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Thermal Oxidation of Polypropylene and Modified Polypropylene – Structure Effects

Lyudmila Shibryaeva

*N.M. Emanuel Institute of Biochemical Physics,
Russian Academy of Sciences,
Russia*

1. Introduction

Ageing and stabilization polymers is a major part of materials science. Aging of polymers defined as a set of chemical and physical transformations, leads to the loss of their set the desired properties. The main role in these transformations belong to chemical processes of degradation and crosslinking of macromolecules. Processes decomposition and structuring polymer conjugates include radical - chain, ionic and molecular reactions. Traditionally, the distinction is made between thermal, thermal-, photo-and radiation-chemical aging. Thermal oxidation and thermal-oxidative destruction are the most common and important processes in which polymer materials participate. It accompanies the posed for chemists-experimenters and producers engaged in polymer materials creation is the problem of maintenance of high quality of output, prolongation of its service life at conditions of thermal oxidation influence and thermal-oxidative destruction. Thermal oxidation of polymers leads to a modification and functionalization of the polymer chains. At the same time thermal oxidation is accompanied by the destruction of bonds in the macromolecules and influence the destructive processes. Thermal oxidation of polymers - a radical chain process with degenerate branching of kinetic chains of oxidation. The structure of polymer significantly influences on chain oxidation and destructive processes. Heterogeneity of polymers structures, the presence of regions differing in amplitudes of molecular motions, decrease of segment mobility, reduction of oxygen diffusion coefficient underlie this effect. These factors change kinetics and mechanism of process. As new methods and polymeric materials, researchers returned to the discussion of the induction period of oxidation of polymers. However, often in the literature there is confusion in the very concept and definition of the period induction. For example, when studying the thermal oxidative degradation of PP with different tacticity by thermogravimetric analysis (Chan J.H., Balke S.T., 1997; Nakatani H. and al., 2005) determine the induction period as a time corresponding to the onset of weight loss. I.e in fact, the period induction regarded not as the beginning of oxidation in infancy kinetic chain, and the time corresponding to the branching of kinetic chains in the collapse of hydroperoxide. This is a fundamental difference, so it is important this issue be considered. Often thermal-oxidative degradation is identified with the thermal oxidation. However, in depending on the nature of the polymer,

thermal oxidation process can take place without destruction chains, and with functionalization. As in the case of isotactic polypropylene. The author of the chapters of the book sets the task of separating the concepts related to the kinetics and mechanism.

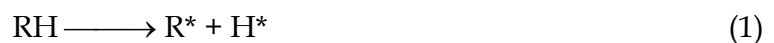
2. The particularities of oxidation of polypropylene

2.1 The kinetics and mechanism of autooxidation of solid polymers

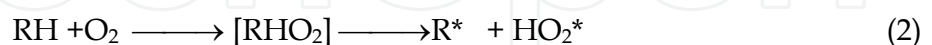
Three types reactions can be in the polymers in the presence of oxygen. 1) Separately occurring molecule reactions. 2) The radical - chain mechanism 3) The products of thermal decomposition and oxidation of polymers catalyze further decomposition of the polymer. The thermal oxidation of polyolefines has been extensively investigated in various works. The investigation of the kinetics and mechanism of oxidation of solid polymers have shown convincingly that this process is a radical - chain with degenerate branching of kinetic chains. In the thermal degradation, thermooxidation and thermal oxidative degradation of polymers play a major role alkyl (R^*), alkoxide (RO^*) and peroxide (RO_2^*) macroradicals and low molecular weight radicals (r^*). The high reactivity of the past towards macromolecules strongly influences on aging processes. The chain reaction of the oxidation of a polymer includes alternate steps of the chain propagation proceeding either inside the same macromolecule or between two molecules. The investigation of kinetics of oxidation of the polymers, containing aliphatic groups ($\equiv C-H$, $-CH_2-$ or $-CH_3$), showed that this process was described by scheme, corresponding to the mechanism of chain oxidation of liquid phase (Denisov E.T. and all., 1975).

2.1.1 Initiation of kinetic chain of oxidation

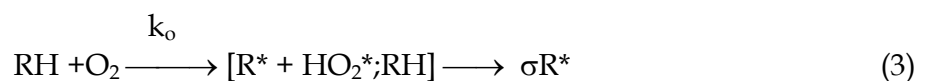
For the oxidation of the polymer to the formation of macroradicals R^* .



Where RH - the monomer units of polymer. Reaction can be triggered by physical factors such as ultraviolet and ionizing radiation, heat, ultrasound, or mechanical treatment chemical factors, such as catalysis, a direct reaction with molecular, singlet or atomic oxygen and ozone. However, initiation by direct interaction of molecular oxygen with the polymer, leads to detachment of a hydrogen atom, was unlikely, because it is endothermic reaction, enthalpy is 126-189 kJ/mol (Chan J.H., Balke S.T., 1997). Often, the birth of the chain portrayed as the bimolecular interaction of oxygen with the monomer units of polymer



HO_2^* radicals, which formed, can enter on reaction with neighboring RH or on reaction of recombination with the primary radical R^*



Therefore, the radical yield (f) is: $0 < \sigma < 2$. RH - may be neighboring monomer units of one macromolecule or belong to different macromolecules. At the origin of the chain oxidation may participate impurities of transition metals, residues of catalysts or initiators, etc. These impurities get into the polymer as a result of receiving or processing the polymer. Table. 1

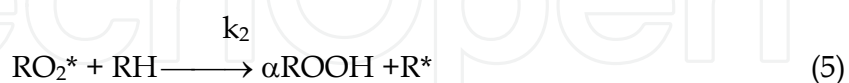
shows the rate of nucleation of chains, obtained by different authors inhibitor method, calculated from the rate of inhibitor consumption in polyethylene, polypropylene and some liquid hydrocarbons. The values of W_0 are small, so usually, when considering the kinetics of the autoxidation of polyolefins, nucleation rate of the chain is neglected compared with the rate of branching.

Substance	T,K	po ₂ , millimeters of mercury	W _{O₂} , mol/l• s	E, kJ/mol
PEHD	404	750	1.3 10 ⁻⁶	117.0
PELD	377	750	3.4 10 ⁻⁷	146.5
PE	391	750	1.5 10 ⁻⁷	-
PE melt	473	300	8.0 10 ⁻⁷	-
PP	405	750	2.1 10 ⁻⁶	92.0
	403	750	2.4 10 ⁻⁶	-
Atactic PP	403	300	<1.2 10 ⁻⁸	-
	423	300	<6.0 10 ⁻⁸	-
Isotactic PP	453	300	< 7.0 10 ⁻⁸	-
	463	300	< 2.7 10 ⁻⁶	-
2-Methylbutane	473	300	< 5.6.10 ⁻⁶	-
	410	4725	2.2 10 ⁻⁹	159.0
n-Heptane	406	4100	1.4 10 ⁻⁹	181.0

Table 1. The kinetic parameters of nucleation reaction chain (RH +O₂) in polyethylene, 7 polypropylene and liquid hydrocarbons

2.1.2 Growth of the chain

The development of the kinetic chain by alternation of two reactions: the formation of peroxide radicals (RO₂ *) and hydroperoxide (ROOH). Macroradicals R*, appeared in the initiation can easily react with oxygen molecules to give peroxide radicals RO₂ *. Peroxide radical can pull hydrogen from another polymer molecules to form polymeric hydroperoxides:



where k_2 - the constant of continuation of kinetic chain rate. α - the yield of hydroperoxide per mole of absorbed oxygen. In the solid polymer free radical R* and hydroperoxide group, formed in reaction (5) can not be away from each other. Part of ROOH is destroyed immediately after the formation of the reaction:

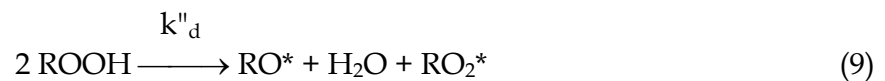
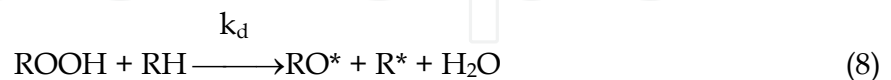


The reaction of (6) leads to a decrease in the yield of hydroperoxides during the oxidation of polymers in comparison with the oxidation of liquid hydrocarbon model. Their output ROOH is close to 100%. In the presence of oxygen even at low concentrations of the radicals

R^* are converted into RO_2^* continue to ROOH. The concentration of the radicals R^* is negligible compared to RO_2^* , so oxidation rate (W_{O_2}) is determined (limited) reaction rate (5). In this case: $W_{O_2} = k_1 [R^*] [O_2] = k_2 [RO_2^*] [RH]$.

2.1.3 The stage of branching of kinetic chain

Branching of the kinetic chain of oxidation occurs in the decay of polymer hydroperoxides. Generally, consider a few basic mechanisms of decomposition of hydroperoxide

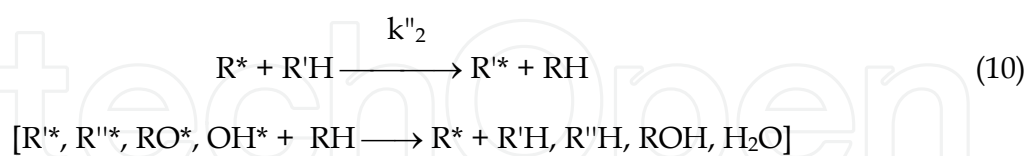


where k_d, k'_d, k''_d - the constants of ROOH decomposition rate.

