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V. M. Gol'dberg^a; G. E. Zaikov^a

^a Institute of Chemical Physics, Moscow, Russia

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Chemical Transformations of Polymers During Processing

V. M. GOL'DBERG and G. E. ZAIKOV

Institute of Chemical Physics, 4, Kosygin str., Moscow, 117334, Russia

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1. INTRODUCTION

Studies of mechanical and thermooxidative degradation and stabilization of polymers were widely developed in late fifties–early sixties. As a result, the main features of these rather complicated processes became more or less clear. Monographs and reviews,^{1–7} summing up the results of investigations in this field, have appeared lately.

The marked place is occupied by transformations in solid phase. Much attention is paid to studies on solution. Degradation in melts is studied much less. Rather high temperatures at which melts are achieved appear to be one of the reasons. A great number of reactions, running at sizable rates in these conditions, hamper investigations of their mechanism and kinetics. Chemistry of degradation in melts seemed not to differ much from reactions in concentrated solutions.

It is important to point out, that the processing is not too complicated from the point of view of initiated changes chemistry. In this case we can consider mechanical and thermooxidative degradations, which occur simultaneously during a short period at high temperatures. According to the most general considerations it is possible to suppose, that the influence of mechanical load on the totality of reactions in this case will give additive initiation of thermooxidation.†

Thus, during the processing the mechanically initiated autooxidation is going on. The nature of organic compounds oxidation is well-known.¹¹ However, conditions of its realization during the processing appear rather difficult to be model and study. There are few publications on the primary stage of general degradation during the processing—mechanodegradation in melt. It may be connected with difficulties in quantitative characterizing the flow of polymer melt in processing

†The works of N. S. Enicolopov and co-authors^{8–10} on solid-phase thermal processes under pressure with a shear, point out the considerable influence of elastic deformation on the mechanism of the processes. But in the case under consideration (melt) the conditions of a chemical process occurrence are quite different.

machines. It is not easier to measure the radical yield at high temperatures. Their behavior is always complicated by side reactions. As a result the mechanism of chemical transformations during the processing is usually evaluated through changes of polymer properties and content in the dependence on conditions. The situation is complicated by interconnection of some of conditions during the processing. For example, in extruder such "chemically inert" parameter as its output, does influence: i) viscosity, because of non-Newton flow; ii) the duration of degradation, iii) the rate of mechano-chemical initiation of radicals, and in some cases iv) temperature as a result of self-heating.

The pulse of aging, the polymer product receives during birth (processing), is materialized in molecular weight changes, carbonyl and hydroperoxide groups accumulation. It is reflected not only on the "momental" changes of properties, but life-time left. From a practical point of view it is very important to know, for how many years of aging in exploitation conditions minutes of polymer presence in processing machine correspond.

There is one more scientific-technical problem, to solve which it is necessary to know the mechanism of degradation. It is modification, i.e. dosed regulation of polymer properties in this process. Such directions in investigations and technology are being intensively developed during last years. One of them, connected with initiator usage, was named "reactive extrusion." Reactive extrusion during polymer mixture processing helps to solve the problems of molecular weight regulation and increasing of compatibility because of block-copolymers creation.

The processing of secondary polymer also includes a number of problems, being solved through usage of mechano-initiated thermooxidation processes. These processes could partly compensate the irreversible changes of properties during exploitation, connected with reactions of crosslinking or ruptures accumulation of hydroperoxide groups.

The aim of this review is the attempt to understand peculiarities of polymer degradation mechanism during the processing. In comparison with usual mechano-degradation at low temperatures and usual thermooxidation under constant oxygen concentration they are:

1) Thermal rupture of a macromolecule, activated by mechanical load is just the initial stage of a complicated chain process, and not the only one, as it often happens at low temperature in solid phase.

2) The process of thermooxidation is going on in a closed volume with limited oxygen concentration. In this case we are speaking of greatly decreased concentrations while melt movement during processing, and not of diffusion limitations.

3) Chemical reactions are going on in polymer matrix at temperatures by tens of degrees higher, than those of crystallization or glassing, and very often under mixing. That is why the influence of overmolecular structures on process rates seems less probable.

4) The mechanism of polymer molecular weight changes during processing is, apparently, the principal difference from "pure" thermooxidation. The difference lies in highly probable appearance of chain processes in macromolecules growth when alkyl radical R' interacts with double bond.

2. MECHANICAL DEGRADATION

General features of mechanical degradation at low temperatures in solid phase and solution are studied well enough.⁷ Investigations of solutions are of great interest for studies of nature of mechanical degradation in melts. Two series of works on the behavior of isolated macromolecules in longitudinal hydrodynamical field were published lately.¹²⁻¹⁷ Theoretical interpretation of macromolecule degradation in "stretching" flow is based on the works of I. Frenkel.¹⁸ Experimentally such flow can be achieved in sets of different types: cross-like slit,¹⁹ contrary nozzles,²⁰ channels with sharply changing diameter.²¹

Conformation of macromolecules transforms from the cloud to the straightened form in the longitudinal stream. It happens when a certain critical deformation rate $\dot{\epsilon}_c$ is reached. The $\dot{\epsilon}_c$ value varies in inverse proportion to viscosity η_s of the solution and molecular weight $M^{1.5}$.

However, sometimes it is not enough for macromolecular chain rupture to reach this rate. The rupture occurs after reaching $\dot{\epsilon}_f$, which is inversibly proportional to M^2 , according to application of Stocks law to the spring-ball model. While the molecular weight growth $\dot{\epsilon}_c$ decreases faster, than $\dot{\epsilon}_f$. For greater values of M it means $\dot{\epsilon}_c = \dot{\epsilon}_f$. Thus, large macromolecules can't be straightened without rupture. Appropriate molecular weight for atactic polystyrene is $M = 3 \cdot 10^7$. The force necessary for chain rupture is estimated as close to the value for C—C bond splitting, experimentally measured.

However, according to Stocks law parabolic distribution of molecular weights should be awaited as a result of degradation of macromolecules with nearly equal length. In experiments with polymer with narrow distribution of molecular weights^{12,15,19} a new polymer appears with narrow distribution and half the mo-

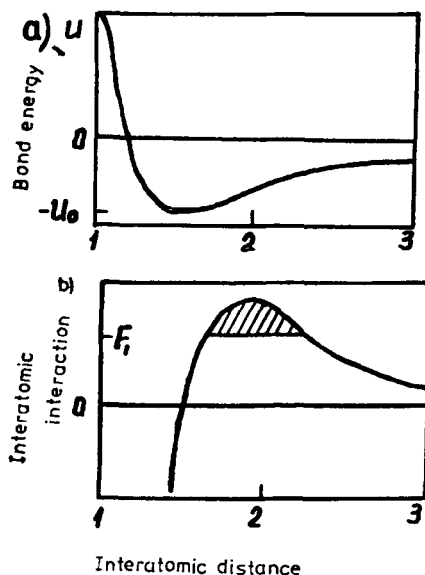


FIGURE 1 a) Morse-function for covalent C—C bond. b) Interatomic interaction (force), received from Morse-function.

lecular weight. It means, that macromolecules rupture near the centre. Such results were predicted.^{18,23} The model for description of these phenomena was developed in References 13 and 20. The authors base on a well-known Morse-function, describing the potential energy as the function of the distance of two carbon atoms (Figure 1a). Energy to force transformation leads to the function shown on Figure 1b. Shaded area corresponds to activation energy of rupture, if the bond is loaded by force F . It is supported traditionally, that the rupture occurs, when thermal fluctuations "throw" the bond higher, than energetic barrier, which is decreased by chain strain in stretching flow. According to the model the rate constant of chain rupture reaction K_d is proportional to:

$$K_d \propto \exp[-u_0/kT + (a/l)\beta N^2/8] \quad (1)$$

where u_0 = bond strength; β = proportional to $\dot{\epsilon}$; k = Boltzmann constant; T = temperature; N = number of molecular chains; a = length of a strained bond; l = length of a monomeric chain.

The results of model calculations for atactic polystyrene with $M = 1 \cdot 10^7$ are shown on Figure 2.^{12,13} The rate of ruptures is seen to be equal to zero below $\dot{\epsilon}_f \approx 1 \cdot 10^3 \text{ s}^{-1}$ and increases very sharp, and the width of distribution of rupture places relative to the centre—decreases.

It is necessary to point out, that ratio (1) is quite close to the usual formula, received in thermofluctuational theory of durability. The difference lies in the fact, that the item responsible for the mechanical load input to the rate constant is not dependent on temperature.

