VII) and bimolecular (VIII) hydroperoxide decomposition will be examined in the following sections.

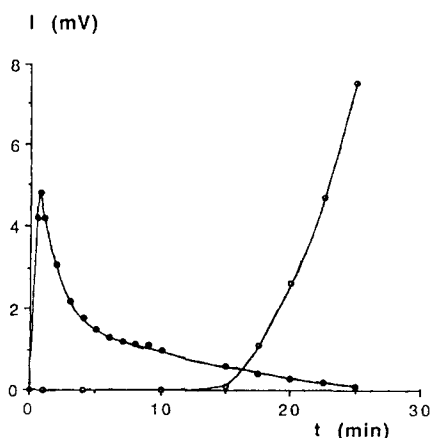
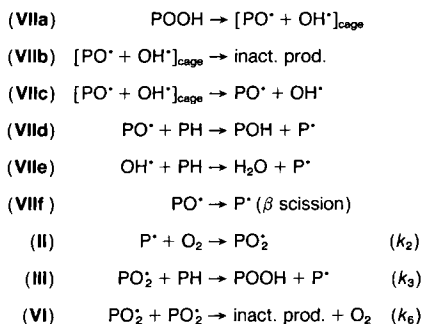


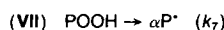
Figure 2. Chemiluminescence kinetic curves at 160°C for an epoxy (●) and a polypropylene (○) sample. The samples are preheated under nitrogen and then oxygen is abruptly admitted in the test chamber at time 0.

"UNIMOLECULAR CLOSE LOOP" SCHEME

The sequence of reactions valid in the general case would be:



It is easy to show that in stationary state, the sequence of reactions $k_{7a} - k_{7f}$ is kinetically equivalent to



where

$$\alpha k_7 = \frac{2k_{7c}k_{7a}}{k_{7c} + k_{7b}}$$

We now have to consider the ensemble of reactions VII, II, III, and VI. Application of the hypothesis of stationary state to this scheme leads to a set of differential equations from which we obtain:

$$[\text{PO}_2^\bullet] = \left[\left(\frac{\alpha k_7}{k_6} \right) y \right]^{1/2} \quad (3)$$

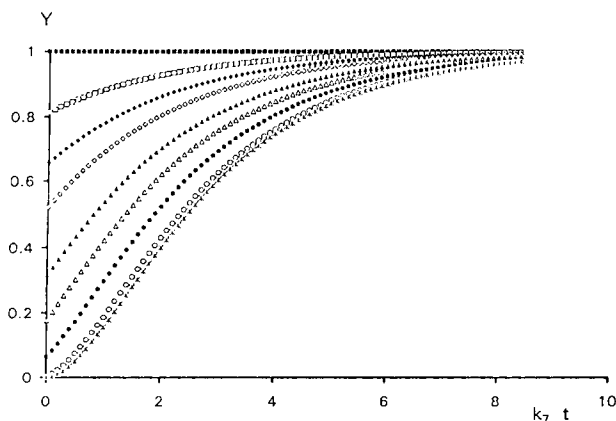


Figure 3. Hydroperoxide reduced concentration (see text) against reduced time $k_7 t$ in the case of unimolecular POOH decomposition. The curves correspond to the following values of the initial reduced POOH concentration: $Y_0 = 1$ (■), 0.95 (□), 0.85 (◆), 0.75 (◇), 0.65 (▲), 0.5 (△), 0.25 (●), 0.1 (○) and 0.0001 (×).

and

$$\frac{dy}{dt} = ay^{1/2} - k_7 y \quad (4)$$

where $y = [\text{POOH}]$ and $a = k_3[\text{PH}](\alpha k_7/k_6)^{1/2}$.

The integration of eq. (4) leads to:

$$y = \frac{a^2}{k_7^2} \left[1 - 2\delta \exp\left(-\frac{k_7 t}{2}\right) + \delta^2 \exp(-k_7 t) \right] \quad (5)$$

and

$$\frac{dy}{dt} = \frac{a^2 \delta}{k_7} \left[1 - \delta \exp\left(-\frac{k_7 t}{2}\right) \right] \cdot \exp\left(-\frac{k_7 t}{2}\right) \quad (6)$$

where $\delta = 1 - (k_7/a)y_0^{1/2}$, y_0 being the initial POOH concentration.

