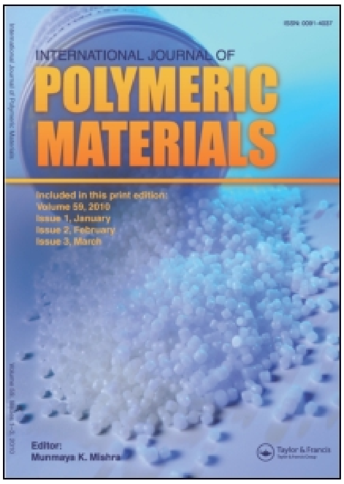

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Shlyapnikov, Yu. A.(1990) 'Specific Features of Polymer Oxidation', International Journal of Polymeric Materials, 13: 1, 1 — 16

To link to this Article: DOI: 10.1080/00914039008039457

URL: http://dx.doi.org/10.1080/00914039008039457

Intern. J. Polymeric Mater., 1990, Vol. 13, pp. 1–16
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Printed in the United Kingdom

Specific Features of Polymer Oxidation

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The role of long-chain structure of polymer in the polymer oxidation kinetics is discussed.

The chain reaction of a polymer oxidation includes the same steps as the oxidation of its low-molecular analogues but the rates and the roles of these steps may differ considerably. The chain propagation step may proceed either intramolecularily, or intermolecularily. Great role in oxidation of some polymer play low-molecular free radicals formed in the reaction. Irregularity of polymer structure results in irregularity of low-molecular compounds, oxygen including, distribution over the polymer volume. All these phenomena affect the polymer oxidation kinetics.

KEYWORDS: Oxidation, antioxidants, chain propagation, chain termination, solubility, radicals, segment mobility

Polymers consist of long chain-like molecules combining the properties of extremely low translational mobility and of high vibrational one. The chain structure of macromolecules results in microanisotropy of polymers: the directions along and across the polymer chain are substantially different. Consider the sequences of this difference.

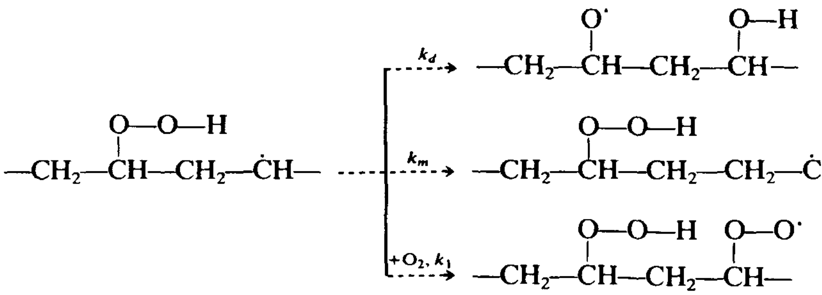
The chain reaction of polymer oxidation includes the alternate steps of chain propagation. If a polymer contains the alifatic groups $\equiv$C—H, —CH$_2$—, or —CH$_3$, the chain propagation follows the scheme;

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot} \quad (1)$$

$$RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot} \quad (2)$$

where RH denotes the polymer chain fragment. This fragment may be either a part of the same macromolecule the $RO_2^{\cdot}$ radical belongs to or a part of the neighbouring molecule. The consequences of intra- and intermolecular chain propagation will be different.

The intramolecular chain propagation results in formation of several active groups in a small section of the polymer chain. If the reaction follows the scheme (1)–(2) these will be hydroperoxide groups ajacent to free alkyl radical $R^{\cdot}$. Among reactions of this radical the interaction of the latter with fresh-formed hydroperoxide group is of special interest because the result of this reaction is decrease of the hydroperoxide yield. In the simplest case of polyethylene oxidation these reactions are:



(3)

Considering these reaction steps we find the expression for the hydroperoxide yield per oxygen consumed α:

$$\alpha = \frac{k_m + k_1[O_2]}{k_d + k_m + k_1[O_2]} \tag{4}$$

According to (3) the hydroperoxide yield α must depend on the oxygen concentration (i.e. on oxygen pressure). In the same time, the oxygen concentration must affect the distribution of hydroperoxide and other oxygen containing groups along macromolecules and in the polymer bulk thus affecting the hydroperoxide properties.

Experiment proved this conclusion: both the rate constant of polypropylene hydroperoxide decomposition and the yield of the hydroperoxide were the functions of the oxygen pressure at which the hydroperoxide has been prepared[1] (Figures 1, 2). The hydroperoxide yield was calculated by comparing its maximum concentration ($d[\mathrm{ROOH}]/dt = 0$) with the oxygen consumption rate,

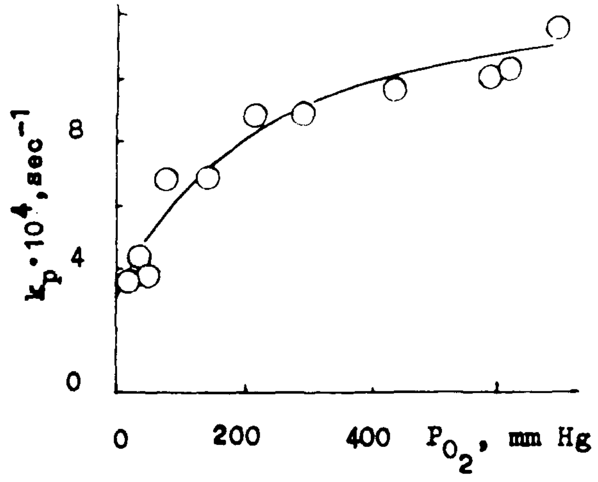


FIGURE 1 Rate constant of polypropylene hydroperoxide decomposition as a function of oxygen pressure at which the hydroperoxide was formed in the polymer oxidation. Temperature 130°C.