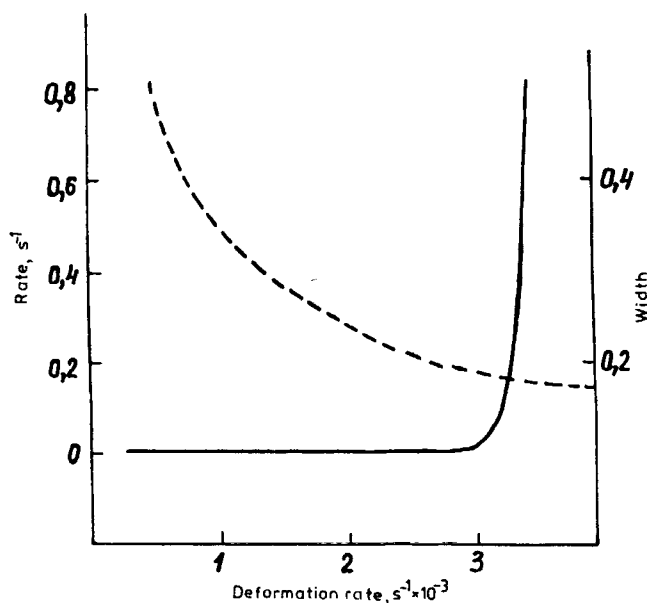


FIGURE 2 General rate of scissions (continuous line) and the width of scission distribution (dashed line) among the centre as a function of deformation rate according to the prediction of the theory for PS ($1 \cdot 10^7 M_w$).

In paper¹⁵ the method of estimation was worked out in conditions of polystyrene (PS) solution flow between two co-axis capillaries. The value of the deformation rate was $3.3 \cdot 10^3 \text{ s}^{-1}$, PS concentration in bromoform $C = 6.6 \cdot 10^4 \text{ g/dl}$, $M_n = 8.25 \cdot 10^6$, $M_w/M_n = 1.21$. It was found, that ϵ_c being predetermined, K_d decreases during degradation because of low-molecular polymers accumulation. M_n twice decrease corresponds to 12-fold K_d decrease.

Critical deformation rate $\dot{\epsilon}_c$ does not practically depend on temperature, and critical rate of ruptures $\dot{\epsilon}_f$ decreases slowly with temperature increase. Thus, for PS with $M_n = 8 \cdot 10^6$ and $M_w/M_n = 1.06$ $\dot{\epsilon}_f$ decreases linearly from $4.5 \cdot 10^3$ to $1 \cdot 10^3 \text{ s}^{-1}$,¹² while temperature increases from 25 to 150°.

For the time being it is impossible to maintain, that the theory of macromolecule rupture is finally worked out. Other models for macromolecule conformation in mechanical field are being supported. Thus in Reference 24 the "yo-yo" model was suggested. According to it only central part of the molecule becomes straight, and the end remains in the form of clouds. According to this model, deformation rate, that is critical for the rupture

$$\dot{\epsilon}_f \propto M^{-1.1}$$

under the regime of quick transitional (non-quasistationary) flow for part cloud straightening. Experimental arguments to prove this model have been received recently.^{26,27} Dependences of degradation rates on concentrations and deformation rates are of principle for the extrapolation of theoretical and experimental results of mechanical degradation in diluted solutions, where macromolecules are supposed isolated, to processing conditions with much higher viscosity, concentration and degradation time, but essentially lower deformation rates and molecular weights.

Degradation rate (in percentage of macromolecules degraded during one pass)[‡] is shown on Figure 3¹² for samples of two molecular weights $10.7 \cdot 10^6$ and $8.1 \cdot 10^6 \text{ g/mole}$. The form of the initial parts is close for both curves. It is connected with small transformations of macromolecules. Sharp increase of reaction rate ν_c could be marked with rise of deformation rate $\dot{\epsilon}$. Thus, for the sample with $M = 8.1 \cdot 10^6$ increase of $\dot{\epsilon}$ from $2 \cdot 10^4$ to $3 \cdot 10^4 \text{ s}^{-1}$ is followed by reaction rate increase from 0.5 to 2% for a pass. Taking into account the fact, that degradation time for one pass varies, reaction speed increases 6-fold. Curve (1) reaches its stationary level because of decrease of initial macromolecule number during the pass itself.

As concentration increases and interaction between macromolecules rises it is to be expected that the rupture site—molecular centre—will gradually lose its locality because of entanglements. However, as the experiments¹² show, even at PS concentration of 0.3% in decaline the yield of ruptures in the centre is high enough. The reason for a small part of statistical ruptures occurrence, lies, evidently, in the fact that the number of entanglements decreases with $\dot{\epsilon}$ rise. Nevertheless, total rate increases in comparison with diluted solution. However, until macromolecules are isolated, there is no concentration dependence.

[‡]The authors have chosen the dimension which can't fully coincide with that of the item "chemical reaction rate," as one pass at different deformation rates corresponds to different degradation times. Though, the form of the curves seems not to change quantitatively.

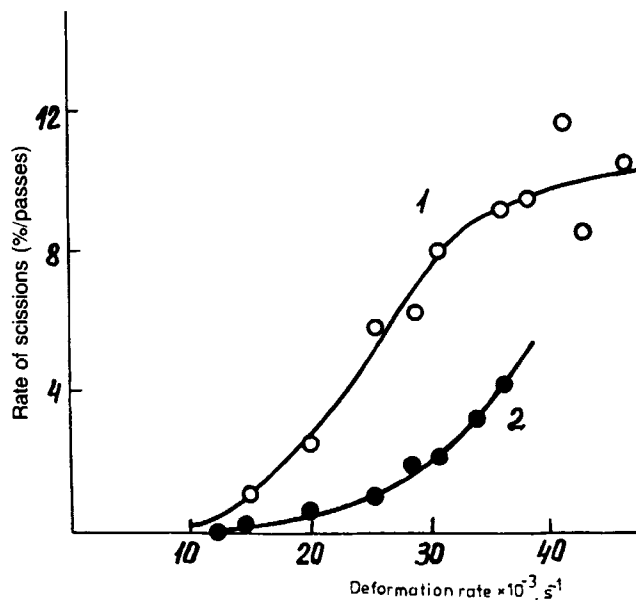


FIGURE 3 The rate of scissions as a function of deformation rate for diluted solutions of a-PS in decaline at room temperature. 1) $M_p = 10.7 \cdot 10^6$, $M_w/M_n = 1.2$; 0.01%. 2) $M_p = 8.1 \cdot 10^6$, $M_w/M_n = 1.07$; 0.02%. M_p = molecular weight, corresponding to the situation of maximum on gel-chromatogram.

This definite conclusion is in contradiction with published data. Both positive,²⁸⁻³⁰ and negative³¹⁻³⁴ concentration dependence during shear flow were observed, and its complicated form³⁵⁻³⁶ or even absence.³⁷⁻⁴⁰ The contradiction is supposed¹² to be induced by a complicated character of shear flow in experimental devices, insufficient characterization of the conditions; turbulence.

Unfortunately, attempts to use the data of degradation theory of macromolecules in diluted solution for the prediction of processing results are unsuccessful even on a qualitative level. The extrapolation scales are too large—each of the key parameters, affecting the degree degradation: molecular weight, viscosity, shear rate, polymer concentration, time, change by several decimal orders and they act in different directions. The situation is complicated by the fact, that mechanical degradation is just the beginning of many staged processes in the presence of oxygen and at high temperature. That is why it is hard to point out in real processing, what causes the observed changes, mechanical degradation or thermal oxidation. However, more simple models are used to answer this question. Thus, extrusion is simulated by squeezing through capillary.

In papers^{41,42} polystyrene bars were studied layer by layer after their squeezing through capillary.

