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The Photooxidation of Isotactic Polypropylene as a Nonhomogeneous Process

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The experimental data on the photooxidation of isotactic polypropylene (PP) have been reviewed. The photooxidation of PP has three main features. Firstly the process proceeds with different rates in different regions of polymer volume. Secondly the reactivity of peroxy macroradicals of solid PP strongly depends on the spectral distribution of incident light, duration of irradiation and the mechanism of the photoinitiator action. Thirdly, the photooxidation occupies only a small part of amorphous phase of the solid polymer. The proposed mechanism of photooxidation includes nonuniform distribution of free radicals and hydroperoxides in the polymer volume, photobranched oxidation chains and the termination *via* reactions of first and second orders. The nonhomogeneous kinetic model based on the proposed mechanism is in good agreement with the different kinds of oxidation kinetics observed with, during and after irradiation.

KEY WORDS Isotactic polypropylene, photooxidation

1. INTRODUCTION

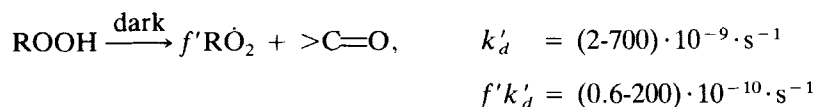
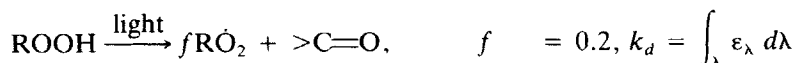
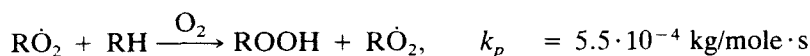
The photooxidation of PP has been studied extensively over the last two decades. By the middle of the first decade the common scheme of PP photooxidation had been established and it had been shown that liquid phase kinetics describes all the data available.^{1,2} Ever since, many data have been obtained which are in contradiction with this conclusion. Furthermore, the old data disagree with the new values of the kinetic parameters of PP oxidation. For example the values of the chain kinetic parameter obtained by many authors (Table I) differ by a factor 20. What value is reasonable?

Scheme I shows the main reactions of the photooxidation of pure PP and the present values of its kinetic parameters.

Now it is known that one discrepancy in the data given in Table I is due to the dependence of the rate constant for termination on the history of the radical generation and on the nature of the sample.^{7,9} One can see (Scheme I) that the values of the rate constant for termination are over an interval of more than four orders of magnitude for long chains of oxidation the peroxy radicals transform many times before recombination and the history of the radicals has no importance

TABLE I
Kinetic parameter of the chain oxidation of PP at 25°C

Initiator	$k_p \cdot k_t^{-1/2}$ (kg/mole · s) ^{1/2}	Reference
Dicumylperoxide	$1.3 \cdot 10^{-5}$	3
Benzophenone	$3.6 \cdot 10^{-5}$	4
Di-tert-butylperoxide	$6.4 \cdot 10^{-5}$	5
Hydroperoxide of PP	$1.9 \cdot 10^{-4}$	6
1,4-trichloromethylphenylene	$2.4 \cdot 10^{-4}$	7
γ -radiolysis	$2.7 \cdot 10^{-4}$	8



SCHEME I Photooxidation of PP.

if the reaction is homogeneous. So an importance of the history indicates a non-homogeneous nature for the termination.

The rate constant for the propagation of chains does not depend on the history of the sample and has values close to the liquid and solid phases.¹⁰ Even in the crystalline phase, the rate constant for propagation is lowered by only one order of magnitude.¹¹ However, oxidation does not occur in the crystalline phase of PP. So the propagation may be considered as a homogeneous reaction.

Photodecomposition of hydroperoxides occurs for every photon absorbed by ROOH and should not depend on the location of the ROOH. So this reaction may also be considered as homogeneous. Thermal decomposition of ROOH is negligible in comparison with the photodecomposition under usual experimental conditions.

Thus, at least one stage of PP photooxidation among the others (termination) proceeds nonhomogeneously through the polymer volume. Consequently a question arises about the influence of one nonhomogeneous reaction on the process of photooxidation as a whole.

There are many studies of polymers where only one reaction proceeds nonhomogeneously with so called "polychrone" kinetics. But there is no study where the reaction with "polychrone" kinetics is accompanied by a number of homogeneous reactions. So an attempt will be made to analyze the effects concerned in this case. At first the termination stage will be considered in some detail.

2. KINETICS OF RADICAL DECAY

At usual concentrations $[\text{RO}_2] < 10^{-3} \text{ M}$ the kinetic law of peroxy radical recombination in solid PP differs from both the 1st and the 2nd order kinetics⁷:

$$[\text{RO}_2]/[\text{RO}_2]_0 = \frac{1}{1 + \bar{k}t}, \quad (1)$$

where \bar{k} is the average rate constant of the first order reaction in a wide range of initial concentrations $[\text{RO}_2]_0$.