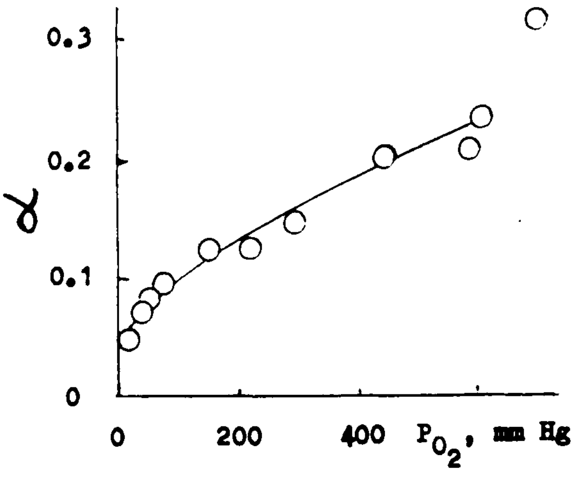


FIGURE 2 Yield of polypropylene hydroperoxide per oxygen consumed as a functon of oxygen pressure 130°C.

using the formula:

$$\frac{d[\mathrm{ROOH}]}{dt} = \alpha W_{O_2} - k_{\mathrm{eff}}[\mathrm{ROOH}] \tag{5}$$

where W_{O_2} is the oxygen consumption rate and k_{eff}, the rate constant of decomposition of hydroperoxide prepared at the same oxygen pressure.

Polymer oxidation is accompanied by destruction and (or) scission of the polymer chains. If the chain reaction of the polymer oxidation proceeds mainly inside one macromolecule, the result of such intramolecular process will be one chain scission and formation of several low-molecular fragments not registered at measurement of molecular weight (Figure 3). Thus if the number of the chain reaction step in the same macromolecule is long enough each act of oxidation process initiation or transfer results in chain scission:

$$W_s = W_0 + k_{\mathrm{tr}}[\mathrm{RO}_2^{\cdot}] \tag{6}$$

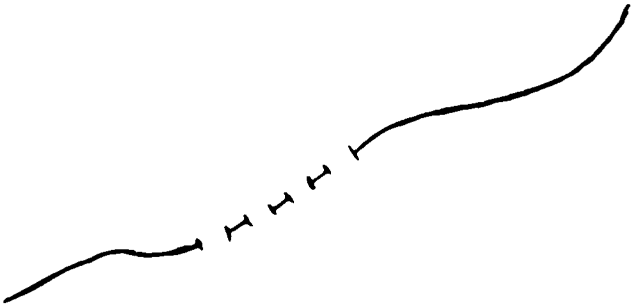


FIGURE 3 Several scissions in one short region of the polymer chain are regarded as one chain scission (scheme).

(supposing that the oxygen pressure is great enough we neglected reactions of alkyl radicals $R^{\cdot}$). If the constant of chain transfer is low, that is the process proceeds mainly in the same macromolecule $W_s = W_0$, i.e. the registered rate of the polymer chain scission will be equal to that of chain initiation, but if in the each act of chain propagation reaction transfers from one macromolecule to another one, the observed rate of the polymer chain scission will be equal to the real one and proportional to the overall concentration of $RO_2^{\cdot}$ radicals.[2]

Another consequence of chain structure of polymer chains is topological irregularity of polymeric substance.

Some polymers, including non-polar polyolefins, are non-homogeneous, they contain the elements of crystalline and amorphous phases. Both phases coexist in certain intervals of temperature and pressure, the ratio of crystalline and amorphous substance reversibly changing. According to Gibbs Phase Rule:

$$F + P = C + 2 \tag{7}$$

where F is the number of freedom degrees ($F = 2$—temperature and pressure), P—that of phases, and C—the number of components. Opposite to (7), an individual polymer ($C = 1$) containing both crystalline and amorphous phases ($P = 2$) behaves as at least two phase system. It has been proposed to consider the multitude of various topological structures: the ends and entanglements of the polymer chains, to be that deficient second components.[3,4]

It is well known that the sorption of many additives by polymers from gas or liquid phases obeys Langmuir sorption Law, that is the additive concentration in polymer is related to its concentration in surrounding medium by formula

$$[A]_p = \frac{a[A]_m}{1 + b[A]_m} \tag{8}$$

($[A]_p$—the concentration of additive A in the polymer, and $[A]_m$—that in surrounding medium). The expression (8) can be derived supposing that the low-molecular additives are reversibly sorbed by certain centers Z:

$$A + Z \overset{K_a}{\rightleftharpoons} K_a AZ \tag{9}$$

To explain transport of the additive A to the centers Z it is necessary to assume that there exists a certain, though very low solubility of A in amorphous zones of the polymer besides that in the sorption centers. Assuming also that this solubility obeys the Henry Law ($[A] = \gamma[A]_m$) we obtain the expression

$$[A]_p = [A] + [AZ] = [AZ] = \frac{\gamma K[Z][A]_m}{1 + \gamma K'[A]_m} \tag{10}$$

which is equivalent to (8).

Equation (10) can easily be transformed into

$$\frac{1}{[A]_p} = \frac{1}{[Z]} + \frac{1}{K[Z]\gamma[A]_m} \tag{10a}$$

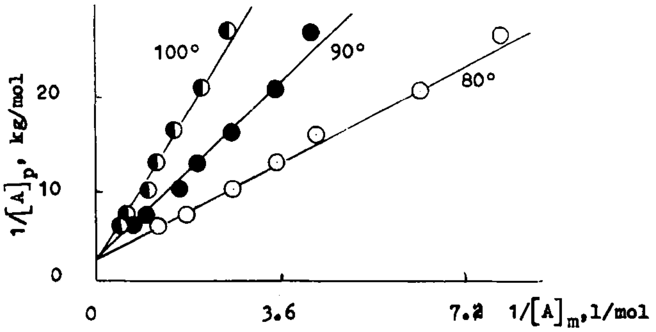


FIGURE 4 Concentration of phenyl benzoate in polyethylene as a function of its concentration in the gas phase surrounding the polymer sample, in coordinates $1/[A]_p$ vs $1/[A]_m$.