Monomolecular decay (7) comes with a large activation energy (140-160 kJ / mol). It occurs only in the oxidation of hydrocarbon fluids in the case of low concentrations of ROOH in solvents not containing weakly bound hydrogen atoms. Are more favorable reaction (8) and (9). Heat of reaction (9) is ~ 36 kJ / mol, and for reaction (8) varies widely depending on the binding energy of the R-H. Reaction (9) dominates at high concentrations of hydroperoxide, the reaction (8) - in small quantities. In polymers containing weakly bound hydrogen atoms are predominant mechanism (8). As usual $[ROOH] \ll [RH]$, ROOH decay is described by a kinetic equation of first order.

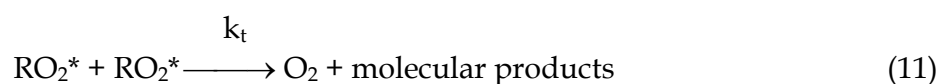
2.1.4 Chain transfer

The particularity of harden phase oxidation of polyolefyne is reaction of chain transfer - interaction of alkyl (R^*) or alkoxy radical (RO^*) with polymer competitive to its reaction with oxygen:



2.1.5 Chain termination

Break radical chain due to the interaction of free radicals with each other to form inactive products. There is quadratic termination of peroxide radicals at high pressure of oxygen:



Chain termination at low pressure of oxygen is quadratic termination of alkyl radicals



and alkyl with peroxide radicals:



Where k_t, k_4, k_5 – the constants of chain termination rate.

2.2 The kinetics and mechanism of autooxidation PP

Oxidation PP occurs in the amorphous regions of the polymer. Localization process in the amorphous regions was confirmed by small-angle X-ray scattering, by direct measurements of oxygen solubility in the samples with varying degrees of crystallinity, by the spin-paramagnetic resonance and other methods. The soluble oxygen, impurities, that contribute to the initiation of oxidation (traces of polymerization catalysts, traces of carbonyl groups, hydroperoxide and unsaturated groups) are localized in the amorphous regions polymer. This leads to a higher initiation rate in the amorphous areas compared to the total weight of the polymer. In the crystalline phase of PP on steric reasons, prohibited further kinetic chain reaction of oxidation. Even with the presence of peroxide radicals in the crystalline phase are not involved in the development of kinetic chains of oxidation of the crystallites. These radicals can formed by the action of γ - radiation on the polymer. RO_2^* slowly dying in the crystallites by the decay of education low-molecular radicals, which may go into an amorphous phase, initiating there oxidation.

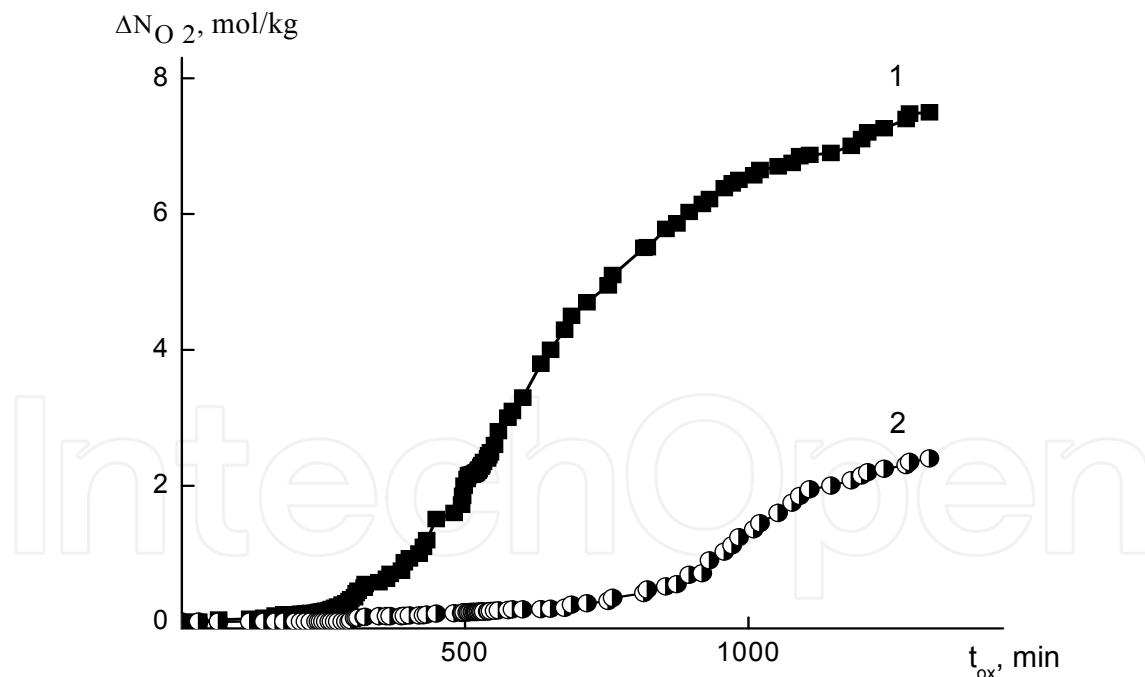


Fig. 1. The kinetic curve of oxygen absorption PP (1), and PE (2) $T_{\text{ox}} = 110^\circ\text{C}$, $p_{\text{O}_2} = 600 \text{ mm Hg}$

Oxidation of polypropylene describes the kinetic curve of oxygen absorption, which has an S-shape (fig.1). This curve is characterized by an induction period of self-acceleration and deceleration of oxidation in a deep stage of the process. A typical kinetic curve of oxygen uptake for isotactic PP is shown in Figure 1. For comparison, the kinetic curve for polyethylene (PEHD). The kinetic equation represents the dependence of the amount of

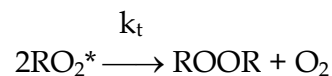
absorbed oxygen from the oxidation time was determined applied to the polypropylene in (Emanuel N.M., Buchachenko A.L., 1982). With this purpose it was used a special mathematical model for handling the above proposed scheme of oxidation of solid polymers. It was suggested the following approach: the origin of kinetic chain occurs at hydroperoxide decomposition (equation (8)). The rate of this reaction (which is reaction of degenerate branching of kinetic chains) in the early stages process considerably exceeds the rate of primary initiation (1). This allows to neglect the primary initiation reaction (1) and assume that the nucleation rate kinetic chain is the speed of degenerate branching. In this case, the initiation rate is determined from the equation:

$$w_i = 2\delta k_d[RH][ROOH]$$

where δ - probability going out of the radicals on one hydroperoxide group which is broken, i.e. probability of degenerate branching, 2δ - number of kinetic chains, born of every molecule of hydroperoxide decomposed. Type of reaction, limiting the development of kinetic chains (4) or (5), depends on the oxygen concentration $[O_2]$, consequently on the concentration of radicals R^* and RO_2^* . Concentration ratio $[R^*]/[RO_2^*]$ from the condition

$$k_1[O_2][R^*] = k_2[RH][RO_2^*]$$

whence $[R^*]/[RO_2^*] = k_2[RH]/k_1[O_2] \cong 10^{-2} \div 10^{-4}$. Thus, the kinetic chain termination occurs only with peroxide radicals. The termination of kinetic chain occurs by a quadratic law:



Kinetic equations for determining the rate of oxygen absorption can be obtained from the kinetic equations for the intermediate concentrations of particulate matter:

$$d[R^*]/dt = 2\delta k_d[RH][ROOH] + k_2[RH][RO_2^*] - k_1[O_2][R^*] \quad (14)$$

$$d[RO_2^*]/dt = k_1[O_2][R^*] - k_2[RH][RO_2^*] - k_t[RO_2^*]^2 \quad (15)$$

$$d[ROOH]/dt = k_2[RH][RO_2^*] - k_d[RH][ROOH] \quad (16)$$

Since the slow processes of oxidation can be applied to the quasi-steady concentration of radicals, i.e. $d[R^*]/dt = d[RO_2^*]/dt = 0$. From the equation (14) and (15) follows the expression

$$[RO_2^*] = (2\delta k_d[RH][ROOH]/k_t)^{1/2} \quad (17)$$

Where the rate of oxygen uptake

$$\begin{aligned} d[\Delta[O_2]]/dt &= k_1[O_2][R^*] = 2\delta k_d[RH][ROOH] + k_2[RH][RO_2^*] = \\ &= 2\delta k_d[RH][ROOH] + k_2(2\delta k_d/k_t)^{1/2}[RH]^{3/2}[ROOH]^{1/2} \end{aligned} \quad (18)$$

$\Delta[O_2]$ - means the amount of oxygen, which absorbed at a given moment of time.