As can be seen from Equation (1), the rate of radical decay is proportional to radical concentration. Hence the radical decay occurs via a 1st order reaction. Obviously Equation (1) is due to the distribution of peroxy radicals in reactivity k . If $r(k) dk$ is the amount of radicals with the rate constant k in interval from k to $k + dk$ at time $t = 0$, Then

$$[\text{RO}_2]/[\text{RO}_2]_0 = \int_0^\infty r(k)\exp(-kt) dk \quad (2)$$

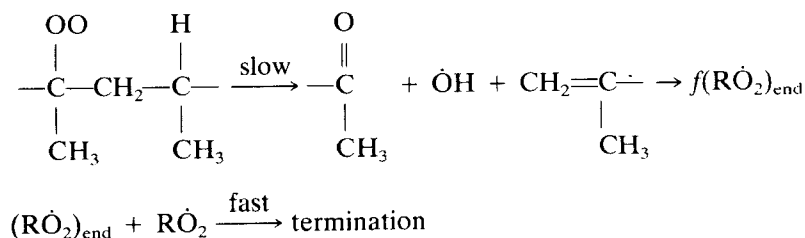
The solution of Equation (2) with Equation (1) gives the function $r(k)$ for radical distribution

$$r(k) = (1/\bar{k})\exp(-k/\bar{k}) \quad (3)$$

The radical distribution may be caused by the nonhomogeneity of the amorphous phase of the polymer, defects of structure, differences in molecular mobility in different sites of the polymer volume and the location of photoinitiator, etc.

To explain the linear termination we propose a new hypothesis (Scheme II). The decomposition of the peroxy radical is known to produce hydroxyl radical $\cdot\text{OH}$ and scission of macromolecule.^{10,12} As a result, the radical $\cdot\text{OH}$ must be for a certain time in the vicinity of two ends of the polymer chains. The radical $\cdot\text{OH}$ has a very high reactivity and probability for the reaction of $\cdot\text{OH}$ with an end group of the chain might be significant (as in the cage).

Thus, the decomposition of the central peroxy macroradical produces an end peroxy macroradical because of this cage effect. The end macroradicals are known



SCHEME II Linear termination of chains.

to possess much higher rate constants of recombination than central macroradicals due to their high molecular mobility and large radius of motion. Therefore after the decomposition of the radical the fast reaction of termination occurs with a rate that is limited by the former slow reaction. As a result the bimolecular termination shows 1st order kinetics.

Scheme II shows that the rate constant k for linear termination equals to double rate constant for radical decomposition. This radical decomposition may be sensitive to molecular environment because of its concert mechanism of simultaneous rupture of O—O, C—H and C—C bonds. The dependence of the rate constant for radical decomposition on local molecular structure and mobility may account for the distribution of peroxy macroradicals on reactivity k .

It should be noted that the linear termination is preferred over the 2nd order termination at low concentrations of peroxy radicals. At higher concentrations of peroxy radicals, the 2nd order termination will be predominant because of its stronger dependence on radical concentration.

3. PHYSICAL MODEL OF PHOTOOXIDATION

In order to integrate the kinetic differential equations of Scheme I and II a certain physical model is needed. Let us assume that the polymer consists of a number of microreactors with different rate constants k for linear termination, the peroxy radical concentrations $r(k, t)$, the hydroperoxide concentrations $P(k)$ and volume $r(k) dk$. To some extent this assumption is close to reality because PP contains about 50–80% crystalline phase and large amounts of macromolecules in an amorphous phase are separated from one another by the crystals, i.e., radical centres and —OOH groups of such macromolecules are attached to a definite location of polymer volume. Diffusion transfer from one microreactor to another may be negligible if the coefficients of diffusion and the difference in concentrations for two neighbouring microreactors are very low.

The average concentrations of radicals and product are determined by Equations (4) and (5) respectively:

$$[\text{RO}_2] = \int_0^{\infty} R(k, t)r(k) dk \quad (4)$$

$$[\text{ROOH}] = \int_0^{\infty} P(k, t)r(k) dk \quad (5)$$

The diffusion flow of radicals from one microreactor to another will increase with an increase of radical concentration and will mix the radicals from different microreactors. So the second order termination, which is preferred at higher concentrations of radicals, is expected to be homogeneous, i.e., its rate constant k_t is averaged through polymer volume.

Thus the 1st order termination occurs with the different rate constants k at low

concentrations of radicals and the 2nd order termination with one rate constant k_t occurs at higher concentrations of radicals.

4. OXIDATION OF PP

Equations (3–5) have been used for the numeric calculation of the photooxidation of pure PP. The average parameter $\bar{k} = 0.005$ s has been measured earlier from the kinetics of radical decay in PP at 25°C.⁷ The most reliable value of k_t can be obtained at higher concentrations of radicals. So $k_t = 0.5$ kg/mole · s has been taken as measured at the highest concentrations 0.002–0.004 M.¹³ This value is in agreement with the theoretical value for k_t , based on the relay segmental diffusion model.¹⁰

At the start of reaction, the initial concentrations of ROOH in all microreactors has been taken to be the same: $P(k, 0) = (1-5) \cdot 10^{-4}$ M. At zero time of reaction all $R(k, 0) = 0$. The results of the calculation are shown in Figure 1.