Experiments have shown that the sorption isotherms of many low-molecular compounds corresponding to different temperatures, sometimes below and above the melting temperature of the polymer, intersect in the same point on the ordinate axis if plotted in coordinates $1/[A]_p$ vs $1/[A]_m$ (Figure 4). According to (10a) it shows that the concentration of sorption centers Z for the same compound is independent of temperature, i.e. these centers are real physical structures. It has been supposed that the sorption centers are formed around topological structures mentioned above.

To confirm the sorption mechanism discussed the effect of the second low-molecular compound B on the sorption of the first one A has been studied. It was shown that introducing of the second compound into the medium surrounding polymer and containing constant concentration of the first additive A the concentration of A in the polymer decrease with increasing $[B]_m$ (Figure 5). This

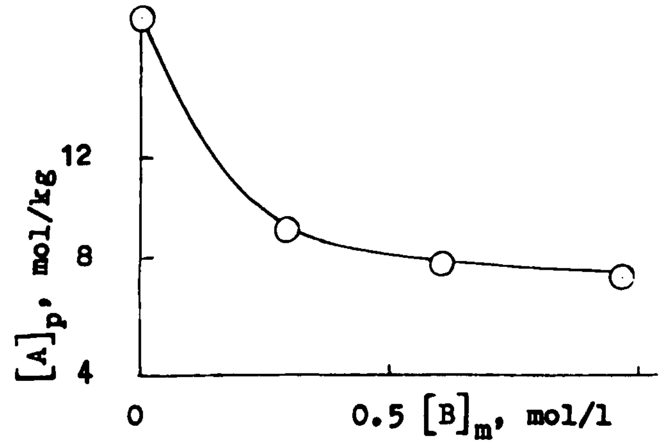


FIGURE 5 Concentration of azo-bisisobutyronitrile in isotactic polypropylene $[A]_p$ as a function of the phenylbenzoate concentration in benzene solution surrounding the polymer $[B]_m$. 40°C, $[A]_m = 0.60$ mol/l = const.

phenomenon may be explained by the scheme:

$$AZ + B \leftrightarrows A + BZ \tag{11}$$

The zones of short range order violation formed around the polymer chains ends and entanglements contain the most oxygen dissolved in the polymer. The mobility of polymer chains in the zones is greater than in surrounding ordered substance. So these zones may be considered as microreactors in which the polymer oxidation mainly proceeds surrounded with less reactive substance deprived of oxygen. Consider the consequences of this model.

If one free valence penetrates into such zone it initiates the chain reaction of polymer oxidation deprived of the chain termination step except that of the free valence exit from the zone. The average concentration of free radicals $[R^\cdot] + [RO_2^\cdot]$ in such zone will be one radical per the zone volume

$$[R^\cdot]_z + [RO_2^\cdot]_z = 1/V_z \tag{12}$$

To simplify consideration we accept $V_z = \text{const.}$, and $[R^\cdot]_z \ll [RO_2^\cdot]_z$.

The reactive groups in a zone in which free valence is present will be consumed according to the first order Law, i.e.

$$\frac{d[RH]_z}{dt} = -k_2[RH]_z[RO_2^\cdot]_z = -k_2[RH]_z V_z^{-1} \tag{13}$$

or

$$[RH]_z = [RH]_{z0}\exp(-k_2 V^{-1} t) \tag{14}$$

The average concentration of reactive groups RH in a zone $[RH]_z$ must be lower than that in the polymer bulk. During the time equal to $t_z = 5k_2^{-1}V_z$ these reactive groups in a zone will be wholly consumed.

Two cases are possible. If the average time during which free valence remains in a zone δ_z is less than t_z, the only difference between reaction kinetics in polymer and in analogous low-molecular liquid will be that in a polymer only a part of monomeric units will participate in the reaction. If $\delta_z > t_z$ all reactive monomeric units in zones will be consumed long before the free valence transit into another zone, so the observed reaction rate will be equal to the product of amount of reactive compound in the zone, overall $RO_2^\cdot$ concentration in the polymer and the inverse time of free valence presence in the same zone δ_z^{-z}:

$$W = V_z[RH]_z\delta_z^{-1}[RO_2^\cdot] \tag{15}$$

and the apparent rate constant of chain propagation $k_{2\text{eff}}$ will be independent of the real kinetical constant of the reaction $RH + RO_2^\cdot$, namely k_2:

$$k_{2\text{eff}} = V_z[RH]_z[RH]^{-1}\delta_z^{-1} \tag{16}$$

where [RH] is the average concentration of monomeric units in the polymer bulk. The scheme of reaction is shown in Figure 6.

The rate of chain termination, according to the model, will be equal to the rate of two valences getting in the same time to the same zone, i.e.

$$W_t = 2[Z]^{-1}\delta_z^{-1}(1 - \varepsilon)[RO_2^\cdot]^2 \tag{17}$$

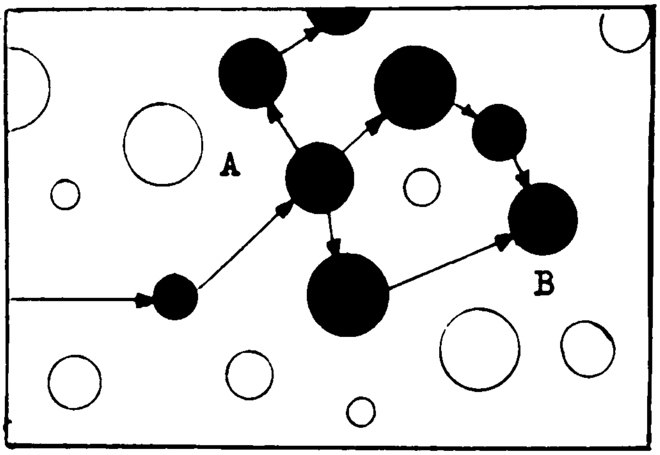


FIGURE 6 Scheme of polymer oxidation corresponding to the zone theory. A—chain branching site, B—chain termination site. Open circles—the zones before, black circles—zones after oxidation.