It followed from these data, that oxidation, though the experiments were performed in inert atmosphere, was the main reason of degradation, and mechanical degradation does not play an essential role. On the other hand, in polyisobutene melt pure mechanical degradation was observed.⁴³

As during PS degradation in solution,¹⁵ the degradation rate (M fall) decreased quite quickly with the degradation degree increase. Authors⁴³ connected the fact

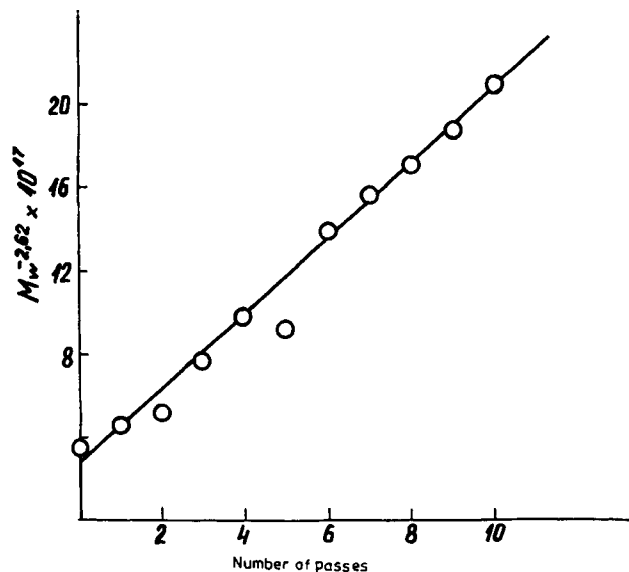


FIGURE 4 The dependence of changes of molecular weight M_w on the number of passes of polyisobutylene melt through capillary at 80°C.⁴⁴

with melt viscosity decrease—shear strain decreased with constant shear rate maintained. Analysis of these experimental results⁴⁴ showed, that the rate of molecule number change ($d(M_n^{-1})/dt$) is proportional to the square of shear strain τ . The melt of a rather high-molecular polymer ($M_w = 1.98 \cdot 10^6$, $M_w/M_n = 1.1 \cdot 10^6$) was characterized by extremely sharp dependence of its rate on molecular weight in spite of viscosity dependence on M_w being not too strong, probably because of non-Newton flow. The total order of M_w rate change against M_w equals to 3.7. The linear anamorphosis of experimental kinetic curve is shown at Figure 4.⁴⁴ Satisfactory description of experimental data by straight line tells about the constancy of chemical parameters of degradation rate during the whole process. In other words, the rate of C—C bonds rupture could be constant, if during this reaction the strain τ and shear rate $\dot{\gamma}$ were kept constant. No deceleration occurs, though visible efficiency of the processes decreases.

These data, from the first view, are in contradiction with conclusions of the theory of mechanical degradation of isolated macromolecules in solution, where square¹² or linear^{25,26} dependences of degradation rate on molecular weight are supposed.

However, it is necessary to take into account, that conditions of the flow in Reference 43 are quite far from those, realised in stretching flows in diluted solutions in References 12, 21 and 26. That is why direct comparison seems impossible in this case.

In this way, it is very hard to choose even on the level of comparatively simple models, what is the main-mechanical degradation or thermal oxidation. An attempt was made to create a general picture of degradation during the processing,⁴⁴ in which both classes of chemical reactions are included as components (Figure 5). According to this hypothesis mechanical degradation as the source of alkyl radicals

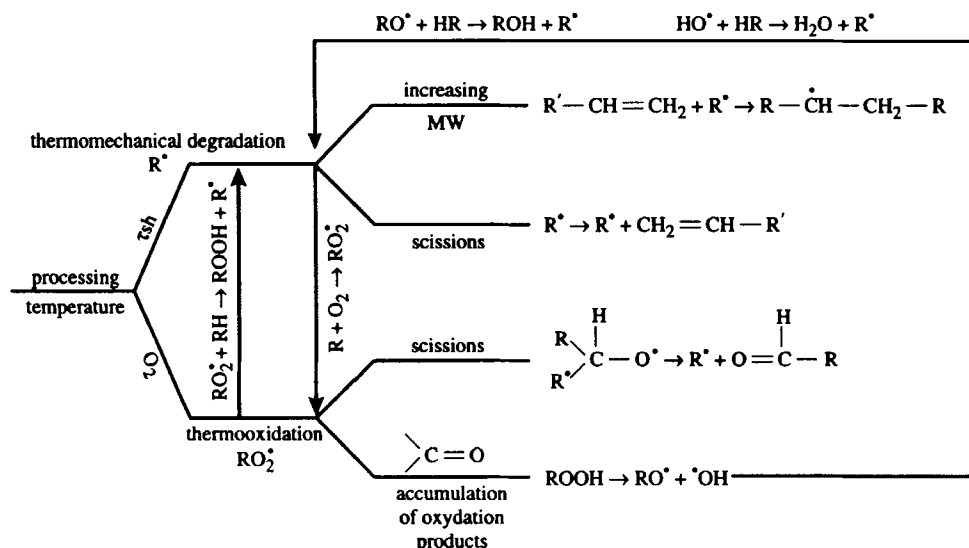
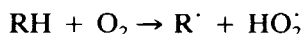


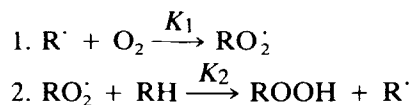
FIGURE 5 The scheme of transformation of macromolecules during the processing.

is one of the initial stages of thermal oxidation. From this point of view it does not differ from thermooxidation initiation^{1,p.124} by oxygen reaction with C—H-bond:



In this case superposition of mechanical degradation and thermal oxidation is expressed in increased radical R^\cdot concentration as compared with that for pure autooxidation. It is supposed that the influence of mechanical strain on reactional ability of C—H bonds in melt is negligible opposite to that in solid phase,^{45,p.120} where it is noticeable.

The interaction of mechanical degradation and oxidation is described by two reactions, well-known in oxidation kinetics as propagation of kinetic chains:



Both radicals take part in processes, which bring to molecular weight change. Alkyl radicals can both be “linked up” to double bonds of macromolecules with the creation of middle radical of greater molecular weight and degradate thermally with the creation of end radical and double bond.

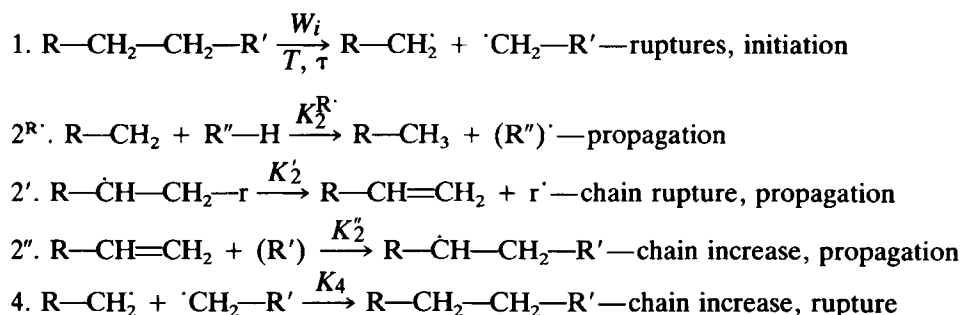
Peroxide radical as a reaction centre of oxidation gives the contribution only in molecular weight decrease through degradation of RO^\cdot alkoxy radical. The deg-

radation mechanism during oxidation is to be discussed below. There is a quite low probability of RO_2 radical to be responsible for macromolecule growth at high temperatures. Created peroxide bond is thermally unstable and degrades with half-time of about 1 minute at temperatures about $200^\circ C$.

Thus, in a complicated system of mechanically initiated and thermooxidation processes during processing of carbochained polymers it is possible that two reactions of degradation with participation of R' and RO' radicals and one more connected with increase of macromolecule size occur.

In this case an elementary kinetic calculation could be made for appropriate scheme, corresponding to the rate of macromolecule concentration changes in polymer (molecular weight) during processing.

Oxygen influence not taken into account, the following reactions will occur in the system:



For concentration of R' radicals:

$$d[R']/dt = W_i - K_4[R']^2 \approx 0$$

It follows from this, that for the process of molecular weight changes the acts of initiation W_i and kinetic chain terminations could be not taken into account, because their rates are nearly equal (according to the rule of radical quasistationarity), and directions are opposite.