From equations (14) and (16)

$$d(\Delta[O_2])/dt = d[ROOH]/dt + (1+2\delta)k_d[RH][ROOH] \quad (19)$$

From equation (19) that since the maximum concentration of hydroperoxide ($d[\text{ROOH}]/dt = 0$), the rate of oxidation is proportional to the speed of its disintegration. The proportionality factor $((1+2\delta))$ can vary from 1 to 3 (as $0 \leq \delta \leq 1$). Substitute equation (17) in the equation (16) gives:

$$d[\text{ROOH}]/dt = k_2(2\delta k_d/k_t)^{1/2}[\text{RH}]^{3/2}[\text{ROOH}]^{1/2} - k_d[\text{RH}][\text{ROOH}] \quad (20)$$

Integration (20) at $[\text{RH}] = \text{const}$, gives the equation:

$$[\text{ROOH}] = [\text{ROOH}]_{\text{max}} \{1 - [1 - ([\text{ROOH}]_o / [\text{ROOH}]_{\text{max}})^{1/2}] \exp(-k_d[\text{RH}] t / 2)\}^2 \quad (21)$$

Where $[\text{ROOH}]_{\text{max}} = (2\delta k_2^2 / k_d k_t) [\text{RH}] t$; $[\text{ROOH}]_{\text{max}}$, $[\text{ROOH}]_o$ - maximum and the initial concentration of hydroperoxide, respectively. So far as $[\text{ROOH}]_o \ll [\text{ROOH}]_{\text{max}}$, value ratio $[\text{ROOH}]_o / [\text{ROOH}]_{\text{max}}$ - infinitely small quantity, which can be neglected. In this case the expression (21) takes the form:

$$[\text{ROOH}] = [\text{ROOH}]_{\text{max}} [1 - \exp(-k_d[\text{RH}]t/2)]^2 \quad (22)$$

Substituting equation (19) in (15) and integrating gives the expression

$$\begin{aligned} \Delta[\text{O}_2] / [\text{ROOH}]_{\text{max}} = & k_d(1+2\delta)[\text{RH}]t + 2(1+4\delta)[\exp(-k_d[\text{RH}]t/2) - 1] - \\ & - 2\delta[\exp(-k_d[\text{RH}]t) - 1] \end{aligned} \quad (23)$$

Equation (23) represents the integral form of the dependence of the amount of absorbed oxygen from the oxidation time. This dependence is valid for shallow oxidation, we can neglect the flow of the polymer and assume $[\text{RH}] = \text{const}$. Expanding the exponential terms in the series for small t , and only the first three terms, gives the expression:

$$\Delta[\text{O}_2] = (k_2^2 \delta k_d [\text{RH}]^3 / 2k_t) t^2 = \Phi^2 t^2 = 1 / 2 [\text{ROOH}]_{\text{max}} k_d^2 [\text{RH}]^2 t^2 \quad (24)$$

So, oxygen uptake at the beginning of oxidation should be proportional to t^2 ; Φ - self-acceleration factor of the reaction.

$$\Phi = (1 / .2^{1/2}) (k_2 / k_t^{1/2}) (\delta k_d)^{1/2} [\text{RH}]^{3/2} \text{ or } \Phi = (1 / .2^{1/2}) [\text{ROOH}]_{\text{max}}^{1/2} k_d [\text{RH}] \quad (25)$$

Substituting this expression in (20) and assuming that the oxidized monomer units of the polymer in the subsequent oxidation do not participate, gives:

$$d[\text{ROOH}]/dt = k_2(2\delta k_d / k_t)^{1/2}([\text{RH}]_o - \Delta[\text{O}_2])^{3/2}[\text{ROOH}]^{1/2} - k_d([\text{RH}]_o - \Delta[\text{O}_2])[\text{ROOH}] \quad (26)$$

$$d(\Delta[\text{O}_2])/dt = k_2(2\delta k_d / k_t)^{1/2}([\text{RH}]_o - \Delta[\text{O}_2])^{3/2}[\text{ROOH}]^{1/2} - 2\delta k_d([\text{RH}]_o - \Delta[\text{O}_2])[\text{ROOH}] \quad (27)$$

From some point set a quasi-stationary concentration of hydroperoxide,

i.e $d[\text{ROOH}]/dt = 0$. Under this condition, equation (26) can be simplified

$$[\text{ROOH}] = k_2^2 \delta / k_d k_t = ([\text{RH}]_o - \Delta[\text{O}_2]) \quad (28)$$

i.e quasistationary concentration of hydroperoxide is proportional to the concentration of unoxidized polymer. When substituting this relation into equation (27) can be obtained

$$d(\Delta[\text{O}_2])/dt = 2(1+2\delta) \delta k_2^2/k_t ([\text{RH}]_0 - \Delta[\text{O}_2]) \quad (29)$$

After integrating the initial condition $\Delta[\text{O}_2] = (\Delta[\text{O}_2])_1$ and $t=t_1$, is obtained

$$1/([\text{RH}]_0 - \Delta[\text{O}_2]) = 2(1+2\delta)(\delta k_2^2/k_t)t_1 + \alpha \quad (30)$$

whence

$$\alpha = 1/([\text{RH}]_0 - \Delta[\text{O}_2]) - 2(1+2\delta)(\delta k_2^2/k_t)t_1, \quad (31)$$

where t_1 means the time from which the concentration of hydroperoxide can be considered quasi-stationary. It is still time to reach maximum concentration of hydroperoxide. Another model, describing the kinetics oxidation of PP, based the same pattern as discussed in (Shlyapnikov Yu. and al., 1986). This work identified two stages of the oxidation process. The initial stage of reaction and phase deep oxidation. At the initial stage of the reaction rate of hydroperoxide significantly higher than the rate of its thermal decomposition. The latter can be neglected. The equation of balance of free radicals and hydroperoxide in amorphous material in the absence of a linear chain termination is as follows:

$$d[\text{RO}_2^*]/dt = W_0 + \alpha k_d[\text{RH}][\text{ROOH}] - 2k_t[\text{RO}_2^*] \quad (32)$$

$$d[\text{ROOH}]/dt = \alpha k_2[\text{RH}][\text{RO}_2^*] \quad (33)$$

System of equations (32) and (33) is solved in a quasistationary approximation $d[\text{RO}_2^*]/dt=0$; $d[\text{ROOH}]/dt \neq 0$. The solution of equation (31) has the form:

$$[\text{RO}_2^*] = \{W_0 + \sigma k_d[\text{RH}][\text{ROOH}]/2k_t\}^{1/2}, \quad (34)$$

where $W_0 = f k_o [\text{RH}] [\text{O}_2]$ - rate of nucleation of chain, which negligible compared with that of chain branching in the early stages process. Substituting the values of $[\text{RO}_2^*]$ (34) and (33) and integration of this expression gives the variation of the expression ROOH concentration in time:

$$[\text{ROOH}] = \alpha N_{\text{O}_2} = \alpha \cdot 2\sigma k_2^2 k_d [\text{RH}]^3 t^2 / 8k_t = At^2 \quad (35)$$

So manner of equation (35) shows that in the initial stage reaction oxidation of the amount of oxygen absorbed during oxidation, and concentration hydroperoxide proportional to the square of oxidation time. This is consistent with the conclusion drawn in previous work (Emanuel N.M., Buchachenko A.L., 1982). Comparison (36) and (37) provided in the form of dependence changes in the concentration oxygen from the oxidation time:

$$\Delta[\text{O}_2] = (k_2^2 \delta k_d [\text{RH}]^3 / 2k_t) t^2 = \Phi^2 t^2 \quad (36)$$

$$N_{\text{O}_2} = (\sigma k_2^2 k_d [\text{RH}]^3 / 4k_t) t^2 = At^2 \quad (37)$$

show that the process oxygen uptake in the initial phase described by a parabolic law. For PP parabolic law is obeyed up to $\Delta[\text{O}_2] = 1$ mole/kg. At a more profound stage of a deviation from this law. Deviations from parabolic law is also observed at short times of oxidation, when still not satisfied quasistationarity the concentration of hydroperoxide (in the induction period).

2.3 Oxidation polymer on the deep stage

At deep stages of oxidation the rate of decomposition of hydroperoxide increases with its concentration. The rate of quadratic chain termination is proportional to the square concentration of radicals. At this point plays an important role expenditure monomer units of the polymer. Nucleation rate of the chain compared with the rate of branching can be neglected. The reaction is carried out at a high concentration of oxygen and the contribution reaction $R^* + RO_2^*$ is negligible, $[R^*] \ll [RO_2^*]$. For these conditions, the balance equation of free radicals and hydroperoxide is:

$$d[R^*]/dt = k_2[RH][RO_2^*] - k_1[O_2][R^*] + \sigma k_d[RH][ROOH] \quad (38)$$

$$d[RO_2^*]/dt = k_1[O_2][R^*] - k_2[RH][RO_2^*] - 2k_t[RO_2^*]^2 \quad (39)$$

$$d[ROOH]/dt = \alpha k_2[RH][RO_2^*] - k_d[RH][ROOH] \quad (40)$$

Using the method of quasistationary concentrations for $[RO_2^*]$ can be obtained:

$$[RO_2^*] = (\sigma k_d[RH]/2k_t)^{1/2} [ROOH]^{1/2} \quad (41)$$

$$d[ROOH]/dt = \alpha \sigma^{1/2} \{k_2 k_d^{1/2} [RH]^{3/2} / \sqrt{2k_t^{1/2}}\} [ROOH] - k_d[RH][ROOH] \quad (42)$$

The solution of equation (40) $[ROOH]_0 = 0$ has the form:

$$[ROOH] = [ROOH]_{\max} [1 - \exp((-k_d[RH])/2) t]^2 \quad (43)$$

$$[ROOH]_{\max} = \alpha^2 \sigma k_2^2 [RH] / 2k_d k_t \quad (44)$$

$[ROOH]_{\max}$ - limit sought by the concentration of hydroperoxide in the case of $[RH] = \text{const}$.