where ε is the probability for two free valences present in the same zone to leave it without interaction. Assuming this probability to be zero we may write the expression for rate constant of chain termination

$$k_t = W_t/[RO_2^{\cdot}]^2 = 2[Z]^{-1}\delta_z^{-1} \tag{18}$$

According to the model discussed the low hydroperoxide yield is due to the great local concentrations of radicals $R^{\cdot}$ and groups —OOH, resulting of decomposition of a part of hydroperoxide in reaction with $R^{\cdot}$ ($R^{\cdot} + ROOH \rightarrow ROH + RO^{\cdot}$).

Low-molecular compounds, using as radical acceptors, are mainly present in the same zones where the hydroperoxide groups are present and can react with radicals which left the primary cage but are still present in the zone. This phenomenon explains too high yields of free radicals when measured by inhibitor methods.

To convert the rate constants from dimension cm^3/sec used in deriving expressions (16) and (18) to l/mol sec they must be multiplied by $10^3N_A = 6.02 \cdot 10^{26}$.

The zone model explains the rapid decrease of the oxidation rate when only a small part of monomeric units is consumed: only a part of these units present in the zones in which the oxidation proceeds.

It has been shown that even in atactic polypropylene melt only near 50% of monomeric units participate in the rapid oxidation reaction which is usually registered in investigation of polymer oxidation. At the oxidation of alifatic polyamides only about one percent of the polymer participate in this reaction.[5]

Topological irregularity of polymers and existence of centers in which the molecules of low-molecular compounds present mainly result also in considerable deviations from the simple kinetical laws of reactions of such compounds dissolved in a polymer.

The zone of short order violation formed around the polymer chains entangle-

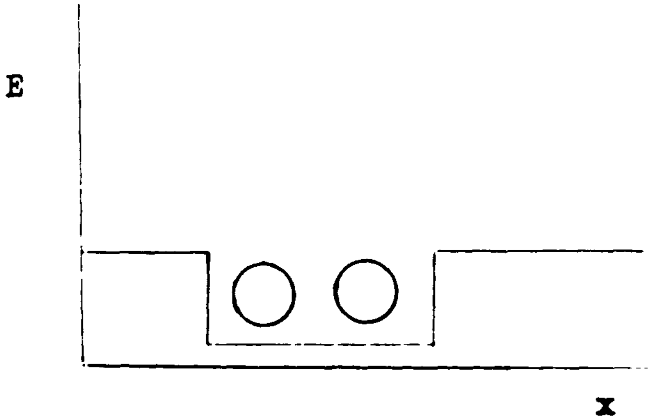


FIGURE 7 Potential energy of particles dissolved in a polymer inside and around the sorption centre E; x is the coordinate.

ment is the site in which the potential energy of a particle present in the polymer is minimal. For this reason the reaction of decomposition of a certain compound A

$$\mathrm{A} \rightleftharpoons (\mathrm{X}^{\cdot} + \mathrm{X}^{\cdot}) \rightarrow \text{products} \tag{19}$$

in polymer medium will be slower than in a low-molecular solvent because if the radical pair ($\mathrm{X}^{\cdot} + \mathrm{X}^{\cdot}$) is formed in the zone the yield of radical $\mathrm{X}^{\cdot}$ from the zone requires some energy (Figure 7).[6]

The molecules of decomposing compound (A) that are outside the sorption centers will decompose with greater rate than those inside because the separation of the radical pair outside the center requires no energy.

In general the reaction rate will be the sum of its rates inside and outside the centers, i.e.

$$W_a = k_a[A] + k_{az}[AZ] = \left(k_{az} + k_a \frac{[A]}{[A]_p}\right)[A]_p \tag{20}$$

where $[A]_p = [A] + [AZ]$—the overall A concentration in the polymer.

The ratio $[A]/[A]_p$ may be found by transformation of expression (10) and solving the resulting quadratic equation. In the simplest case when all centers Z are equal in their properties it is:

$$\frac{[A]}{[A]_p} = \frac{K_a[A]_p - K_a[Z] - 1 + \sqrt{(K_a[A]_p - K_a[Z] - 1)^2 + 4K_a[A]_p}}{2K_a[A]_p} \tag{21}$$

Dependence of the ratio $[A]/[A]_p$ on dimensionless additive concentration (ratio $[A]_p/[Z]$) for different values of equilibrium constant K_a is shown in Figure 8. The ratio is seen to increase with $[A]_p$, especially when $[A]_p$ becomes greater than $[Z]$, the curves for high additive concentration converging with increasing K_a value.

In agreement with formula (20), the rate constant of benzoyl peroxide decomposition in polypropylene increases with the peroxide concentration, resembling the curves of Figure 8. Special treatment of the polymer for increasing

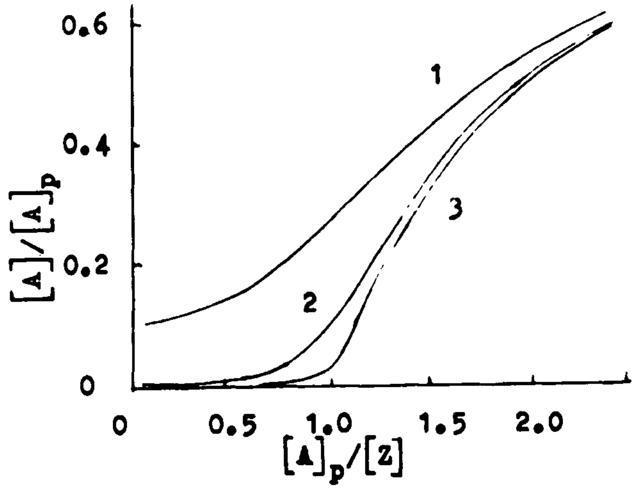


FIGURE 8 The ratio of concentrations of additive A outside and inside the sorption centers $[A]/[A]_p$ as a function of $[A]_p/[Z]$ calculated from Eq. (21). $K_a = 10$ (1), 100 (2), and 1000 (3).

peroxide solubility (i.e. Z) results in a marked decrease of the rate constant at the same peroxide concentration, according to (21) in which both terms with $[Z]$ are negative (Figure 9).