The rate of macromolecule concentration change (molecular weight) should be described by following equation:

$$dn/dt = (W_i/K_4)^{1/2}(K_2' - K_2'')C=C \quad (2)$$

According to the Equation (2) general effect of mechanical degradation—increase or decrease of molecular weight—depends on the sign of the second multiplicand in the right part. If $K_2' > K_2''$ $C=C$, then $dn/dt > 0$ and degradation is observed, in the other case molecular weight will increase. The effective activation energy of R' radical degradation reaction should be higher than that for a bond joined to a double bond. The latter is 3–5 kcal/mole.⁴⁶ That is why the change of general direction of mechanical degradation could happen as the temperature increases—molecular weight increase will be changed by decrease. It really happens.⁴⁴

The influence of oxygen, that should increase the relative concentration of $\text{RO}_2\dot{\text{C}}$ radicals and the degradative component of the general process, could be taken into account on a half-quantitative level. Degradation rate for initiated oxidation depends on oxygen concentration as follows:

$$dn/dt = [W/K_4(1 + \pi)]^{1/2}(K'_2 - K''_2)C=C\langle \rangle + K_{\text{eff}}^{\text{RO}_2}\pi/(1 + \pi)^{1/2} \quad (3)$$

where π = dimensionless oxygen concentration

$$\pi = K_1[\text{O}_2]K_6^{1/2}/K_2[\text{RH}]K_4^{1/2}$$

K_1 and K_2 = rate constants of kinetic chain propagation for O_2 and RH correspondingly. K_4 and K_6 = rate constants of recombination of $\text{R}\dot{\text{C}}$ and $\text{RO}_2\dot{\text{C}}$ radicals. K_{eff} = effective rate constant of $\text{RO}_2\dot{\text{C}}$ radical decay, whose concentration is proportional to that of decaying $\text{RO}\dot{\text{C}}$ radical in the regime of oxidation quasistationary by hydroperoxides.

According to formula (3) the rate of degradation is directly proportional to oxygen concentration, the latter being small $\pi \ll 1$ in usual conditions of polymer processing.

In References 44 and 47 experimental proofs of the mechanism suggested are cited. The main of them are: i) sharp change of molecular weight increase to decrease with temperature increase during mechanical degradation; ii) presence of 3 temperature regions of molecular weight change: low temperature oxidative degradation, intermediate region of mechanically initiated molecular weight increase and high temperature mechanical degradation; iii) correspondence between concentration changes of macromolecules and double bonds.

Additional proofs appeared in the work,⁴⁸ where behavior of HDPE under repeated extrusion was investigated. It was found, that in the dependence on vinyl group content samples behave themselves in different ways: HDPE with vinyl group concentration of 993 mole/10⁶ atoms, received by synthesis on C_2 -containing catalyst by "Philips" (HDPEPh) is mainly being linked together as a result of extrusion, while HDPE, synthesised on Ti, Ziegler catalyst (HDPEZ) in the main degrades. Extrusion regimes were usual for laboratory onescrew extruder, with temperature varying within 4 zones of heating from 200–220°C to 260–280°C.

In Figure 6,⁴⁸ the dependence of double bond concentration on reverse M_w change is shown to be linear. Corresponding angle coefficient $\Delta\langle \rangle C=C\langle \rangle / \Delta M_w^{-1} = 12$. It approximately corresponds to distribution width and means, that changes of macromolecule concentration—linkage formation in this case—occurs by the consumption of double bonds. Such a conclusion on a qualitative level was made,⁴⁹ where molecular weight increases in HDPE was observed only for the samples, containing vinyl double bonds. In hydrogenized HDPE fluidity decrease of melt does not occur during processing.⁵⁰

These data testify to the fact, that the molecular weight change happens during processing on the stage of chain propagations, and not initiation (primary rupture) or termination (recombination) of kinetic chains. Nevertheless, even in those works, where this conception is experimentally proved, for explanation of the degradation the whole list of all possible reactions is adduced (see, for example References 48

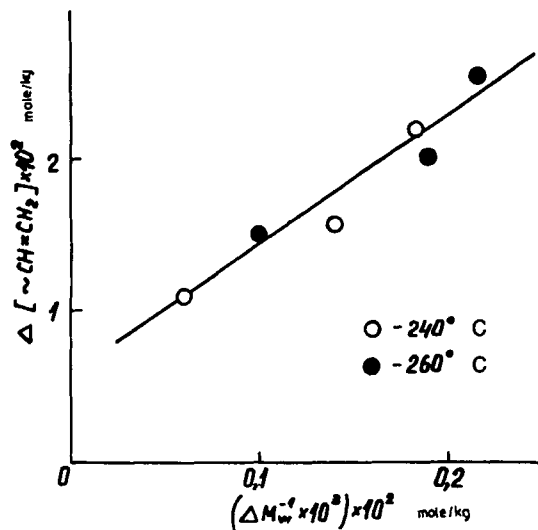


FIGURE 6 The interdependence between changes of concentrations of double bonds and macromolecules.

and 49). Such point of view just hampers understanding of mechanism, quantitative interpretation of experimental data, the possibility of true prognosing about influence of processing conditions on changes of material properties.

This mechanism of molecular weight changes obviously does not concern low temperature degradation processes, initiated by different influences: γ -irradiation, UV-light, mechanical load. The situation here will be opposite—initiation rates are high, and kinetic chains are short. So it is quite possible, that in these conditions initiation and kinetic chain termination will be responsible for molecular weight changes.

Lately direct proof has appeared, that free radicals are the cause of chemical reactions during processing. In Reference 51 they were found by ESR-method under the extrusion of PP melt in the presence of space-hindered amines as a radical trap. It was found, that radicals appeared are analogous to those, that are formed during grinding in a spherical mill below 77°C. During processing of secondary PE in disk extruder⁵² momental freezing of extrudate in liquid nitrogen made it possible to measure radical concentrations. According to data of Reference 52 the Melt Flow Index (MFI) passes through maximum during growth of disk revolution rate. In Reference 52 it is explained by degradation rate increase with shear rate increase.

We made an attempt to estimate rates of degradation processes, which pass under disk extrusion. To do it a suggestion was made, that during registration of melt flow index the flow had a Newtonian character, and viscosity η_{eff} depended on molecular weight as power function

$$\eta_{\text{eff}} \approx [\eta]_0 \propto M^{3.5}$$

The value of Melt Flow Index (MFI) is inversely proportional to η_{eff} . In this case

degradation degree, measured by the number of appearing and disappearing bonds, i.e. by difference in macromolecule concentrations, could be estimated as a difference of values of $MFI^{1/3.5}$. However, to get values, connected with degradation rates, it is necessary to relate the appropriate change to the time of melt being under load, which in the first approximation is inversely proportional to $\dot{\gamma}$. In this way, the degradation rate under extrusion

$$W_d \propto \dot{\gamma} (MFI_{\dot{\gamma}}^{0.286} - MFI_0^{0.286}).$$

Figure 7⁵² shows a dependence proportional to degradation rate (1) and radical concentration (2) from shear rate $\dot{\gamma}$. Curves have similar forms. We will use one of the methods of experimental data treatment, accepted in chemical kinetics—method of transformation. We will divide all the values of radical concentrations by the same coefficient κ , which equal in this case:

$$\kappa = 1.26.$$

It is seen from Figure 7, that transformed values of R' concentrations are described by the same curve, as the dependence of degradation rate.

Thus, experimental data from Reference 52, testify to the fact, that radical concentrations and degradation rate in all the ranges of shear rates are connected by the same coefficient. It should mean, that, obviously, radicals are the reason of degradation. It also becomes clear, that linkage is not observed in this case at all. It may occur, but its rate is less than that of degradation. Descending part of

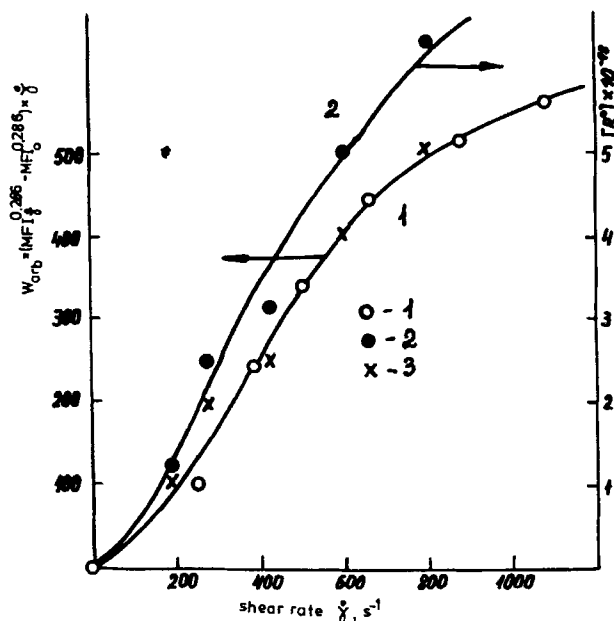


FIGURE 7 The dependence of degradation rate (1) and radical concentration (2) on the shear rate during the processing of secondary PE. Points (3) correspond to transformation of $[R']$.

MFI dependence on γ is explained by the degradation rate deceleration and by the decrease of time presence under load, and not by linking acceleration. It is more or less clear, why no linkage occurs in this case. PE undergoes processing after exposure in the sun and thus, after intensive linkage, during which double bonds may have been removed.