In the same conditions, the rate of oxygen consumption varies as

$$W_{O_2} = dN_{O_2} / dt = \alpha \sigma k_2^2 [RH]^2 / k_d k_t [1 - \exp((-k_d[RH])/2) t] \quad (45)$$

Equations (23), (24) describe the dependence of the amount of absorbed oxygen from the oxidation time and the equation takes into account the flow of the polymer during the reaction (31) allow us to establish the oxidation characteristics of polypropylene and the factors influencing this process. The above equation (35) does not take into account the flow of the polymer during the reaction. Because the rate of consumption of the polymer is the rate of absorption of oxygen:

$$d[RH]/dt = d(\Delta[O_2])/dt, \quad (46)$$

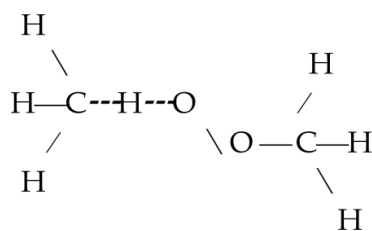
$$[RH] = [RH]_0 - \Delta[O_2], \quad (47)$$

Where $[RH]_0$, $[RH]$ - the concentration of polymer in the beginning of the reaction and at time t ; $\Delta[O_2]$ - the amount of oxygen, absorbed by this time.

2.4 The reaction to continue the kinetic chain of oxidation $RO_2^* + RH \longrightarrow ROOH + R^*$

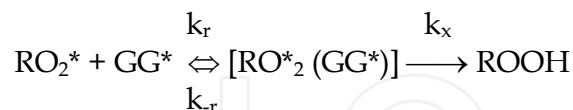
A key step in the radical chain oxidation of polypropylene is the reaction to continue the kinetic chain of oxidation (5). It determines the overall speed of the process leads to spatial

displacement of the free valence, it is the product of hydroperoxide, which is the degenerate branching of kinetic oxidation chains. In polyolefins, the reaction can take place both inside and intermolecularly. The oxidate polymer chain fragment may be a part of one macromolecule to which the RO_2^* radical belongs or a part of the neighbouring macromolecule. The consequences of the intra- and intermolecular chain propagation are different for various polyolefins. So, in polyethylene, the main mode of reaction is intermolecular (Emanuel N.M., Buchachenko A.L., 1982). In contrast to PE, in polypropylene, this reaction is carried out intramolecularly (Shlyapnikov Yu. A. and al., 1986; Rapoport N.Ya. and al, 1986). The reason for the differences between the PP and PE is the conformational structure of the polymer chain. With the continuation of the intramolecular kinetic chain the probability of activated complex optimal structure should depend on the local conformation of the site of a macromolecule carrying a peroxide macroradical. Conformation of the reaction complex is given below:



In this complex bond angles $\angle(\text{H}-\text{C}-\text{H}) = 109^\circ$, $\angle(\text{C}-\text{H}-\text{O}) = 180^\circ$, $\angle\text{HOO} = 100-105^\circ$, the distance between the atoms $\text{O} \cdots \text{H} = 1,4 \text{ \AA}$, $\text{C}-\text{H} = 1,2 \text{ \AA}$. Reaction does not occur, if the distance $\text{O} \cdots \text{H}$ more than $1,8 \text{ \AA}$ (Rapoport N.Ya., Mostovaya E.M., and all 1986). With the help of analysis of molecular models of Stuart-Briegleb, it was show that the probability of formation of activated complex of optimal structure depends on the set of conformations of the macromolecule. For example in PE, the linear activated complex is not formed in a macromolecule, having a straightened conformation of trans - zigzag, consisting of a sequence of trans-conformers ($\sim \text{TT} \sim$). For the occurrence of an intramolecular reaction of the chain oxidation of PE required sequence of two folded gosh-conformers type GG or G-G. Where are the angles of internal rotation around C-C bonds for G and G-conformers are equal to 120° , the angles of internal rotation for T-conformers are equal 0° . However, the equilibrium fraction of dyads GG in PE low, at room temperature it is approximately 9%. On the other hand, in PE not bulky lateral substituents create steric hindrance to intermolecular continuation of the kinetic chain of oxidation. Due to these factors, education linear activated complex with PE in intermolecular reaction is realized in order are more likely than in intramolecular (Popov A.A. and al. 1987). The presence of side substituents in the macromolecule of polypropylene leads to the formation of helical conformation, which consists of a series of trans and gauche-conformers $\sim \text{TGTGTG} \sim$. This sequence forms an extremely straightened conformation of the chain, which is "hard", and corresponds to the minimum energy on potential curve of interaction of valence-not bonded atoms. Folded conformation is formed by alternating joints left-and right dextro-rotatory sites spirals type $\sim \text{TGTGTGG}^* \text{TGT} \sim$. Where G^* - gauche conformer with the angle of internal rotation, deviating from 120° , relevant $\pm 60^\circ$. The relative position of atoms H adjacent tertiary C-H bonds in PP is determined by the type of dyad conformer: TT, TG and GG. Dyad TT in PP is not implemented due to the overlap of methyl groups in dyad TG peroxide radical is shielded from neighboring tertiary connection CH. Education of the reaction complex is most likely if the conformation of the reaction center meets the dyad GG*. This dyad is a

prelaunch conformers for the intramolecular reaction. This explains why in contrast to PE in polypropylene the reaction of $RO_2^* + RH$ proceeds mainly intramolecularly. In (Rapoport N.Ya. and al, 1986), this reaction was considered from the perspective of a reaction "pair" the radical $RO_2^* - GG^*$ -conformer:



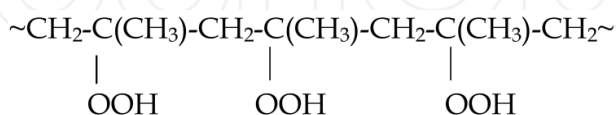
For the case $k_r \approx k_{-r}$ speed of reaction in the quasistationary approximation is:

$$W_2 = (k_x k_r / k_x + k_r) [RO_2^*] [GG^*] = k_{\phi} [RO_2^*] [GG^*]$$

If the limiting stage will be meeting with conformer GG^* - radical, $k_{ef} = k_r$, if the reaction is limited by a pair of $k_{ef} = k_x$; in the intermediate case k_r and k_x are added by law to the kinetic resistances. Thus, in theory, developed in (Rapoport N.Ya. and all, 1986; Popov A.A. and all., 1987) the rate of intramolecular reactions continue oxidation chains, occurring in isotactic PP is proportional to the concentration of GG^* - conformers in the macromolecule. Number of gauche-conformers at the site of a macromolecule depends on the contour length, the distance between the ends of the site. In the PP amorphous phase always there is a distribution on lengths of chains in the intercrystalline regions, hence, on the contour length and concentrations of GG^* - conformers. This leads to the presence distribution on values of the constants k_2 . Determined from the gross - value of the kinetics of k_2 are effective for the average values distribution. The smallest value of k_2 in the crystalline phase of PP, which have macrochain conformation of the helix. In (Roginsky V.A., 1977; 1982) studied the reaction of the chain oxidation crystal PP-phase at 200-300°C. Estimate of the effective values gave the value of $k_2 = 2.10^{-5} \text{ s}^{-1}$, it is 3 orders of magnitude lower than in the amorphous phase k_{2ef} PP. Hence, PP different grades with different molecular weight distribution have different width of the distribution on values of k_2 and values constants k_{2eff} .

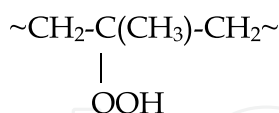
2.5 The reactions of accumulation and disintegration of hydroperoxide PP

As has been shown, PP oxidation occurs predominantly intramolecularly, the kinetic chain moves along the macromolecule. Macroradical RO_2^* , formed by the oxidation of polypropylene, reacts with a hydrogen atom from the tertiary C atom located in the β -position relative to the peroxide radical of their molecules. As a result, intramolecular transfer of a macromolecule oxidized PP formed "blocks" of several adjacent OH-groups.

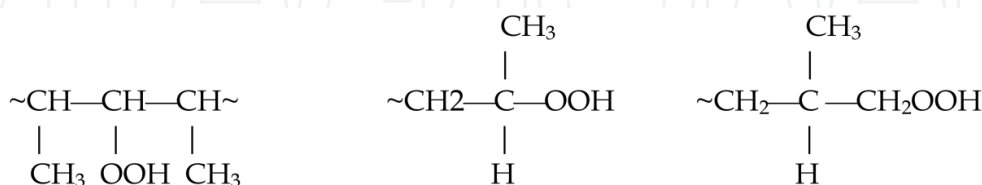


However, the low-temperature oxidation of solid polypropylene (70-110°C) proceeds with alternating intramolecular and intermolecular chain transfer. Intramolecular kinetic of extension chains is limited to small parts of the macromolecule with a favorable set of conformations. As a result, blocks of hydroperoxide can be short. In the solid polypropylene has found about 60% of paired units and about 20% of triads, the share of units with a higher number of hydroperoxide groups is small. It should be noted that in other carbon-chain polymers increases the probability of intramolecular reaction at the high rate of conformational motions. For example, in the polymers with a saturated C-C bond (such as

PE), the kinetic chain are transmitted preferably via a carbon atom (in γ -position), in other polymers (with unsaturated bonds, heteroatoms, phenyl rings, etc.) the transfer of kinetic chains are statistically. In oxidizing polypropylene along with the main hydroperoxide:



hydroperoxides can be formed type:



These hydroperoxides are formed as a result of intermolecular transfer of kinetic chains of oxidation. In the PP also form low molecular weight hydroperoxides such as methyl, ethyl, etc. The hydroperoxide, obtained by thermal oxidation of polypropylene, is not an individual compound, but is a combination of $-\text{OOH}$ and other oxygen-containing groups, and the concentrations and location of these groups in the polymer are not unambiguous functions of the hydroperoxide concentration.