Bimolecular reaction in which two low-molecular compounds take part can proceed in a polymer only if the molecules of both reactants simultaneously get into the same elementary volume V^*. Two molecules present in different volumes cannot react. For this reason there are three possible ways for reaction A + B:

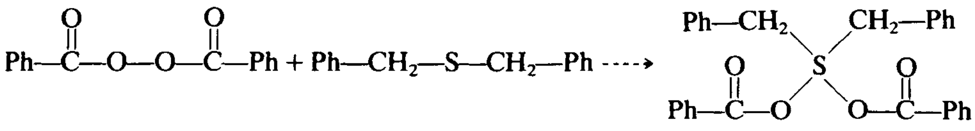
$$\mathrm{A} + \mathrm{B} \rightarrow \text{products} \qquad (22)$$

$$\mathrm{AZ} + \mathrm{B} \rightarrow \text{products} \qquad (23)$$

$$\mathrm{A} + \mathrm{BZ} \rightarrow \text{products} \qquad (24)$$

If the concentrations of mobile molecules A and B are small, we may neglect the first reaction (22).

As seen from Figure 10, the rate constant of reaction of benzoyl peroxide with dibenzylsulfide[7]



$$\mathrm{Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Ph + Ph{-}CH_2{-}S{-}CH_2{-}Ph} \dashrightarrow$$

$\dashrightarrow$ products (25)

varies with reactant concentrations decreasing at low and increasing with high ones. The increase of apparent rate constant (i.e. of the ratio $W_{ab}/[A][B]$, where W_{ab} is the rate) with increasing concentrations of both reactants may be explained by corresponding variation of mobile molecules concentrations shown in Figure 9, but reactions (22)–(24) cannot explain the decrease of the rate constant at low concentrations.

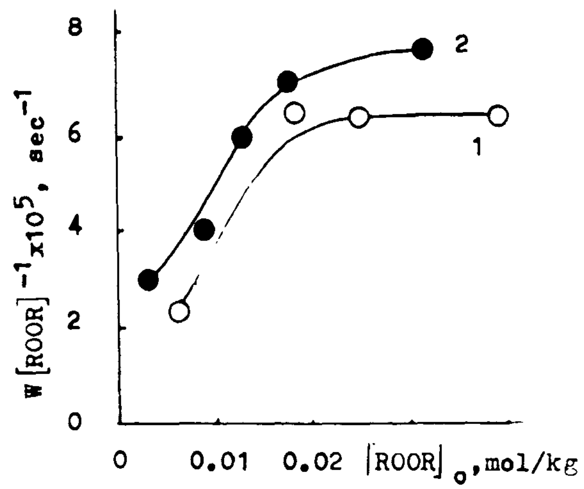


FIGURE 9 Rate constant (the ratio $W/[\mathrm{ROOH}]$) of benzoyl peroxide decomposition in isotactic (1) and atactic (2) polypropylene as a function of peroxide concentration 80°C.

To explain this decrease the scheme (22)–(24) must be supplemented with monomolecular transformation of ABZ^* complexes, consisting of one big center Z^* and two reactant molecules:

$$ABZ^* \xrightarrow{k_{ab}} Z^* + \text{products} \tag{26}$$

Concentration of such complexes will be:

$$[ABZ^*] = \frac{K_{ab}[Z^*][A][B]}{1 + K_{ab}[A][B]} \tag{27}$$

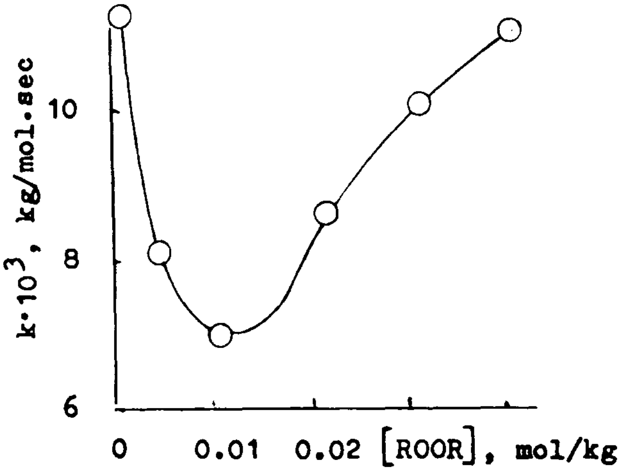


FIGURE 10 Rate constant of interaction of benzoyl peroxide and dibenzyl sulfide as a function of the peroxide concentration in atactic polypropylene. 50°C.