3. THE INFLUENCE OF OXYGEN CONCENTRATION ON OXIDATION AND DIFFUSIONAL LIMITATIONS OF OXIDATION

The processing of polymers happens in unusual oxygen conditions. In dependence on the type of processing O_2 access to polymer will be either free during rolling, or limited casting under pressure, extrusion. In the last case, when oxidation rates are rather high, the concentration of oxygen dissolved in the melt will decrease during processing. So processing is connected with oxidation under variable and low O_2 concentrations. In this connection two problems appear for quantitative description of the degree oxidation in processing: i) The dependence of the oxidation rate on oxygen concentration, ii) Diffusional limitations on the oxidation rate.

Both problems have been investigating for a long time. It is necessary to point out a certain incorrectness, that has become the general place in raising up a problem of calculation of kinetics diffusion limited of oxidation. It is asserted, that diffusional limitations appear, when chemical reaction is fast, and diffusion is slow. ^{1, p. 151; 4, p. 195}

Here the case of the regime with stationary oxygen concentration is considered, when the rates of diffusion and chemical processes are equal (for monodimensional diffusion).

$$d[O_2]/dt = D(d^2[O_2]/dx^2) - W([O_2]) = 0 \quad (4)$$

It is obvious, as it is a chemical reaction being the motive force, i.e. the reason for diffusion, by creation of oxygen concentration gradient at the expense of its consumption.

There would be no diffusional flow without chemical reaction—diffusion would stop as a result of polymer layer saturation by oxygen.

Wide-spread inaccuracy, appeared, evidently, as a result of mixing of items of “external diffusional” and “internal diffusional” area of chemical processes.⁵³ In the external-diffusional sphere the reaction of gas on a solid state surface or liquid happens. The rate of gas feeding, defined by the reagent diffusion in gas phase, is independent on the chemical process rate in condensed phase. Here we can speak about difference of rates of reaction and diffusion.

Polymer oxidation happens, as a rule, in the internal diffusional sphere. Small changes of the reagent concentration across the polymer layer, i.e. slow diffusion corresponds to this kinetic sphere. “Diffusional limitations” appear, when diffusional flow becomes maximally fast because of a high concentration gradient. So, in internal diffusional area diffusional regime corresponds to the fast diffusion and

kinetic one to the slow one. In monograph⁵³ the simple proof of general rule for the internal diffusional area is given.

i) The effective reaction order should be the arithmetical mean between unity and the real index of the chemical reaction.

ii) The effective reaction rate should be the geometric mean for maximally possible diffusion rate and that of chemical reaction.⁵³ The last rule is expressed quantitatively by the following equation:

$$W_{\text{eff}} = 2D/l^2 \left(\int_{[O_2]_l}^{[O_2]_0} W_{(O_2)} d[O_2] \right)^{1/2} \quad (5)$$

where W_{eff} and $W_{(O_2)}$ = effective and true rates of O_2 absorption; $[O_2]_0$ and $[O_2]_l$ = oxygen concentrations on plate surfaces open and inaccessible for oxygen; D = diffusion coefficient; l = plate thickness.

iii) If the reaction order is $n < 1$, then the concentration of diffusing reagent may become zero at a certain thickness l_0 , and both the reaction and the diffusion stop. In this case the external layer is a protective one and prevents the reagent from penetrating down to a larger depth. In case of zero order, for example, it is easy to show, that

$$l_0 = (2D[O_2]_0/W)^{1/2} \quad (6)$$

If oxidation in air at 200°C is spoken about, the oxidation rates in polymers from PS (hard oxidative polymer) to PP (easy oxidative polymer) lie in the range from $1 \cdot 10^{-4}$ to $5 \cdot 10^{-2}$ mole/kg·s. $D \approx 1 \cdot 10^{-5} \div 1 \cdot 10^{-4}$ cm²/s, $[O_2] \approx 1 \cdot 10^{-3} \div 1 \cdot 10^{-4}$ mole/kg.^{1,p.153} The thicknesses l_0 of the complete absorption vary from 20 to 200 μm. The real thickness of samples, in which oxidation occurs in a kinetic regime, should be even smaller.

The difficulty in the situation with oxidation consists in the dependence of the reaction rate on oxygen concentration W_{O_2} , which is not a simple power function. It is interesting, that in first works on diffusional limitations of oxidation in polymers⁵⁴⁻⁵⁷ authors observed the effective first order of oxidation by oxygen under autooxidation in diffusional regime. Because of this the opinion was expressed, that the real reaction order by O_2 should be also the first. However, a usual scheme of oxidation with quadratic termination of kinetic chains leads to a variable order by oxygen.

The corresponding functions are received as follows:

$$W_{O_2} = W_x(1 + \pi^{-1})^{-2} \quad (7) \text{—for autooxidation,}$$

$$W_{O_2} = W_x(1 + \pi^{-1})^{-1} \quad (8) \text{—for initiated oxidation,}$$

where W_{O_2} and W_x = oxidation rates at a given $[O_2]$ and $[O_2] \rightarrow \infty$; $W_x = K_2^2[RH]^2/K_6$ —under autooxidation; $W_x = K_2[RH]W_i^{1/2}/K_6^{1/2}$ —under initiated oxi-

ation; K_2 and K_6 rate constants of the reactions of chain propagation and termination; W_i = rate of initiation; π = dimensionless oxygen concentration.

$$\pi = K_1[\text{O}_2]K_6^{1/2}/K_2[\text{RH}]K_4^{1/2}$$

K_1 and K_4 = rate constants of O_2 adding and alkyl radicals recombination.^{1,11} The analytical expression of function for description of oxygen distribution in diffusional field along the thickness could not be obtained in a general form. For this reason different simplified formulae and models are being suggested, which make calculations for experimental data description^{58,59} easy.

Sometimes such ranges of pressure values are selected, where oxidation rate dependence on oxygen concentration is a simple power function. Thus, for autooxidation rather small oxygen pressures correspond to square dependence, large ones—to zero order, and quite a wide transitional zone given first order. The last explains well very often observed exponential distributions of oxidation products along the thickness—the solution of diffusional equations for a first order chemical reaction of⁵⁴⁻⁵⁷ does give an exponential function.

On the whole, one can state, that the mechanism of diffusional limitations for polymer oxidation is clear enough. However, it is far not so clear, if this phenomenon has any relation to oxidation process during processing. A great number of attempts to model oxidation during processing were described: by oxygen concentration decrease,⁶⁰ by closing or partly opening the mixer camera,⁶¹ by air blowing into the mixer camera.⁶²

It was found, that under conditions investigated the oxidation occurs faster in dynamic rather than in statistic mode. It may be a consequence of both mixing during processing, and the increase of the rate of mechanoinitiation. However, the first being true, the diffusional limitations are taken off or become lower. But if the second is true, they increase.

It is obvious, that this problem is of a great practical importance. In the case, if there are diffusional difficulties, polymer will be oxidized nonuniformly by the initiating product. This nonuniformity will be increased by exploitation. Uneven degradation of the material promotes the appearance of mechanical loads, which can accelerate degradation. Such positive backward connection may bring to the sharp decrease of exploitation duration of the products.

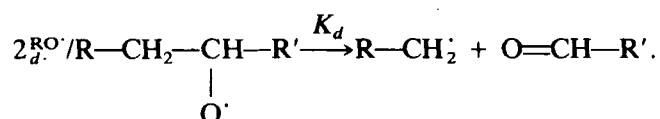
Evidently, it is impossible to answer the question in general case—is there any diffusional limitations during processing or not. The arguments for the benefit of their absence are: mixing, limited space, where oxygen can be injected from, material saturation with oxygen before processing, low rate of oxidation in the presence of antioxidants. However, if mixing is weak, oxidation rate is high, and there is a source of oxygen injection to the melt, the gradient of O_2 concentration along the thickness and consequently the difference in the oxidation rates can appear.

4. OXIDATIVE DEGRADATION OF MACROMOLECULES

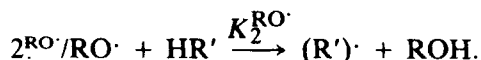
The mechanism of macromolecule ruptures is the subject of careful study. It was important to explain, what stages of oxidation are, responsible for rupture, and

what possibilities of decelerating these reactions exist. The situation was complicated by the fact, that during oxidation two opposite processes—degradation and crosslinking—are going at a time, as far as, volatile products excretion on one side of distribution and gel formation on the other one.