Equation (5) can be simplified using a dimensionless function Y such as $Y = y/y_\infty$, where $y_\infty = a^2/k_7^2$ is the asymptotic value of y . Then:

$$Y = 1 - 2\delta \exp\left(-\frac{k_7 t}{2}\right) + \delta^2 \exp(-k_7 t) \quad (7)$$

with $\delta = 1 - Y_0^{1/2}$.

This function displays an inflexion point if $Y_0 < \frac{1}{4}$. Some representative curves are shown in Figure 3. They correspond to tests performed to a fixed temperature, but with samples differing by the initial POOH concentration (or in other words by the initial initiation rate, r_i). Very interesting is the existence of an asymptotic curve corresponding to $y_0 \rightarrow 0$ and, then, $\delta \rightarrow 1$.

The induction period can be arbitrarily defined by the intersection between the tangent at the inflexion point and the time axis. The calculation from the curve equation leads to:

$$t_i = \frac{2 \ln(2\delta) - 1}{k_7} \quad (8)$$

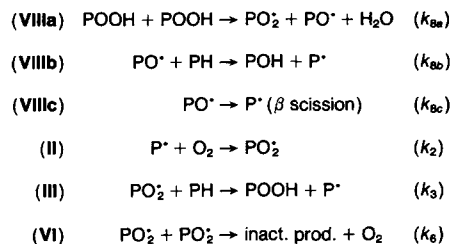
For $y_0 \ll 1$, i.e., for very low initial concentrations of POOH, it comes:

$$t_{i0} \neq \frac{0.386}{k_7} \quad (9)$$

We see another important characteristic of this scheme: the duration of the induction period is only scaled by the rate constant of the POOH decomposition.

"BIMOLECULAR CLOSE LOOP" SCHEME

The following scheme is considered here:



As in the preceding case, the sequence of reactions k_{8a} – k_{8c} can be replaced by



provided that $\beta = 2$. In fact β can be considered as an adjustable parameter taking into account the fact that the initiation yield is not necessarily equal to unity.

The hypothesis of stationary state leads to:

$$[\text{PO}_2^\bullet] = \left(\frac{\beta k_8}{k_6} \right)^{1/2} y \quad (10)$$

$$\frac{dy}{dt} = by - k_8 y^2 \quad (11)$$

where $b = k_3[\text{PH}](\alpha k_8/k_6)^{1/2}$.

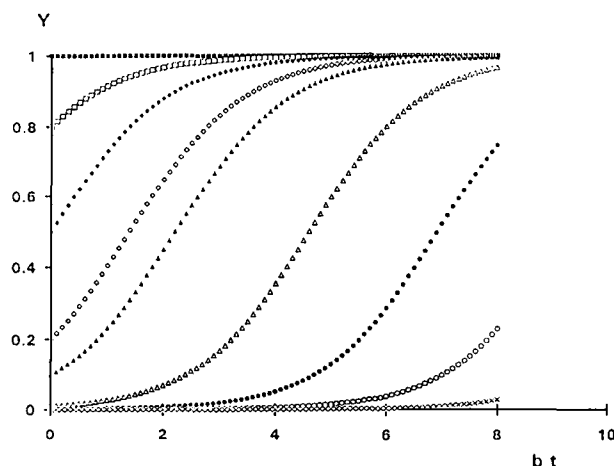


Figure 4. Hydroperoxide reduced concentration (see text) against reduced time bt in the case of bimolecular POOH decomposition. The curves correspond to the following values of the initial reduced POOH concentration: $Y_0 = 1$ (■), 0.8 (□), 0.5 (◆), 0.2 (◇), 0.1 (▲), 0.01 (△), 0.001 (●), 0.0001 (○), and 0.00001 (×).