When $[ABZ^*]$ approaches the limiting value equal to $[Z^*]$ the rate becomes equal to $k_{ab}[Z^*]$ and apparent rate constant of this process becomes $(k_{ab})_{\text{eff}} = k_{ab}[Z^*]/[A]_p[B]_p$ and decreases with both A and B concentrations. The observed reaction rate is the sum of the rates of reactions (22), (23), (24), and (26), first three prevailing at high, and the second at low concentrations.[8,9]

The reaction of two molecules of substituted o-quinone and polymer proceeds as transformation of AAZ^* complexes and its rate tends to the limit equal to $k_{aa}[Z^*]$.[10]

Retardation of polymer oxidation process is based on reaction of low-molecular inhibitor with free macroradicals $R^{\cdot}$ or $RO_2^{\cdot}$:

$$RO_2^{\cdot} + IH \rightarrow ROOH + I^{\cdot} \tag{28}$$

The inhibitor radicals $I^{\cdot}$ formed can react with the polymer regenerating active free radicals $R^{\cdot}$ and then $RO_2^{\cdot}$ ($I^{\cdot} + RH \rightarrow IH + R^{\cdot}$). For this reason the compound IH will retard the oxidation reaction only if a considerable part of radicals $I^{\cdot}$ will be removed from reaction system without formation of active free radicals, for example by reactions of recombination with another $I^{\cdot}$ radical, with the active radicals $R^{\cdot}$ or $RO_2^{\cdot}$, or in disproportionation processes. Experiments have shown that the most of inhibitor added to polymer transforms into non-volatile intensively coloured products, apparently formed in polycondensation of primary radicals $I^{\cdot}$ formed in reaction (28).[11] Some of these products can retard the oxidation process.

Non-volatility of polymers makes possible the investigation of the oxygen consumption kinetics of polymer inhibited oxidation.[12] The inhibitor consumption during inhibited oxidation of low-molecular hydrocarbons has not been studied.

Figure 11 shows the oxygen consumption of the polyethylene oxidation in the presence of various concentrations of 2,2′-methylene-bis(4-methyl-6-tert.butylphenol), the inhibitor, at 200°C. The oxygen consumption kinetics is presented by

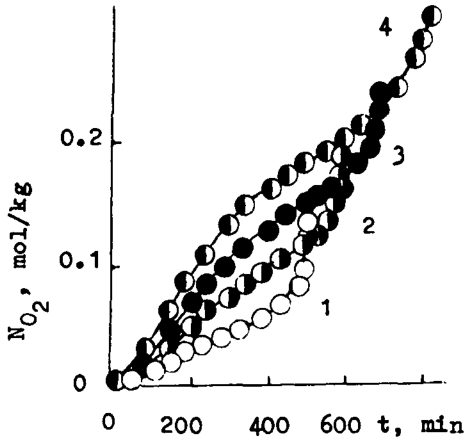


FIGURE 11 Oxygen consumption during polyethylene oxidation in the presence of inhibitor 2,2-methylene-bis(4-methyl-6-tert.butylphenol) at 200°C. Initial inhibitor concentrations 0.02 (1), 0.04 (2), 0.06 (3), and 0.08 (4) mol/kg, oxygen pressure. 300 mm Hg.

complicated curves: in initial stage of induction period (i.e. of the period of retarded oxidation) the oxygen consumption rate increases, then slowly decreases, and at the end of induction period rapidly increases. Beginning from the certain value of inhibitor concentration the initial rate increases with the concentration, in the same time increases the induction period. The inhibitor consumption during the most part of the induction period follows the first order law, that is its rate is direct proportion to its concentration. Comparing these dependences one may conclude that the main route of inhibitor consumption in this period is interaction with oxygen:

$$\mathrm{IH} + \mathrm{O}_2 \rightarrow \mathrm{I}^{\cdot} + \mathrm{HO}_2^{\cdot} \qquad (29)$$

The products of this reaction can initiate the polymer oxidation, for example as $\mathrm{RH} + \mathrm{HO}_2^{\cdot} \rightarrow \mathrm{R}^{\cdot} + \mathrm{H}_2\mathrm{O}_2$. When reaction of chain termination needs the mobile inhibitor molecule and immobile macroradical getting together, the undesired reaction (29) involves the mobile oxygen molecule and its rate only slightly depends on inhibitor molecule mobility. For this reason the inhibitor molecule sorbed by the center Z cannot participate in chain termination but can react with oxygen participating in chain initiation.

The critical inhibitor concentration, i.e. the minimal effective one,[13] can be determined from condition that at this concentration the rate of chain branching, which in developed reaction is equal to $\alpha\sigma k_2[\mathrm{RH}][\mathrm{RO}_2^{\cdot}]$, is equal to the rate of chain termination $k_3[\mathrm{RO}_2^{\cdot}][\mathrm{IH}]$. Taking into account that in the chain branching reaction hydroperoxide group is formed, and subsequent decomposition of this group results in formation of free radicals (average yield is σ), this condition may be written as

$$\alpha\sigma k_2[\mathrm{RH}][\mathrm{RO}_2^{\cdot}] = (1-\sigma)k_3[\mathrm{RH}_2^{\cdot}]\mathrm{IH} \qquad (30)$$

or

$$[\mathrm{IH}]_{\mathrm{cr}} = \frac{\alpha\sigma k_2[\mathrm{RH}]}{(1-\sigma)k_3} \qquad (31)$$

As told above, decrease in mobility of IH molecules will result in increase of $[\mathrm{IH}]_{\mathrm{cr}}$.

When the inhibitor concentration is much greater than the critical one, the inhibitor in polymer oxidation reaction is consumed according to the first order law relatively its current concentration. Denoting the rate constant of inhibitor consumption k_{eff} and assuming that the induction period, which corresponds to the slow stage of oxidation reaction, ends when inhibitor concentration becomes equal to the critical one, we obtain the expression:

$$\tau = \frac{1}{k_{\mathrm{eff}}} \ln \frac{[\mathrm{IH}]_0}{[\mathrm{IH}]_{\mathrm{cr}}} + \tau_{\mathrm{cr}} \qquad (32)$$

where τ is induction period and τ_{cr} that corresponding to the case when $[\mathrm{IH}]_0 = [\mathrm{IH}]_{\mathrm{cr}}$. According to (32) the increase in inhibitor critical concentration results in decrease of induction period.