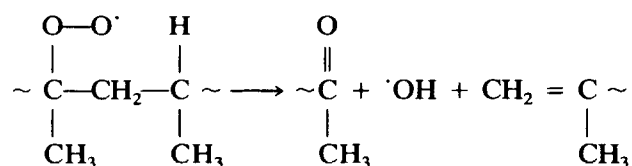
Linkage during oxidation seems to be a nontrivial fact. Cases, cited in the literature, on the molecular weight increase during autooxidation are connected, as a rule, either with the lack of oxygen^{60,63} or with the primary stages of the reaction, when its rate is rather low. It is quite possible, that this is induced by the reactions of alkyl radical R'. However, during oxidation RO₂ radical is the main active centre. Therefore, the question is actively discussed—what oxygen-containing radicals: RO₂· or RO'—are responsible for macromolecule ruptures.^{1,p.171} The degradation mechanism of RO' radicals has been accepted long ago and is now traditional:



This reaction runs fast, as the energy of generated C—O bond is rather high—about 80 kcal/mole. The reaction of hydrogen subtraction, competing with the degradation one, also runs comparatively fast:



The hypothesis of RO₂ radical degradation was created recently and is being developed actively.⁶⁴⁻⁶⁶ For PP this reaction runs as follows:



Kinetic and chemical proofs of such reactions were adduced for the initiated oxidation of PP and PE in solution ($t^0 \approx 100^\circ\text{C}$) and for the decay of peroxide radicals of PS. The rate of degradation was proportional to the first power of [RO₂·], double bond concentration corresponded to scissions. During recombination of RO₂· marked by O¹⁸ it was labeled water arising from hydroxyl radical, that was being eliminated and not marked oxygen. However, in conditions of autooxidation at much higher temperature the degradation of macromolecules does go on due to RO' radical decay. The form of kinetic curve of scission accumulation as cubic parabola is a very characteristic proof of this.

The corresponding dependence appears theoretically due to the fact, that con-

centration of both RO^\cdot radicals, and hydroperoxides—their direct predecessor—at the primary stages of oxidation is proportional to the square of time:

$$dn/dt \propto [\text{RO}^\cdot] \propto t^2$$

It follows

$$n \propto t^3.$$

This circumstance was emphasized in the last monographs on polymer degradation.^{1,p.172;4,p.203} It is necessary to take into account, that here we are talking only about primary stages of autooxidation. In conditions, stationary about hydroperoxides the rate of oxidation will be constant. The ratio between different radicals will also be held constant with time.

The behavior of an important parameter, characterizing oxygen efficiency as degradating agent, differs in principle at the primary stage of oxidation and at that stationary by hydroperoxides.

In the first case the quantity of oxygen absorbed for one scission should decrease with time

$$[\text{O}_2]/n \approx t^{-1}.$$

In the last one—the rate of oxidation $d[\text{O}_2]/dt$

$$d[\text{O}_2]/dt = 3K_2^2[\text{RH}]^2/4K_6 \quad (7)$$

(taking into account oxygen, eliminated during the recombination of RO_2^\cdot radicals); the degradation rate of RO^\cdot radicals dn/dt .

$$dn/dt = K_d K_2^2 [\text{RH}]^2 / 4K_6 (K_2^{\text{RO}^\cdot} [\text{RH}] + K_d) \quad (8)$$

and the quantity of oxygen for one scission

$$d[\text{O}_2]/dn = 3(K_2^{\text{RO}^\cdot} [\text{RH}] + K_d) / K_d \quad (9)$$

are constant with time.

The formula (9) shows, that this quantity must be 3 or higher. Number 3 is received in suggestion, that the coefficients of radical yield during hydroperoxide degradation and hydroperoxide yield in the reaction of chain propagation are equal to unity. In this case for the formation of one RO^\cdot radical not less, than 3 molecules of O_2 should be absorbed—one after the formation of alkyl radical R^\cdot and two—after hydroperoxide degradation into 2 radicals. At low temperatures, when $K_2^{\text{RO}^\cdot}/K_d$ has higher value because of much lower activation energy of the reaction

of H atom subtracting by $RO\cdot$ radical, more O_2 is necessary for each scission, at high temperatures—less.

The cubic dependence of scission quantity on time at primary stages of oxidation are observed experimentally quite frequently for various polymers: HDPE,⁶⁷ LDPE,⁶⁸ PS.⁶⁹

Detailed investigation of thermooxidation degradation of PE at temperatures of 140°C and lower was carried out in the work.⁷⁰ The analysis of experimental data from this work shows, that kinetic curve of scissions represents a cubic parabola. Figure 8 shows the dependence of the number of scissions per molecule on cube of time during HDPE oxidation. The temperature of the oxidation was 100°C. It is seen, that during the whole period of observations the linear dependence is implemented. This is a serious argument for the benefit of degradation through $RO\cdot$ radical decay. However, the authors of the work⁷⁰ suppose, that the chain scission in oxidation process represents the superposition of many stages. As the base for such a hypothesis the following suggestion was made: according to the data of Reference 71 half-time of PE hydroperoxide decay is 6.4 hours, and the period of induction of PE oxidation is 35 hours. Therefore the authors of Reference 70 have come to the conclusion, that they observed the stationary part of oxidation, where the quantity of oxygen, necessary for one scission realization should be constant.

However, the increase of this value was observed experimentally. In reality the kinetics of absorption of O_2 in Reference 70 pointed out, that observations were made at the primary stage of oxidation, and not at the stationary one. Figure 9 shows the kinetic curve of O_2 absorption built in double logarithmic coordinates. The corresponding straight line has pitched with $tg\alpha = 4$. Thus, O_2 absorption is described here by the parabola of the fourth power. It is not clear, what is the cause of this phenomenon, as usually the initial parts of kinetic curves of oxygen

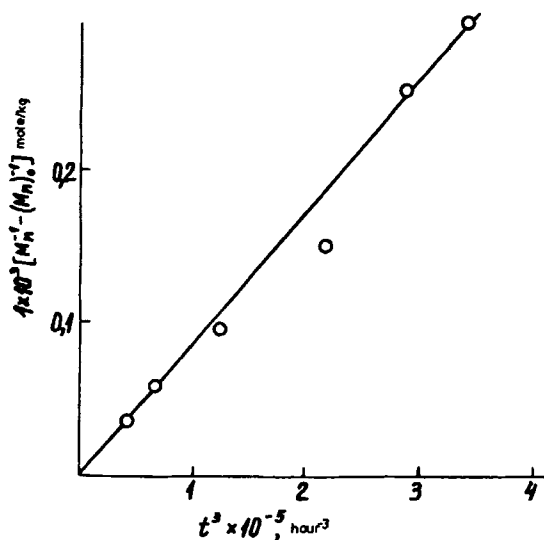


FIGURE 8 The dependence of scission number on cubic time,⁷⁰ calculated per macromolecule at PE oxidation (air, 100°C).

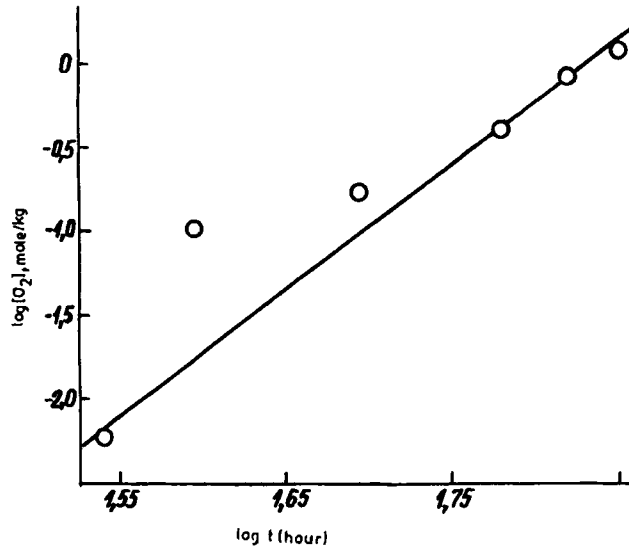


FIGURE 9 The dependence of O_2 absorption on time in double logarithmic coordinates (PE oxidation at $100^\circ C$).

absorption during the autooxidation of polyethylene and many other hydrocarbons are quadratic parabolas. Evidently, it is caused by peculiarities of either measurement methods, or studied sample. Then the growth of oxygen consumption per scission becomes clear—the rate of oxygen absorption increases with the time faster, than the rate of scission accumulation. While in the stationary regime of the oxidation of PE and PP the specific consumption of oxygen remains constant⁷² and is about 6 mole O_2 /scission. Another reason for decrease of O_2 quantity necessary for one scission at the beginning of the reaction can exist. In many cases there is a component of scissions, independent on the oxidation kinetics. In Reference 73 the experimental data on this problem are analyzed. During PS oxidation up to a stationary regime about hydroperoxides the kinetics of oxygen absorption is of autoaccelerated character, and the kinetics of scissions—autoretarded one.⁷⁴

Scissions appear in PS even without oxygen.⁶⁹ The rate of this process is decreased. Evidently, in this case a scission occurs and then gradual consumption of the so-called “weak” bonds takes place. The concentration of these bonds being small $\sim 1 \cdot 10^{-2}$ mole/kg, the degradation kinetics should be described by a first order reaction (Figure 10) this is observed in reality—the half-logarithmic plots of the kinetic curve 1 gives a straight line (curve 2).