2.6 The yield of hydroperoxide per mole of absorbed oxygen

Relationship between the concentration of hydroperoxide and absorption rate of oxygen stored in various pressures of oxygen and described by the following empirical equation:

$$W_{\text{O}_2} = a[\text{ROOH}]^{1/2} + b[\text{ROOH}], \quad (48)$$

where $a = k_2(\delta k_d/k_t)^{1/2}$, $b = \sigma k_d[\text{RH}]$; k_d - the constant of ROOH decomposition rate; δ - the probability of degenerated branching of kinetic chains; $\delta = \alpha\sigma$, σ - the yield of radicals from cell; α - the yield of hydroperoxide per mole of absorbed oxygen. The rate of polymers oxidation depends on concentration and constant of ROOH destruction. In its turn concentration of ROOH depends on yield per mole of absorbed oxygen. To determine the hydroperoxide yield may be used balance of hydroperoxide in the oxidation of solid polypropylene. For this the obvious fact may be used that at the maximal hydroperoxide concentration the rates of its formation and decomposition are the same.

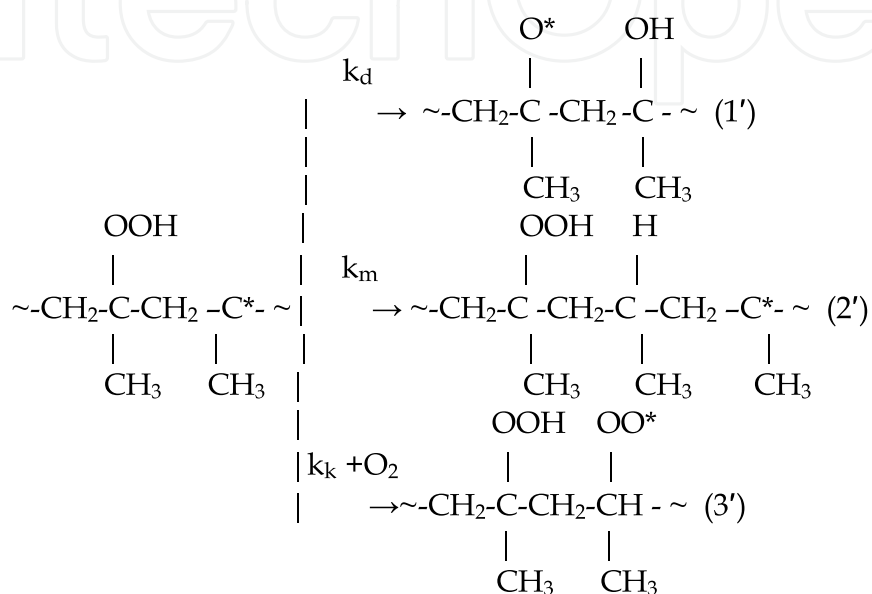
$$d[\text{ROOH}]/dt = \alpha W_{\text{O}_2} - k_d[\text{ROOH}]^n, \quad (49)$$

where n - the order of decomposition reaction of hydroperoxide. Substituting the experimental values for apparent rate constant of hydroperoxide decomposition k_p , and its maximal concentration at which $d[\text{ROOH}]/dt$ becomes zero. Assuming that the initial stage of polyolefin hydroperoxide decomposition obeys the first-order law, we get:

$$\alpha = k_d[\text{ROOH}]_{\text{max}} / (W_{\text{O}_2})_{\text{max}} \quad (50)$$

In liquid-phase oxidation of hydrocarbons the rate of oxygen uptake equals the rate of accumulation of hydroperoxide. The yield ROOH per mole of absorbed oxygen $\alpha=1$. In the autoxidation of solid polymer α much less than unity. For isotactic polypropylene,

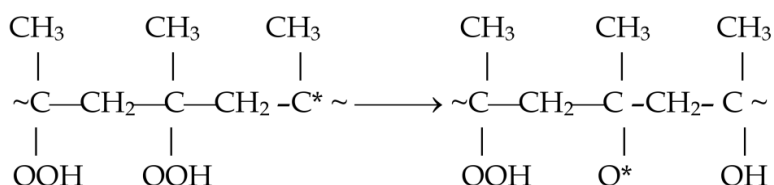
polyethylene, poly-4-methylpentene from (Emanuel N.M., Buchachenko A.L., 1982) $\alpha \approx 0,2-0,5$. This means that only 20-50% of the absorbed oxygen passes into the hydroperoxide, the remaining 80-50% goes into the reaction products, bypassing the stage education hydroperoxide. According to (Shlyapnikov Yu.A. and al, 1986) for PP $\alpha = 0,05-0,3$. There are several reasons for the drop out hydroperoxide per mole of absorbed oxygen. As a result of intramolecular chain transfer to ROOH appears next to the free valence and forms β -hydroperoxyalkyl radical. The interaction of the free valence with a freshly formed hydroperoxide group can occur in three ways, according to reactions (1'), (2') and (3').



The first way to becoming peroksilalkil radical would lead to the death of hydroperoxide group (1'), the second and third - the removal of the reaction center and stabilize the group. The yield of the stabilized hydroperoxide is equal to the sum of relative rates of reactions (2') and (3') to the sum of the rates of all three reactions, i.e. the expression for the yield of hydroperoxide (α) in PP is:

$$\alpha = \frac{k_k[\text{O}_2] + k_m}{k_k[\text{O}_2] + k_m + k_d} \text{ or } \frac{1}{\alpha} = 1 + \left\{ \frac{k_d}{k_k} \left([\text{O}_2] + \frac{k_m}{k_k} \right) \right\} \quad (51)$$

In the works (Kiryushkin S.G., Shlyapnikov Y.A., 1975; 1986), reaction (1') is considered as " induced" decay of hydroperoxide. The kinetic chain is moved along macromolecules formed alkyl macroradical who takes a step "backwards", reacts with the preceding neighboring hydroperoxide group to form alcohol and alkoksiradikal.



It should be noted that "return motion" of the kinetic chain $R^* + ROOH \longrightarrow RO^* + ROH$, which leads to the induced decomposition of hydroperoxide not necessarily occurs intramolecularly, it can also occur when the intermolecular kinetic extension chains. Only the probability of the latter case will be considerably less than intramolecular reaction, when the local concentration of ROOH and R^* is high and partners reactions can not break up the diffusion way. Intramolecular continuation of the kinetic chain of oxidation is not the sole reason for the low yield of hydroperoxide per mole of absorbed oxygen. If the kinetic chain oxidation of long, almost all oxygen passes into the hydroperoxide, with short chains, much of it remains products in the termination of kinetic chains, so α depends on the length kinetic chain. The oxidation of polypropylene in the induction period (long kinetic chain) $\alpha = 0.85$, almost all the oxygen passes into the hydroperoxide. For short chains of about 30% absorbed oxygen is consumed in the initiation of intracellular processes and termination of kinetic chains, with what shorter kinetic chain, the lower yield of hydroperoxide. On the same reason, the value of α particularly low in crystalline polymers, where kinetic chains are short. Thus low the value of α is not a strict criterion of intramolecular oxidation. It may also be a sign of short kinetic chains. Kinetic chain length (ν) - the number of molecules absorbed oxygen or hydroperoxide at a kinetic chain is

$$\nu = W_{ROOH}/W_i = k_2[RH]k_t^{-1/2} W_i^{-1/2} \quad (52)$$

(Emanuel N.M., Buchachenko A.L., 1982). Another reason low yield of hydroperoxide is the decay of the peroxide macroradical before it turns into a hydroperoxide. In this case, kinetic chain extension occurs without the formation of hydroperoxide. However, the decay of peroxide radicals PP is small compared with the probability of becoming it hydroperoxide. The collapse of the radical RO_2^* can occur at temperatures above 200-300°C. According to eq.(49) the hydroperoxide yield in the polymer oxidation must depend on the oxygen pressure over the polymer (on its concentration in the polymer). At the same time, oxygen concentration, affecting the ratio of the reaction rates, must affect the hydroperoxide structure, i.e. the distribution of hydroperoxide and other oxygen - containing groups along macromolecules and in polymer bulk. This distribution must affect the hydroperoxide properties. Experiments have proved this conclusion: the rate constant of hydroperoxide decomposition varies depending on the oxygen pressure at which the hydroperoxide has been prepared.

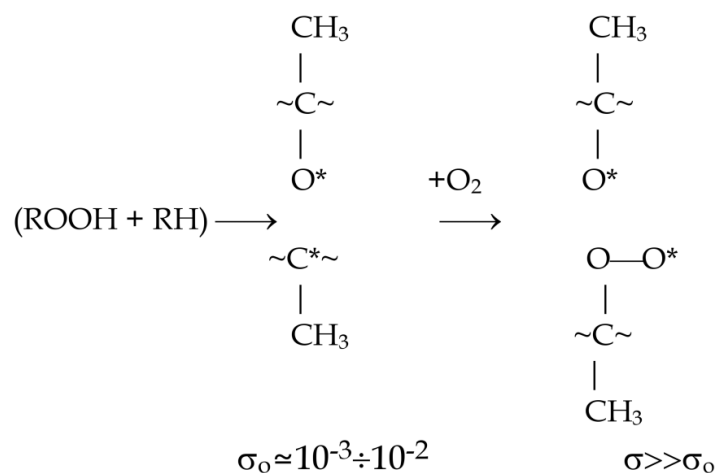
2.7 The probability of degenerate branching

The effectiveness of the emergence of new kinetic chains in the decay of the hydroperoxide has two features. First, the radical yield on one broken hydroperoxide group is small and amounts to several percent. Second, the probability of extinction branching depends on the oxygen pressure. The yield of low molecular weight hydrocarbons (methane, propylene) - the decay products of alkoxide and terminal alkyl macroradicals with an increase in oxygen pressure is not reduced to zero, and reaches a limiting finite value, independent of pressure oxygen. This means that oxygen is not only reduces the concentration of alkyl radicals, converting them into peroxide, but also participates in the reactions of their formation, by increasing output radicals from the cage. Calculated from data on collapse GP isotactic polypropylene dependence of d on the oxygen pressure in 100°C meet view $d = (7.10^{-3} + 1.10^{-4}) \cdot p_{O_2}$, where p_{O_2} in mm Hg. Probability degenerate branching of the oxygen pressure for isotactic PP and PE are found from the kinetics of autoxidation is presented in the table.2.