According to expression (21) the greater is the sorption center concentration the lower is that of mobile molecules IH and, consequently the apparent rate constant k_3 and the critical inhibitor concentration $[IH]_{cr}$. In the same time the rate of direct oxidation of inhibitor molecules in the centers Z will be only slightly smaller than that in the centers. The resulting effect will be a marked decrease of induction period at low inhibitor concentration and increase at high concentrations.[14] The opposite effect: the increase of inhibitor effectivity at low concentration and decrease at the high ones can be achieved by adding to the polymer low-molecular compound which do not participate in the oxidation reaction but substitutes a part of inhibitor in the centers Z increasing the concentration of mobile molecules.[15]

Thus the topological polymer irregularity must be taken into account and can be used in polymer stabilization.

The polar groups of the polymer behave similarly to the sorption centers. Some of these groups can form the stable complexes with the polar inhibitor molecules:

$$IH + X \rightleftharpoons IH \cdot X \tag{33}$$

thus decreasing the inhibitor concentration outside the centers. This explains low effectivity of the polar "usual" inhibitors in polyamides and other polymers containing polar groups compared to polyolefins.

Morphological polymer irregularity results from the presence in the same polymer of crystalline and amorphous zones. These zones can form the large polycrystalline formations seen in optical mycroscope. This irregularity affects the regularities and the rates of polymer oxidation.

The elementary crystalline groups—crystallites—are characterized by long-range order in arrangement of macromolecules and of monomeric units the macromolecules consist of. The oxygen solubility in the crystallites is extremely low or zero, so the $R^\cdot$ radicals present in the crystalline zones of the polymer cannot transform into peroxide ones (i.e. to $RO_2^\cdot$). On the other hand these radicals (or, that is more precise, the free valences) can move inside the radicals by the sequence of reactions $R^\cdot + RH$.

The capture of free radicals by crystals will be equivalent to the kinetic chain termination if these radicals "stick" in the crystallite or recombine in them. It may be shown that if the radicals are only kept inside crystallites for a certain time it will be in some cases equivalent to chain termination.

Denote the total concentration of radicals $R^\cdot$ and $RO_2^\cdot$ r_a if these radicals are present in amorphous part of the polymer and r_c if they are present in crystalline part. Assuming that the individual elements of both phases are small and the gradients of radical concentrations in these elements may be neglected, and that the probability of radical recombination is also small and can be neglected, we obtain the equation of the radical balance in the crystalline part:

$$\frac{dr_c}{dt} = \frac{S}{x}(k_{ac}r_a - k_{ca}r_c) \tag{34}$$

where x is the polymer crystallinity, S—the area of the border between crystalline and amorphous zones of the polymer, k_{ac} and k_{ca}—the apparent rate constants of free radical transition from amorphous zones to crystalline ones (k_{ac}) and in the opposite direction (k_{ca}).

The solution of Eq. (34) depends on the character of r_a variation. If $r_a = \text{const.}$ we have:

$$r_c = r_a \frac{k_{ac}}{k_{ca}}\left\{1 - \exp\left(-k_{ca}\frac{S}{x}t\right)\right\} \tag{35}$$

and the rate of chain termination equal to that of radical accumulation in crystallites will be

$$W_t = x\frac{dr_c}{dt} = r_a k_{ac} S \exp\left(-k_{ca}\frac{S}{x}t\right) \tag{36}$$

We see that this rate will tend to zero with the reaction time.

If the free radical concentration in amorphous phase increases with time following the exponential law ($r_a = r_{a0}\exp(\varphi t)$), the solvation for Eq. (36) will be:

$$r_c = \frac{Sk_{ac}r_{a0}}{Sk_{ac} + \varphi x}\exp \varphi t \tag{37}$$

and apparent rate constant of chain termination will be really constant:

$$k_t = \frac{W_t}{r_a(1-x)} = \frac{Sxk_{ac}}{(Sk_{ca} + \varphi x)(1-x)} \tag{38}$$

Thus in the period of exponential increase of the reaction rate, specific for initial stages of branched chain reactions, the free radical transport from amorphous phase where the reaction proceeds to crystalline phase will be equal to the first order (i.e. linear) chain termination. According to (36) when reaction rate becomes constant this mechanism works no more.

As seen from Figure 12, the kinetic curves of crystalline and amorphous polypropylene oxidation in the coordinates $N_{O_2}^{1/2}(1-x)^{-1/2}$ vs time, which follows

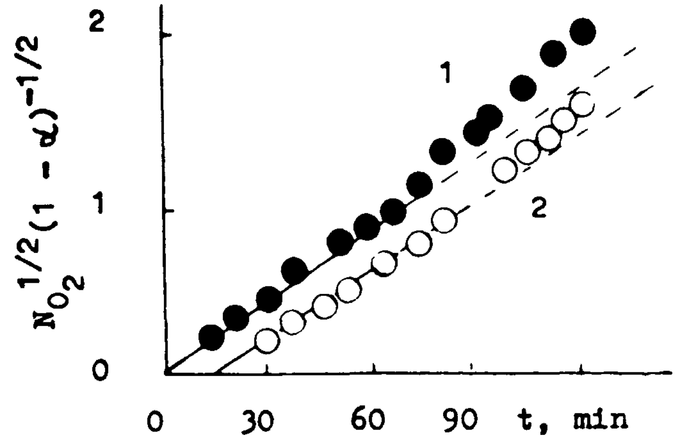


FIGURE 12 Oxygen consumption in atactic (1) and isotactic (2) polypropylene oxidation in the coordinates $N_{O_2}^{1/2}(1-x)^{-1/2}$ vs oxidation time. 130°, oxygen pressure 300 mm Hg. N_{O_2} is the amount of oxygen consumed in mol/kg, x—the polymer crystallinity.

from an assumption that oxidation involves only the amorphous part of the polymer (here x is crystallinity) and that the kinetic chains terminate via a second order process, are parallel lines with the same slope, however the line for the crystalline polymer does not originate from the zero point but from the point t_0, not coinciding with the coordinate origin, as if there were a certain induction on period. This shows that at the beginning of the crystalline polymer oxidation there is an additional chain termination process, not observed in amorphous polymer,[16] in accordance with the assumption discussed.