Scissions at primary stages of LDPE oxidation are insensitive even for inhibitor addition—the rate of corresponding process remains constant for different concentrations of inhibitor (Figure 11).⁷⁴ Only the change of oxygen to vacuum decreases the rate of degradation. So in LDPE there exist two more components of degradation additional to that of chain oxidation—non-chain one with O_2 participation and “quasithermal” without oxygen.

The problem of inhibitor influence on scissions is not quite clear at the present time. According to the data of Figure 11⁷⁴ the inhibitor (Nonox WSP) does not influence the degradation rate. The results from References 75 and 76 show, that

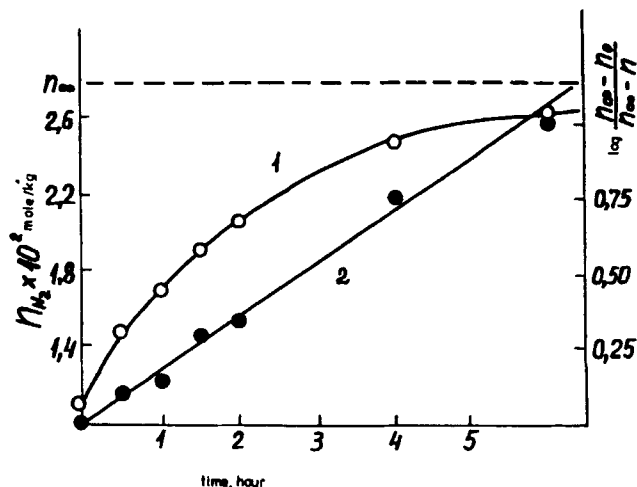


FIGURE 10 PS degradation in nitrogen: 1) kinetic curve, 2) semilogarithmic anamorphosis of curve 1.

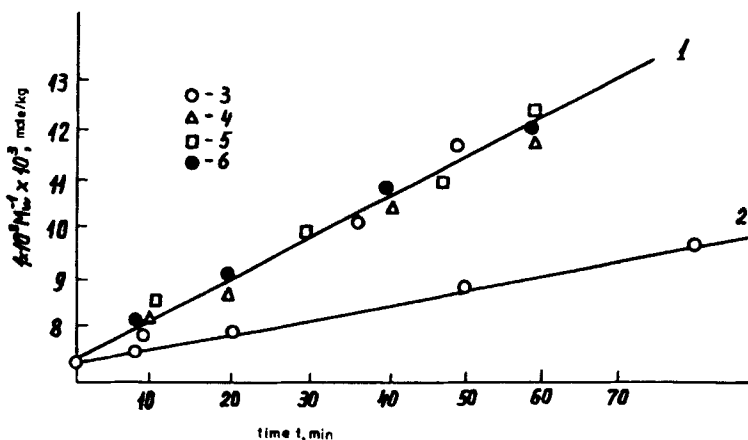


FIGURE 11 LDPE degradation at autooxidation and different inhibitor concentrations in O₂ atmosphere ($p_{O_2} = 150$ torr) (1) and in vacuum (2) $t^0 = 180^\circ\text{C}$, inhibitor Nonox WSP. $[\text{InH}]_0 \cdot 10^2$, mole/kg: 0 (3); 1.4 (4); 2.4 (5); 3.8 (6).

this influence is also not observed for analogous antioxidant at 200°C . However,⁷⁰ it was shown, that at 100°C the HDPE degradation is linear versus absorbed oxygen, and the inhibitor retards it to the same degree as the oxidation. Evidently, “non-oxidation” scissions are displayed with comparable rates at high temperatures only. In PP the rate of degradation is approximately proportional to the current concentration of the inhibitor.⁷⁷ However, some hydroperoxide reducers, for example diphenylisooctylphosphite, retard PP degradation at high concentrations of the inhibitor.⁷⁸ These data indicate that in this case pure “oxidation” scissions occurs— at high concentrations of the inhibitor the rate of oxidation increases with its concentration. The role of phosphites is a decay of hydroperoxides, the direct predecessor of alkoxy RO^\cdot radical. However, in this case there is a possibility,

that the inhibitor and the hydroperoxide inhibitor influence the processes of crosslinking. The increase of rate of crosslinking should make the impression of degradation retardation.

The behavior of the molecular weight distribution function is sensitive to two kinds of influence during oxidation—the chemical nature of reactions of degradation and crosslinking and spacial location of polymer regions with different rate of oxidation.

The second case is realized during oxidation in the solid phase. It occurs in the amorphous phases, while crystalline ones are not affected by oxidation. Another variant of spacial nonuniformity of oxidation appears under the diffusion limitations of oxidation rate. Near the surface the oxidation occurs faster than macromolecule degradation on the bulk. In deeper layers, enriched in alkyl radicals, crosslinkages can occur. In much deep layers the material remains untouched because of the absence of oxygen. Apparently, in such case edges of the distribution according to molecular weights will “crawl away” because of the appearance of molecules of lower and higher weights. The same effect will occur also in the kinetic field because of morphological inhomogeneity of oxidation. Even if no crosslinking occurs, the width of the distribution will increase, because a part of the material will degrade, and a part will remain practically untouched.

However, in conditions of processing only chemical influences on the width of MWD of polymer may be expected. Meanwhile superposition of mechanical degradative influence, described previously, thermal and oxidative ones may occur. The rates of primary mechanoinitiated scissions depend on the molecular weight. Therefore the influence of mechanical field on the MWD-function is specific. Its high molecular part is being cut off and width of MWD is narrowed along with the degradation. But if kinetic chains are rather long—low rates of initiation—then the primary specific influence largely will be camouflaged by the secondary reactions of radicals, with scissions having a most probably statistical character. As to the oxidation and thermal (the scission of “weak” bonds) initiation, the scissions here are expected to occur by random law. It is stated in works on the mechanodegradation.¹²

In Reference 70 the MWD-functions of oxidized HDPE samples were measured. The initial width of MWD was $M_w/M_n = 18.1$. After occurrence of 0.3 scissions per macromolecule it increased to 21.1, and then decreased gradually with the number of scissions increase. The value of $M_w/M_n = 3$ was reached, when the average number of scissions per macromolecule became equal $S = 2.5$. The authors of Reference 70 pointed out the following feature of oxidation influence on molecular weight; at the beginning the average weight M_w falls sharply—by 80% of the initial value, however, average numeral M_n during the same period decreases only by 15%. It corresponded to the transition time from induction period to autoaccelerated regime.

It is well-known, that under degradation the MWD of a sample of any initial width after 3–4 scissions directs to the most probable one, which has the value $M_w/M_n = 2$ for radical degradation through disproportionality and $M_w/M_n = 1.5$ under recombination. For the mechanism of degradation during oxidation it is

important to know, whether the process of M_w and M_n changes is purely statistic or includes the nonchance component.