The resolution of eq. (11) gives:

$$y = \frac{b}{k_8} \frac{1}{1 + \left(\frac{b}{k_8 Y_0} - 1 \right) \exp(-bt)} \quad (12)$$

Using the same reduced function Y as in the preceding chapter with $y_\infty = b/k_8$, eq. (12) becomes:

$$Y = \frac{1}{1 + c \exp(-bt)} \quad (13)$$

where $c = (1 - Y_0)/Y_0$.

If the induction time t_i is defined as precedingly by the intersection of the tangent at the inflexion point with the time axis, we obtain:

$$t_i = \frac{1}{b} (\ln c - 2) \quad (14)$$

which becomes, for very low initial POOH concentrations:

$$t_i \approx \frac{1}{b} \left(\ln \frac{1}{Y_0} - 2 \right)$$

Thus, the kinetic curves of POOH build-up (Fig. 4) are apparently the same as in the case of unimolecular POOH decomposition, however there are two big differences:

1. There is no asymptotic kinetic curve when $Y_0 \rightarrow 0$.
2. The induction time is scaled by b (a composite rate constant) whereas it was scaled by k_7 (the rate constant of initiation) in the former case.

DISCUSSION

Physical Meaning of y_∞

According to the foregoing schemes, the system tends in principle towards an equilibrium at which the formation and destruction rates of POOH are equal. Mathematically, $y_\infty (a^2/k_7^2)$ for unimolecular POOH decomposition, b/k_8 for bimolecular POOH decomposition) is the POOH equilibrium concentration. In fact, there are many possible reasons why such equilibrium would not be experimentally accessible. It could for instance correspond to high conversions at which secondary reactions, not taken

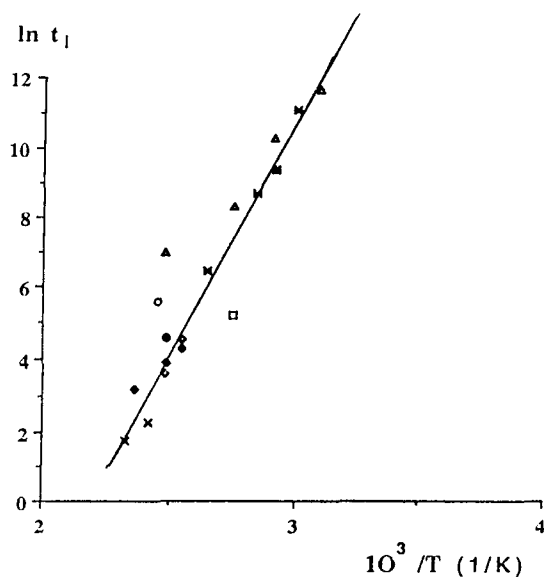


Figure 5. Arrhenius plot of induction time for polypropylene autooxidation from the following literature data: (×) Ref. 17; (◆) Ref. 18; (●) Ref. 19; (◇) Ref. 20; (○) Ref. 21; (□) Ref. 22; (×) Ref. 23; (△) Ref. 24, and (■) Ref. 25.

into account in the mechanistic scheme, would become important. In practical cases, for instance for PP, the POOH concentration first increases until a maximum and then decreases,^{16,17} which is not consistent with the mechanisms under study and any other mechanism which would only differ from the latter by the initiation step. Thus, for us, y_{∞} will appear only as a constant having the dimension of a concentration but not necessarily derivable from the experimental curves $y = f(t)$ in their final part.

Induction Time Versus Initial Concentration and Temperature

Both types of mechanisms display as expected an autoaccelerated character in the case of low initial POOH concentration, but the corresponding induction time varies in distinct ways with $[\text{POOH}]_0$ and temperature. When y_0 tends towards zero at fixed temperature, t_i tends towards a finite value: $t_{i0} = 0.386/k_7$ in the case of the unimolecular mechanism, whereas it increases continuously in the case of the bimolecular mechanism.