$p_{O_2, \text{mmHg}}$	0	50	100	200	400
σ_{pp}	0.017	0.12	0.25	0.40	0.65
σ_{pe}	-	-	0.26	-	0.32

Table 2. Probability degenerate branching for isotactic PP and PE

To explain the dependence of δ on oxygen pressure offered two hypotheses. Firstly, the probability of degenerate branching, δ is the initiating ability of ROOH depends on its structure and hence on the oxygen pressure at which the obtained hydroperoxide. Initiation efficiency block hydroperoxides, an order of magnitude higher than the efficiency of initiation isolated groups. However, this hypothesis is realized at low pressures oxygen (less than 150-200 mm Hg). Second, it increases the oxygen probability of degenerate branching root in the primary radical pair converts it into the secondary:



The radical yield of primary pair (σ_o) very low, and from the secondary - much higher, order of unity. The higher the oxygen pressure, the greater the concentration in the polymer, the greater the contribution secondary pairs, and, consequently, the higher the probability of degenerate branching.

2.8 Autoxidation induction period of the PP

The changes, occurring at oxidation of the polymer are laid in the induction period, so it is important establish the nature of this stage of the oxidation process. The parabolic law of oxidation of isotactic PP is established not immediately but after some time. This time was proposed to call the true induction period of uninhibited oxidation (Rapoport N.Ya and all 1986; Popov A.A. and al., 1987). For example, in PP at 403K the true induction period is equal $\sim 80\%$ of the experimental period, which correspond to time of absorbed oxygen $[\text{No}_2] \sim 0,1 \text{ mol/kg}$. Probably mechanisms of oxidation of the polymer in the period induction and on the stage of more extensive oxidation are different. In the literature discusses the possible reasons for the differences of the kinetics of oxidation PP in the induction period, and after leaving it. The following explanation of the features mechanism of oxidation in the induction period are offered in the literature. First, the initial stage oxidation corresponds to the accumulation of hydroperoxide. However, the quasi-steady on hydroperoxide do not run in the induction period. The low yield of hydroperoxide per mole of absorbed oxygen, and low initiating ability of hydroperoxide, which formed at the initial stage, leads to slow

down the rate of process of branching of kinetic chains (Popov A.A. and al, 1987). Secondly, the induction period may be associate with the low rate constant of radical decay. The rate constant of radical decay is changed during oxidation. Low - molecular radicals formed at the beginning of oxidation is exchanged for macromolecular radicals in reactions with hydroperoxide (Roginsky V.A. and al., 1976; 1982; Emanuel N.M. and al, 1982). Third, the existence of the period induction may be explained of the localization of the oxidation in the zones (Shlyapnikov. Yu.A. and al 1986; Richters P., 1970; Graeme A.and all., 1997; Livanova, Zaikov G.E., 1997). Localization of oxidation in the zones of polymer is the consequence of the structural and physical microinhomogeneity, nonequivalence of the structural elements , that differ frequencies and amplitudes of molecular motions. This creates spatial heterogeneity in distribution of the reactants in a polymer. Their local concentration may differ significantly from the average. This leads to distribution of reactivity, rate constants and energies activation, as a result, to polychromatic kinetics. This creates spatial heterogeneity in distribution of the reactants in a polymer. This means that oxidative processes is localized to the centers, "Microreactors", which are amorphous interlayers and interfibrillar areas. Polyethylene and polypropylene are not homogeneous. They have amorphous and crystalline regions. In the PE crystalline regions are impermeable and inaccessible for oxygen. The solubility of oxygen in the crystalline regions of PP on order of magnitude smaller than in the amorphous regions. The oxidation rate, calculated on the unit volume, and the limiting amount of absorbed oxygen are decreased proportionally with increasing crystallinity in both polymers (Bogayevskya TA, and al., 1978). Ther are several models of local oxidation of polymers proposed in the literature. In the framework of the local oxidation, polypropylene is considered as a set of kinetically nonequivalent "zones". This zones are differ of molecular dynamics, values of the radical yield of cells, which initiated the kinetic chains, and of termination rate constants k_t . (Makedonov Yu. V. and al, 1986; George A.G.and al., 1997). High molecular mobility, the velocities of the initiation and radical decay in zones leading to rapid establishment of steady-state concentration of radicals in these zones. In the more hard regions, where the rate constants k_t are low and the rate of initiation are small due to cellular effects the process of establishing steady-state concentration of radicals slows down. Therefore, initiating of the radical process in PP by irradiation with light leads to high rates of population of the soft zones of polymer by radicals with high rates of destruction. At longer initiating of the radicals they inhabit the rigid zones, resulting in the experimentally observed rate constant destruction of free radicals decreases. Thus, induction period of oxidation of PP is explained with in terms of non-homogeneous oxidation. By the end of the true induction period is set steady-state distribution of radicals in the zones, the parameters of oxidation are characterize the process of development and not change during further oxidation. Next "zone`s model" of oxidation of the polymer has been proposed (Shlyapnikov and al,1986; 1989). If in the previous model are considered as zones of amorphous regions as a whole, in the second model - it's part amorphous layers in violation of the short-range order. So, the amorphous interlayers of PP include through-passage chains in the folded conformation. In these areas, are concentrated oxygen and other low molecular weight substances. These areas are possess a high segmental mobility and high activity with respect to oxygen. These zones are considered as microreactors, which are surrounded by a more orderly and, therefore, less reactive substance. The model, which offers Shlyapnikov, has different mechanism of oxidation. From the perspective of this model, free valence, formed in the zone of violation of the order, begins a chain reaction, which has no stage of chain termination. The average

concentration of RO_2^* in the zone will be equal to one particle per volume area (particles / cm^3 or cm^{-3} .) $[RO_2^*]_z = 1/V_z$. Accepted that $V_z = \text{const}$ and we can neglect differences in the individual properties of zones. The expenditure of reactionary capable RH - groups in the some areas (RH_z) are proceeding of the law:

$$d[RH]_z / dt = k_2[RH]_z / V_z. \quad (53)$$

It concentration of groups in the area of RH, which does not coincide with average concentration of monomeric in the polymer. During $t_z = 5k_2^{-1}V$ reactive substance in violation of the order of the area consumed almost completely. Then there are two possibilities. First, if the average time of free valence in a separate zone t_z much less than θ , then the kinetics of reactions in polymer is not significantly different from the kinetics of the same reaction in low molecular weight liquid only in the reaction will not participate the entire polymer and part of it is equal to $[RH]_e = [Z] V_z [RH]_z$, where Z-density zones. Second, if the stay of free valence in the area of more than θ , then reaction rate is determined by the amount of matter in a separate area and speed displacement of the free valence from zone to zone:

$$W = V_z [RH]_z \theta^{-1} [RO_2^*] \quad (54)$$

where $[RO_2^*]$ - average concentration of peroxide radicals, calculated on the entire polymer. At the same time the observed rate constant of chain transfer is

$$k_{2e} = V_z [RH]_z [RH]^{-1} \theta^{-1} \quad (55)$$

and, consequently, will not coincide with the true constant reaction rate $RO_2^* + RH$, where this constant attribute. The rate of chain termination is determined by the frequency hit two free valences in the same area, i.e. will be:

$$W = 2 [Z]^{-1} \theta^{-1} (1-\varepsilon) [RO_2^*]^2, \quad (56)$$

where ε - chance what a pair of free valences, which has appeared in the same area, come out of it without recombination. Assuming, ε we can write $k_{t\text{ef}} = 2 [Z]^{-1} \theta^{-1}$ kinetic parameter of oxidation $k_{2\text{ef}}/k_{t\text{ef}}$ can be:

$$k_{2\text{ef}}/k_{t\text{ef}} = V_z^2 [RH]_z^2 N_{\text{av}} 10^{-6} / 2 [RH]^2 \theta \quad (57)$$

$$\text{where } \theta = V_z [RH]_z [RO_2^*] N_{\text{av}} 10^{-3} / W_{O_2} \quad (58)$$

Substituting (56) into (55) we find:

$$k_{2\text{ef}}/k_{t\text{ef}} = V_z [RH]_z W_{O_2} N_{\text{av}} 10^{-6} Z / 2 [RH]^2 [RO_2^*] \quad (59)$$

substitution (57) into (35) gives:

$$N_{O_2} = \delta k_d [RH] V_z [RH]_z W_{O_2} N_{\text{av}} 10^{-6} Z t^2 / 16 [RO_2^*] \quad (60)$$

Under provision, "the zone model" $[RO_2^*] = 1/V_z$, then one can assume that

$V_z [RO_2^*] = \text{const}$. Whence

$$N_{O_2} = B Z W_{O_2} t^2 \quad (61)$$

$$\text{where } B = \delta k_d [RH] V_z N_{\text{av}} 10^{-3} / 16 [RO_2^*] \quad (62)$$

On the initial stage of oxidation $W_{O_2} = N_{O_2}/t_{ind}$. Substituting this expression (60) we obtain

$$W_{O_2} = B N_{O_2} Z t^2/t_{ind} \quad (63)$$

Simplifying (55), we obtain the desired dependence:

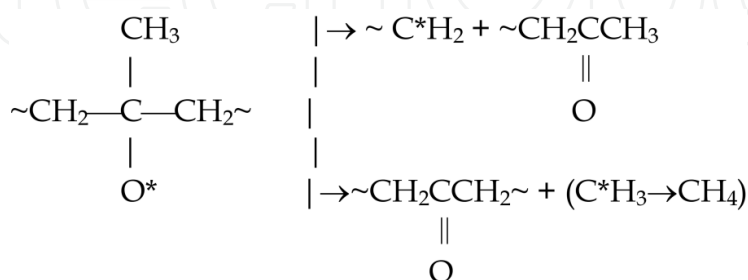
$$t = (t_{ind}/Z)^{1/2} (1/B)^{1/2} \quad (64)$$

Within the "zone's model" of the induction period is correlated with the autoxidation of PP time location of the free valence in the area, the low yield of hydroperoxide a can be explained by high local concentrations UN Teams and the radicals R^* in the zone, which is why the probability of their interaction is significant. Low yield of free radicals in decay. In within the "zone's model" of the induction period is correlated with the autoxidation of PP time finding free valence in the area, low yield hydroperoxide can be explained by a high local concentrations of the ROOH and the radicals R^* in the zone, which is why the probability their interaction is significant. Low yield of free radicals the decay of the polymer hydroperoxides due to the fact that, unlike low molecular weight Fluid pair of free radicals, emerged from the primary cell is a long time in a small volume of zone violations of the order, where the probability of recombination radicals is high. The low molecular weight scavengers of free radicals dissolved in the polymer are in the same zones violations of the order in which reaction occurs, and may react with the radicals issued from the primary cells, but do not go out of the volume of the zone, are able to initiate the reaction of oxidation. Polymer hydroperoxides due to the fact that in contrast to low molecular weight Fluid pair of free radicals, emerged from the primary cell is a long time in a small volume of zone violations of the order, where the probability of recombination radicals is high. The low molecular weight scavengers of free radicals dissolved in the polymer. Zone's model allows us to understand the dependence of the oxidation rate related polymers on the content of foreign links. Expression for the effective rate constants of the chain contains as one of the factors value of V_z - volume of the zone violations of short-range order rate constant of quadratic chain termination depends only on the total concentration of these zones. Introduction to the polymer chain side substituents leads to loosening of the polymer structure and hence, increases the volume of the zone V_z and the rate of oxidation of the polymer. For the same reason, reduces the probability of radical recombination in the area and increases. The transition from PE to PP leads to an increase in the rate of oxidation and reduction induction period (Shlyapnikov Yu. A., 1989). The rate of primary initiation, therefore induction period of oxidation of PP determined not only by the amount and concentration of reactive zones, but also nature of the substances, which are localized in these zones. In the papers convincingly (Livanova, Zaikov G.E., 1997) shown that the polymer (PP) of preexisting primary foci of initiation rate of radicals in which is significantly higher than those in microreactors, which can occur under the influence of stress and other influences on the RH bond PP. The main reason initiation of the primary foci are microscopic debris size (residual polymerization catalysts - transition metal valence and their products conversion).

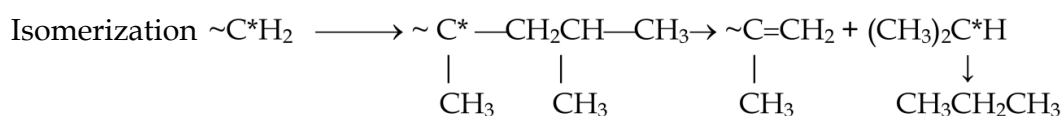
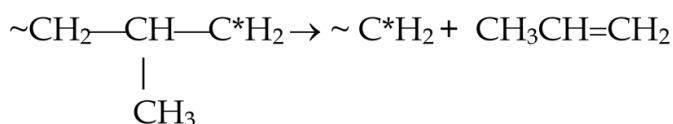
2.9 Thermooxidative degradation of polypropylene

Hydroperoxide is not only branching agent, but also a precursor of low-molecular products and breaks the molecular chains, resulting in to a change in molecular weight and molecular weight distribution (Shlyapnikov Yu. A., and al. 1986; 1989). Basic mechanisms of decomposition of hydroperoxide in the polypropylene - the bimolecular reaction involving communication C-H at the tertiary carbon atom of the macromolecule eq (8). Among decay

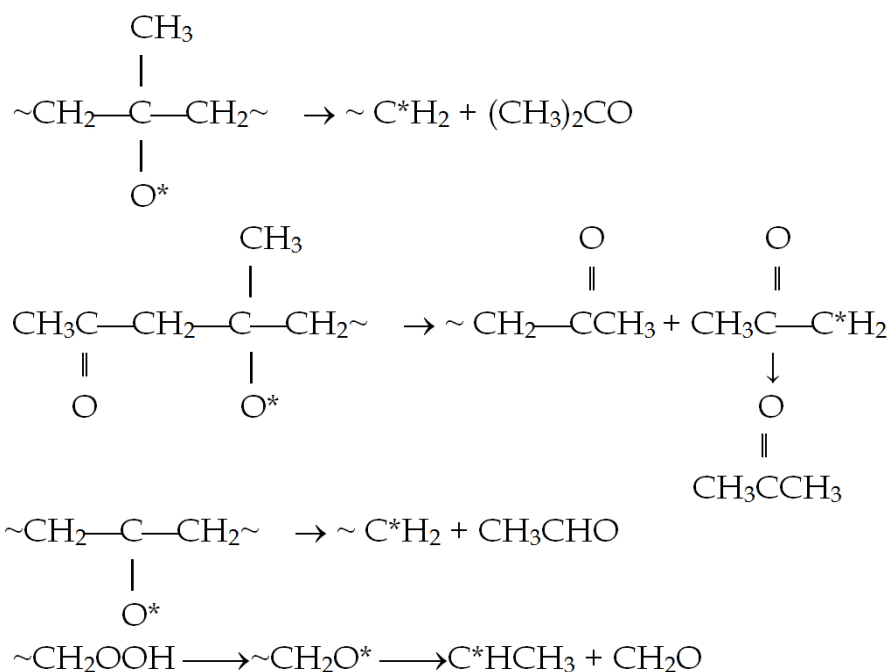
products detected ROOH PP: water, acetone, acetaldehyde, formaldehyde, methane, ethane, propane, propylene, ethylene, etc. The rate of formation of these products proportional to the concentration hydroperoxide. Comparative analysis of oxidation products and degradation products hydroperoxide. in an inert atmosphere, showed the same qualitative and quantitative composition. So products oxidation of PP is mainly formed by the decay of hydroperoxides. The total rate of formation of volatile products (of which the main product water-based) half the rate of decomposition of hydroperoxide. Ie 50% of productsoxidation remains in the solid phase in the form of alcohol, peroxide and ketone groups of macromolecules. The main source of low-molecular products are alkoxide macroradicals:



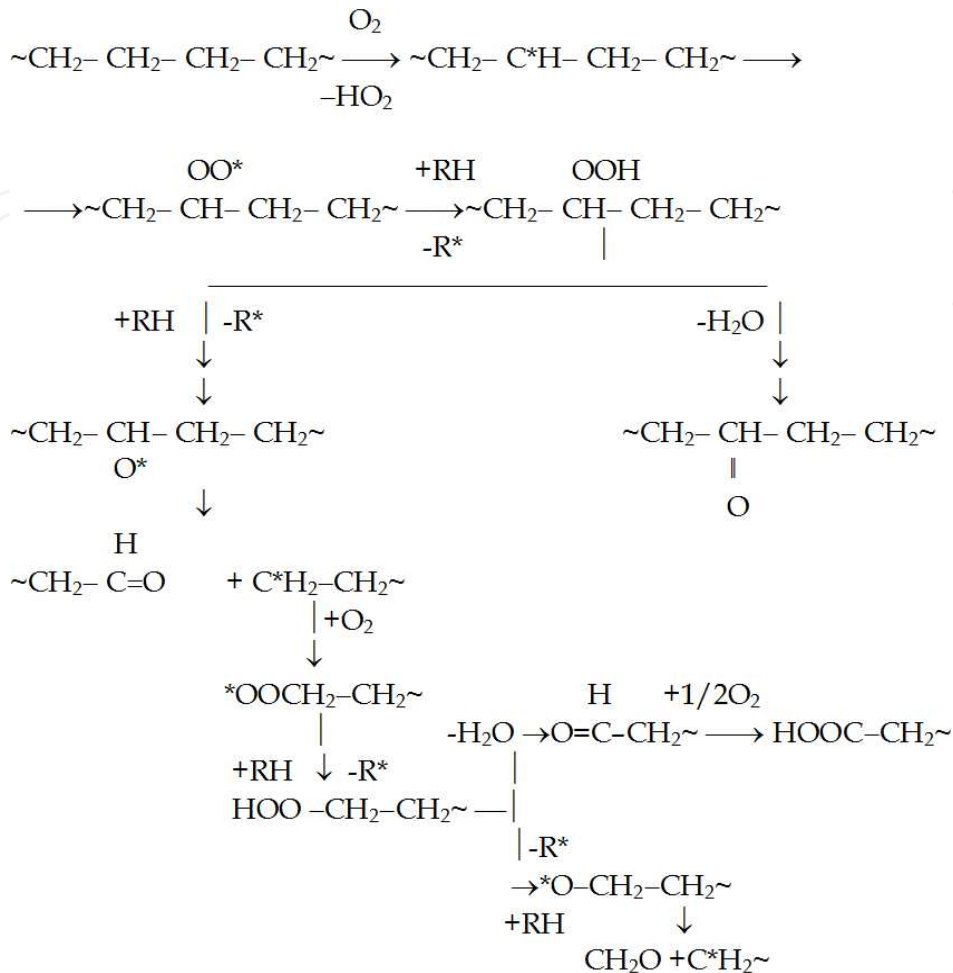
Low molecular weight hydrocarbons obtained from the terminal alkyl macroradicals:



Acetone and aldehydes are obtained of hydroperoxide groups and alkoxide radicals, respectively, located near the ends of macromolecules:



In polyethylene formation of the products described in the following scheme (Ranby B., Rabek J.F., 1978)



Polymer oxidation is accompanied by polymer chain destruction. When measuring the molecular weight of polymer, one can see only large remnants of the polymer chain, and if a short segment of the polymer chain takes place a few breaks they will be treated as one scission. Denoting the probability of the scission of a macromolecule as a result of one step of chain reaction propagation ρ_1 , the probability that there is no scission is $(1-\rho_1)$, and the probability of at least one scission resulting from v_b reaction steps proceeding in the same region (block) of the macromolecule is (Shlyapnikov Yu. A., 1989):

$$\rho_b = 1-(1-\rho_1)^{v_b} \tag{65}$$

The rate of formation of such oxidatized regions (or blocks) of polymer chains is the sum of rates of chain initiation and of chain transition from one molecule to another. Supposing the latter to be directly proportional to the overall concentration of free radicals in the system, gets this:

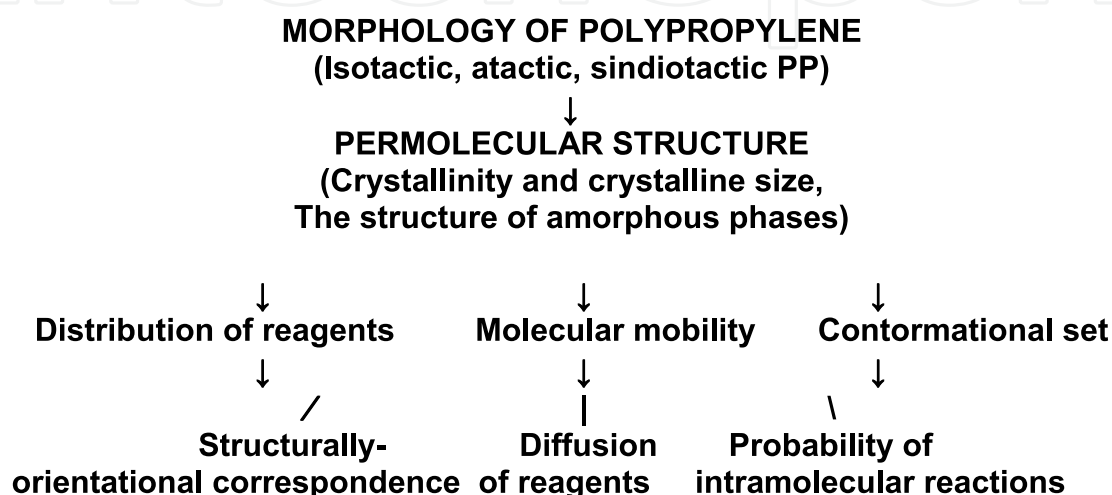
$$W_b = W_o + k_{tr} [\text{RO}_2^*], \tag{66}$$

where W_o is the chain initiation rate. It is assumed that the oxygen concentration is high enough and we can neglect reactions of R^* radicals. The rate of recorded scission formation is proportional to W_b , and if $\rho_b=1$ it is virtually equal to W_b . If the oxidation chains are long

enough, or k_{tr} is small, the rate of polymer destruction, i.e. the rate of recorded scission formation, will be equal to W_o , i.e. to the rate of chain initiation. The rate of chain initiation plus the rate of chain branching are always equal to the rate of chain termination; thus the rate of chain scission is proportional to that of chain termination, and at $\rho_b = 1$ is approximately equal to it (Shlyapnikov Yu. A. 1986; 1989).

3. The effects of structure on thermooxidation kinetics of polypropylene

The direct correlation between initial structure of polymer and kinetics of oxygen absorption is consequent from our scheme (Shibryaeva L.S. and al., 2003; 2006; 2010.)



The thermal oxidation is complex process including chain oxidation of hydrocarbon radicals, destruction of macro-chains and structure formation (cross-linking, crystallization). Thermal oxidation is accompanied by structural-physical processes leading to structure change (structural reconstruction) under the action of high temperature. The mechanism of these processes will depend on polymer's morphology and in its turn will influence on oxidation kinetics. The effect of polymer crystallites in vacuum and on air: the effect of high temperature may lead to perfection of crystallites structure, rise of temperature and melting heat, at the same time at long high temperature effect the destruction of chains occurs and crystallites and decomposed. There are the data demonstrating the influence of annealing temperature on relaxation parameters in polymer which allow concluding that there is significant change of structure of amorphous regions. At that the amorphous regions to a greater extent determine the particularities of oxidation radical reactions kinetics developing in them. With the aim of revealing of the role of structure (conformational set) of polymer macro-chains we also studied structure reconstructions, accompanying oxidation of oriented samples of PP with various extract degree. Structure parameters of PP: crystallites and amorphous regions, make it polymer heterophase system. These parameters of systems will determine localization of oxidation in zones having high segment mobility. In these Section is proposed a model for heterogeneous thermal oxidation of PP. Morphological irregularity of polymer results from the presence of crystalline and amorphous regions in the same polymer. This type of irregularity affects the regularities and rates of polymer oxidation. Crystallites are characterized by long-range order in the arrangement of macromolecules and of their monomeric units. Oxygen solubility in the crystallites is very low or zero, and

the R^* radicals present in crystalline zones of the polymer cannot transform into peroxide ones. On the other hand, these radicals can move inside the crystals by subsequent reactions $R^* + RH$. The capture of free radicals R^* by crystallites is equivalent to the kinetic chain termination if these radicals remain in the crystallites or recombine in them. It was shown (Shlyapnikov Yu.A., 1986) that if these radicals are only kept inside the crystallites for a certain time, this is equivalent to chain termination if the reaction is self - accelerated.

4. Isotactic pp, modified by oil

The given section is devoted to regularities of thermal oxidation and to structural reconstructions in the course of oxidation of model heterogeneous systems (Shibryaeva L.S., 2010). The change of destruction rate of PP chains in the presence of modifier may be explained by the change of mechanism of polymer oxidation. Increase of segment mobility of chain leads to increase of contribution of intermolecular transfer of kinetic chains of oxidation. As a result of this kinetic chains of oxidation become shorter and the number of breakages in macromolecules is increased. But in the case of destruction process acceleration at the stage of kinetic chains continuation at the expense of prevailing of intermolecular transfer in composition of hydroxyl containing products the single OH-groups will prevail. However analysis of products composition did not reveal prevailing of single OH-groups over block ones. Increase of chains mobility is observed not only in the case of PP with compatible additives, but also for incompatible, nevertheless the rate of PP oxidation in its presence is reduced. The most probable reason of oxidation process acceleration in samples of PP with compatible additives, of the rise of PP chain destruction rate is joint oxidation (co-oxidation) of polymer and additives. There are two fundamental hypotheses concerning the mechanism of these reactions which can be derived from the present experimental knowledge of structure and reactivity of macroradicals. (1) Hypothesis of physical migration by which the reactions of reactants are controlled either by mobility of the chains or their parts (segments) with fixed free valence or by diffusion of the low-molecular products of macroradical decomposition, e.i. the so-called radical fragments. (2) Hypothesis of chemical migration by which the reactions of reactants are controlled by various reactions of macroradicals of low-molecular fragments.

5. Experimental part

The samples of Isotactic PP non-inhibited powder of polymerizate was purified by standard technique.

5.1 The methods of investigation

5.1.1 Kinetics of oxidation

The kinetics of oxidation of isotactic polypropylene was investigated in circulating apparatus with freeze-volatile products of oxidation at the temperature of liquid nitrogen. When the film thickness is less than 60 microns maximum rate of oxidation of the sample is proportional to its thickness. Consequently, at a thickness of less than 60 microns ($l < 60$ mcm) kinetic regime is realized, i.e. diffusion of oxygen is a rapid process and does not affect the rate of oxidation. On the contrary, for $l > 200$ microns oxidation occurs in the diffusion regime and the maximum speed calculated for 1 cm^2 the surface is practically independent of the thickness.

5.1.2 The research methods

Differential scanning calorimetry, X-ray analysis, IR-spectroscopy, Electronic microscopy, ESR-study.

6. List of abbreviations

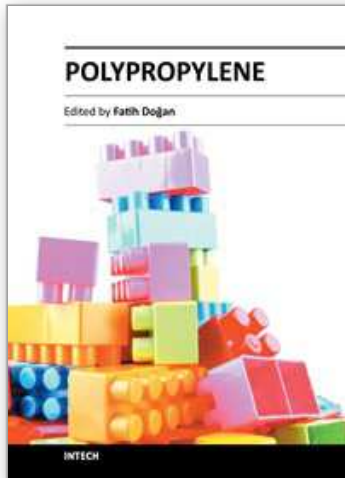
PE	- polyethylene
PP	- polypropylene
PEHD	- polyethylene of high density
PELD	- polyethylene of low density

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University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
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Phone: +86-21-62489820
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