Macroradicals of a polymer are practically immobile, and there are only two ways of two radicals interaction: migration of free valencies through consequent reactions:

$$R^{\cdot} + R_1H \rightarrow RH + R_1^{\cdot} \tag{39}$$

and

$$RO_2^{\cdot} + R_1H \rightarrow ROOH + R_1^{\cdot} \tag{40}$$

where $R^{\cdot}$ and $R_1^{\cdot}$ may be the parts of the same or of different macromolecules, or formation of the light, low-molecular free radicals moving in the polymer by diffusion mechanism.

The diffusion of light free radicals enables us to explain the relatively high rate of kinetic chain termination at the oxidation of solid polymers. In the same time the light free radicals, if exist, can evaporate from the polymer sample into the gas phase. If the sample is thin enough, this evaporation can markedly change the free radical balance in it, i.e. to affect the reaction rate.

As seen from Figure 13, a maximum in the curve of oxidation rate vs the sample thickness was observed in investigating of poly(dimethylphenylene oxide) oxidation.[17] Maxima were observed in both curves of rates calculated per mass unit and per surface area unit. These maxima may be explained assuming that

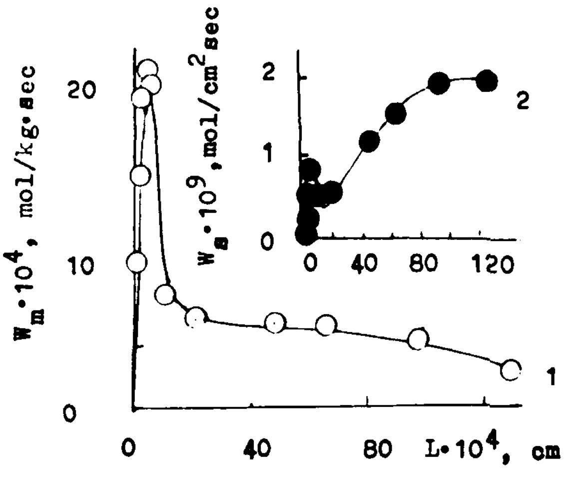


FIGURE 13 The rate of oxygen consumption during oxidation of poly(dimethylphenylene oxide) as a function of sample thickness. The rate was calculated per mass unit (1) and per surface area unit (2). 240°, oxygen, 300 mm Hg.

there are several types of light free radicals in the oxidizing polymer, differing in their mobility and reactivity. The more active radicals participate mainly in kinetic chain propagation, when the less active ones mainly terminate the chains. The greater is the free radical reactivity, the shorter is its lifetime, and consequently the shorter is the way it passes from origin to decay. The loss of less reactive radicals from samples 20–6 microns thick results in decrease of the rate of chain termination and, consequently, in an increase of the rate of the polymer oxidation, when the loss of more reactive radicals at the sample thickness less than 6 microns results in decrease of the rate of chain propagation and, consequently, of the overall reaction rate.

The analogous dependence has been observed at the oxidation of polycarbonate films.[17]

Thus irregularity and low mobility of a polymeric substance determine the specific features of a polymer oxidation, distinguishing this process from oxidation of low-molecular compounds.

It must be noted that a polymeric compound is essentially more sensitive to low degrees of oxidation than the low-molecular ones.

References

1. Yu. A. Shlyapnikov, T. A. Bogaevskaya, S. G. Kiryushkin and T. V. Monakhova, *Eur. Polym. J.*, **15**, 737 (1979).
2. I. A. Shlyapnikova and Yu. A. Shlyapnikov, *Vysokomol. Soedin.*, **B14**, 529 (1972).
3. Yu. A. Shlyapnikov, *Dokl. Akad. Nauk SSSR*, **202**, 1377 (1972).
4. Yu. A. Shlyapnikov, *Europhysics Conference Abstract*, **51**, 311 (1981).
5. T. V. Monakhova, T. A. Bogaevskaya and Yu. A. Shlyapnikov, *Vysokomol. Soedin.*, **A29**, 1033 (1987).
6. A. P. Mar'in and Yu. A. Shlyapnikov, *Dokl. Akad. Nauk SSSR*, **215**, 1160 (1974).
7. W. A. Pryor and H. T. Bickley, *J. Org. Chem.*, **37**, 2885 (1972).
8. N. N. Kolesnikova and Yu. A. Shlyapnikov, *Vysokomol. Soedin.*, **A18**, 2401 (1976).
9. Yu. A. Shlyapnikov and N. N. Kolesnikova, *Eur. Polym. J.*, **23**, 633 (1987).
10. E. S. Torsueva and Yu. A. Shlyapnikov, *Vysokomol. Soedin.*, **B19**, 377 (1977).
11. L. L. Yasina, B. A. Gromov, V. B. Miller and Yu. A. Shlyapnikov, *Vysokomol. Soedin.*, **8**, 1411 (1964).
12. N. K. Tyuleneva, S. G. Kiryushkin and Yu. A. Shlyapnikov, *Dokl. Akad. Nauk SSSR*, **279**, 145 (1984).
13. Yu. A. Shlyapnikov, *Pure appl. Chem.*, **52**, 337 (1980).
14. A. P. Mar'in and Yu. A. Shlyapnikov, *Vysokomol. Soedin.*, **B17**, 582 (1975).
15. A. P. Mar'in, I. V. Yatsenko, S. R. Avetisyan, Yu. A. Shlyapnikov and M. S. Akutin, *Dokl. Akad. Nauk SSSR*, **253**, 159 (1980).
16. Yu. A. Shlyapnikov, T. A. Bogaevskaya and T. V. Monakhova, *Khim. Fiz.*, **3**, 997 (1984).
17. I. A. Serenkova, E. P. Gorelov, Yu. A. Shlyapnikov, *Eur. Polym. J.*, **18**, 5 (1982).