Some literature data¹⁷⁻²⁵ on induction time of unstabilized PP are presented in Figure 5. The logarithm of the induction time t_i , as reported by the authors or graphically estimated from their kinetic curves, was plotted against the reciprocal temperature. Despite the extreme diversity of polymer sources, distinct research groups between 1959 and

1993, the points are remarkably close to a simple straightline corresponding to:

$$t_i = t_{i00} \exp\left(-\frac{E_i}{RT}\right)$$

where $t_{i00} \approx 5.3 \times 10^{-10}$ s and $E_i \approx 100$ kJ mol⁻¹. This result seems to be consistent with the hypothesis of a close-loop scheme with unimolecular POOH decomposition. The values of t_i would be close to the asymptotic one t_{i0} because the concentration of initiating species would be low in the studied samples. In this case, the kinetic behavior of the samples would be dominated by autoacceleration effects and would be practically independent of the polymer origin. Except for a very surprising coincidence, this seems the unique possibility to explain the low dispersion of literature values of t_i .

The temperature dependence of t_i calls for the following comments: in both cases, t_i is expected to obey the Arrhenius law, its apparent activation energy being

$$E_{i1} = E_7$$

for the case of unimolecular POOH decomposition and

$$E_{i2} = E_3 + \frac{1}{2}E_8 - \frac{1}{2}E_6$$

in the case of bimolecular POOH decomposition. It is noteworthy that, since E_3 and $E_6 \ll E_8$ and $E_7 > E_8$,⁸ we expect:

$$E_{i1} \geq 2E_{i2}$$

Here, also, the literature data seems to favor the hypothesis of unimolecular POOH decomposition. As a matter of fact, the activation energy of this process is close to 100 kJ mol⁻¹, whereas a value of 50 kJ mol⁻¹ or lower would be expected for E_{i2} .

There is a simple way of verification of the hypothesis of unimolecular POOH decomposition: to study the isothermal ageing, in inert atmosphere, of pre-oxidized samples and to determine the first-order rate constant for the disappearance of hydroperoxides. This experiment was recently made by Gisjman et al.¹⁷ in the case of PP at 70°C. In this case, the problem is somewhat complicated by the existence of two distinct types of POOH groups for which the respective values of k_7 are 4.2×10^{-6} s⁻¹ and 1.8×10^{-7} s⁻¹ at 70°C.

The corresponding theoretical values of t_{i0} would be respectively 25 h and 538 h. According to the authors, the slowest process would predominate in

the early period of ageing, so that we would normally expect an induction period duration of the same order of magnitude but lower than 583 h. The graphically estimated experimental value is $t_{i0} \approx 200$ h, which agrees reasonably with the chosen hypothesis. The activation energy for the slowest process of POOH decomposition was found to be 93.7 kJ mol^{-1} by the authors, a value very close to the average apparent activation energy found for induction times in Figure 5.

Thus, although analytical data on hydrogen bonding or sequential hydroperoxidation seem to favor the hypothesis of bimolecular POOH decomposition, kinetic data seem to militate clearly in favor of the unimolecular process.

This mechanism offers a simple method for checking, since the duration of the induction period is only scaled by the rate constant of POOH decomposition. Some recently published results¹⁷ seem to agree with this hypothesis, but more detailed verification is needed.

CONCLUSIONS

It has been shown that the "close loop" scheme based on the standard mechanistic scheme for radical oxidation of hydrocarbon polymers, but in which there is no other source of radicals than the unimolecular hydroperoxide decomposition, seems to lead to interesting predictions concerning the autoaccelerated character of the kinetics and the duration of the (arbitrarily defined) induction period. There are two main characteristics of this mechanistic scheme:

1. For low initial content of thermolabile species, the behavior is expected to be practically independent of the polymer composition.
2. The duration of the induction period is of the same order of magnitude as the POOH lifetime in inert atmosphere.

Literature data seem to indicate that polypropylene would correspond to this model.

Is it possible to adapt this scheme to the case of heterogeneous oxidation? Is the observed behavior explainable by a completely different scheme, e.g., the heterogeneous propagation proposed by George et al.⁴? It is not possible to answer these questions on the basis of the data and calculations presented here but the latter indicates that it is too soon to renounce definitively to the classical kinetic analysis on the basis of the argument that oxidation is heterogeneous.

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