We find a good agreement of the calculated curves with the experimental data of Carlsson. Garton and Wiles¹ gives an argument in favour of the nonhomogeneous nature of the photooxidation of PP. It should also be noted that it is impossible to describe the photooxidation of PP on the grounds of the liquid phase kinetics with one set of the rate constants.

The calculated local hydroperoxide concentrations $P(k)$ are much higher than the average concentration by a factor of 20. The values of $P(k)$ of about 4–5 M correspond to the experimental data on the blocks of ROOH, which arise from the reaction of propagating along the polymer chain.

Another important feature of the nonhomogeneous model is a critical phenomena due to the 1st order termination. In the initial stages of photooxidation the hydroperoxide concentration in the microreactor with the rate constant k is changed by the law:

$$P(k, t) = P(k, 0) \exp((fk_p[\text{RH}]/k - 1)k_d t) \quad (6)$$

Equation (6) shows that autocatalysis occurs only if $k < k_p[\text{RH}]$. In our case $f = 0.2$, $k_p = 0.00055$ kg/mole · s, $[\text{RH}] = 23.8$ mole/kg. Consequently photooxi-

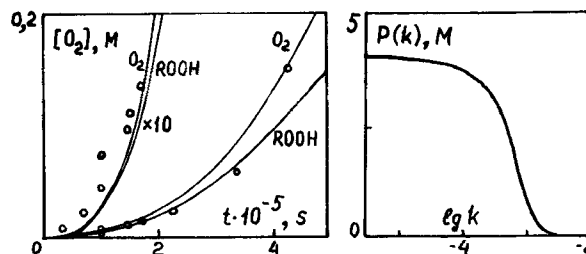


FIGURE 1 Experimental (circles, data of Reference 1) and theoretical (lines) curves for oxygen consumption and accumulation of ROOH under photooxidation of PP in air at 25°C.

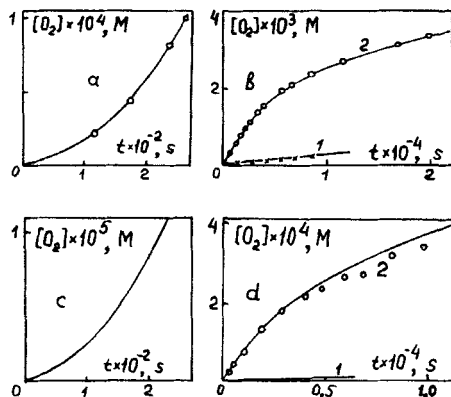


FIGURE 2 Effects of the history of PP samples on photooxidation and post-oxidation in the dark and in air at 25°C (points—experimental data, lines—theroretical curves): (a) photooxidation of PP for 270 s; before this procedure the sample was oxidized up to $[ROOH] = 0.1$ M and then it was held at 25°C for the annealing of peroxy radicals; (b) oxygen consumption of the sample (a) with $[ROOH] = 0.1$ M in dark immediately after irradiation (2) and at the stationary state (1); (c) photooxidation of PP during 240 s; before this procedure the sample was oxidized up to $[ROOH] = 0.003$ M and then it was held for annealing of peroxy radicals; (d) oxygen consumption of the sample (c) with $[ROOH] = 0.003$ M in the dark immediately after irradiation (2) and at the stationary state (1).

dation occurs only in microreactors with the rate constants $k < k^* = 0.0026 \text{ s}^{-1}$. It is easy to find the part of the polymer where the oxidation occurs:

$$V_{loc} = \int_0^{k^*} (1/\bar{k}) \exp(-k/\bar{k}) dk \quad (7)$$

At accepted values of the kinetic parameters Equation (7) gives $V_{loc} = 0.4$ of amorphous phase of PP. Taking into account for that the contents of amorphous phase of PP equals to 0.6, one can obtain value 0.24 that is close to experimental value 0.2 in Reference 1.

The important consequence of the nonhomogeneous oxidation model is the dependence of photooxidation on the history of the polymer sample. Our experimental data on oxidation of PP with different histories and calculated curves are shown in Figure 2. Of course, the set of rate constants used was the same as in the previous case. The count of photooxidation must reproduce all the experimental conditions: time before and after irradiation, duration of oxidation, intensity of light etc. The change in the experimental conditions changes the distribution of peroxy radicals and hydroperoxides on the microreactors. It leads to large changes in the kinetics of photooxidation. The accordance of the calculated curves with the experimental data points out that the model of nonhomogeneous oxidation can predict the phenomena of photooxidation. Preliminary calculations of the oxidation of PP at 130°C show that the nonhomogeneous model may be also useful for understanding the thermal oxidation of PP.

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