It is possible to compare the dynamics of M_w and M_n changes during oxidation, measured in Reference 70, with that, which could be observed, if the polymer of the same initial M_w and M_n was exposed to statistical degradation. Theoretical dependence of the M_w/M_n on number of molecule scissions per macromolecule S , necessary for calculations, was taken from Reference 7, p. 58 for $(M_w/M_n)_0 = 21$. The S value is connected with M_n by the following correlation:

$$(M_n)_s^{-1} = (1 + S)/(M_n)_0.$$

Figure 12 shows the results of calculations for the scissions by the random law (1) and the experimental data (2) from Reference 70 for HDPE oxidation in air at 100°C, in $M_n^{-1} - M_w^{-1}$ coordinates. In both cases the dependence is seen to be linear. Angle coefficients differ not more, than by 10%. Real narrowing of the distribution proceeds a little slower, than it should according to the statistics, but the difference does not exceed experimental deviation. The data from Figure 12 show, that during oxidation degradation is described statistically, and not selectively, as it was supposed by the authors in Reference 70. Sharp M_w decrease at the beginning simultaneous to small decrease of M_n is caused by the fact, that the initial distribution was very wide and under equal probabilities for all the C—C bonds to be scissioned, in large molecules the scission probability is higher. Because

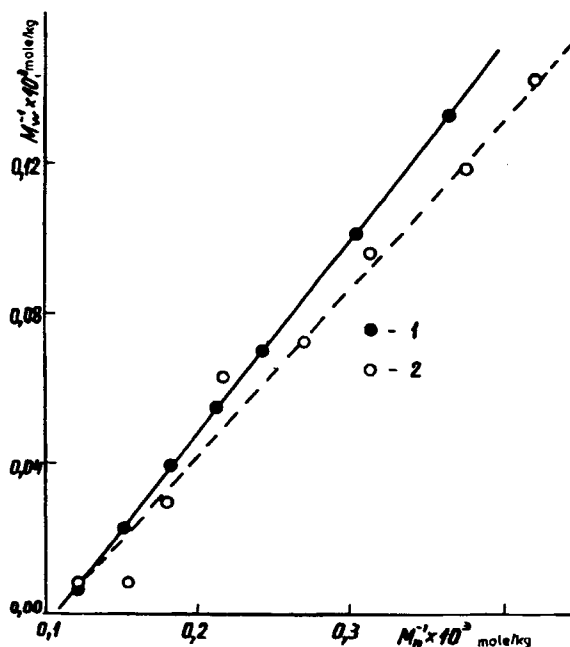


FIGURE 12 The dependence of M_w and M_n in inverse coordinates: 1) Theoretical for scissions according to the chance law (M_n data from Reference 70; M_w was calculated according to Reference 7, p. 58. 2) Experimental from Reference 70.

for wide MWD the initial scissions are followed by a very fast decrease of the width, this provokes the observed decrease of M_w .

It is essential to point out, that M_w , is responsible for the most part of physico-mechanical properties. The width of polyolephines MWD-function, as a rule, is large enough. Therefore, even the very primary degradation stages can essentially affect the exploitation properties of such polymers.

The behavior of MDW-function during the processing is much more complicated, then during oxidation. Two factors can affect it—the sensitivity of the mechano-degradation rate to the size of macromolecule on one hand, and the possibility of crosslinking during the processing on the other. The joint action of these factors can both increase and decrease the width. Thus, in HDPE as a result of the processing⁷⁹ the width of MWD-function decreases noticeably. However, in dependence on the processing conditions and the way of PE synthesis other effects are also observed. In the table the changes of the melt flow index (MFI) and the polydispersion index PI are observed as a result of multiple extrusion of two types of HDPE—Ziegler and “Phillips” firm, produced on the Cr-containing catalyst. In the latter one the concentration of vinyl bonds is much higher.

The data in Table I shows, that the multiple processing of Ziegler HDPE at different temperatures does not really change either the MFI, or the width of (PI) distribution. But Phillips HDPE—with the great concentration of vinyl bonds—decreases its fluidity and increases very much the distribution width in the same conditions. These processes occur practically similar at all the temperatures from 220°C up to 280°C. Mechanochemical transformations seem to be the base of these changes. It is possible, that in comparison with data from Reference 79, where the MWD narrowing was observed for HDPE, analogous to that of “Phillips” firm, in Reference 44 the concentration of $R\cdot$ radicals was higher and that of $[O_2]$ —lower due to construction peculiarities and extruder processing regime.

5. STABILIZERS AND STABILIZATION

The mechanism of stabilizers-antioxidants action is well studied.¹⁻⁴ The principles of their action are known: the change of active peroxide radicals $RO_2\cdot$ by the radicals

TABLE I
The influence of multiple extrusion on fluidity and MWD width of HDPE

| Temperature | 220 | | | 240 | | | 260 | | | 280 | | | |
|--------------------------|-----|-----|-----|------|-----|------|------|-----|------|------|-----|------|------|
| extrusion multiplication | 1 | 3 | 5 | 1 | 3 | 5 | 1 | 3 | 5 | 1 | 3 | 5 | |
| Samples: | | | | | | | | | | | | | |
| Phillips | MFI | 2,0 | 1,4 | 1,2 | 2,3 | 1,5 | 1,2 | 2,8 | 2,0 | 1,0 | 3,4 | 1,7 | 1,1 |
| | PI | 5,9 | 9,7 | 13,2 | 7,4 | 11,2 | 15,7 | 7,8 | 11,6 | 14,2 | 7,5 | 10,0 | 15,4 |
| Ziegler | MFI | 4,2 | 4,0 | 4,1 | 4,3 | 4,1 | 4,3 | 3,8 | 4,0 | 4,2 | 3,9 | 4,6 | 5,2 |
| | PI | 1,2 | 1,5 | 1,5 | 1,0 | 1,3 | 1,7 | 1,3 | 1,7 | 2,3 | 3,6 | 2,8 | 1,02 |

of inhibitor In^\cdot , low active in the reaction of the chain propagation. At the high temperature while usual regimes of the processing the efficiency of stabilizers decreases more or less noticeably because of various reactions of inhibitor radical. The specificities of inhibitor action in solid phase—the influence of morphology on the reaction ability of radicals, nonhomogeneous distribution of inhibitor in the sample⁸⁰—during the processing seem not to play a great role. The chemical component of the stabilizer efficiency may play more considerable role at high temperatures and mixing, than at low temperatures. Under these conditions one should expect that stages running with rather high activation energy—namely, chain propagation by the inhibitor radical In^\cdot , the In^\cdot reaction with ROOH —will contribute noticeably to the totality of reactions of inhibited oxidation.

Such evident reaction, as direct oxidation of the inhibitor by oxygen should also have quite high activation energy. In investigations of inhibited oxidation of polymers, where the inhibitor is being consumed in a first order reaction at constant $[\text{O}_2]$, this reaction has been supposed as the main channel of the inhibitor consumption.^{81,82} It was shown in References 83 and 84, that the oxidation rate of phenols PhOH is proportional to the product $[\text{O}_2][\text{PhOH}]$. Recently⁸⁵ the experimental data on kinetics of different space-hindered phenols consumption in melt and solution in presence and absence of polypropylene were received. Rate constants of reaction K_{O_2} were found to be close. It means, that phenol oxidation runs independently on the radical reactions in polymer.

However, even thermodynamic estimations show, that at 180°C the rate constant of this highly endothermal reaction (47–34 kcal/mole) could not be more than $1 \cdot 10^{-11} \div 4 \cdot 10^{-8}$ kg/mole · sec. But experimentally observed values even under 130°C are higher in several orders of value. The authors⁸⁵ suppose, that in reality the mechanism of phenol oxidation is quite complicated. It runs by the radical-chain way through peroxide formation and branching on them, or through oxidation of phenol radical, presented very often in phenols as admixture. At least, only thus it is possible to explain the anomalous high value of the rate constant of this reaction.

This reaction may occur either through direct oxidation by oxygen, or intermediate compounds may play an important role so that it may run along radical-chain way at high temperatures. Independent on the way of reaction the following problem is of principle for possible consequences—what part in inhibitor consumption is assigned to the presence of substrate of oxidation and radicals formed in the reaction. According to References 81, 82 and 85 it is possible to conclude, that in these conditions the contribution of oxidized polymer into the consumption of inhibitor is not great during the induction period, when $[\text{InH}]$ exceeds $1 \cdot 10^{-3}$ mole/kg. In this case the kind of oxidized polymer does not play any role. The rate of stabilizer consumption will be the same, defined only by chemical nature of the inhibitor and partial pressure of oxygen.

To tell the truth, such conclusion is not in accordance with reality. For easily oxidizable polymers PP the induction periods are shorter than those for PE, and so, the rate of inhibitor consumption is higher.

In Reference 1, p. 197 the minimal value of the activation energy (~ 50 kcal/mole from the endothermity of the process) and maximal predexponential $\sim 10^{10}$ kg/mole · s were used for calculation of the rate constant of the direct phenol

oxidation at 210°C. It was found low in full correspondence with calculations, made in Reference 85. The most active of phenol with respect to direct oxidation α -naphthol is oxidized in chlorobenzene at 200°C with the rate constant of $6 \cdot 10^{-3}$ l/mole \cdot s.^{1,p.257} It is only 6% of the whole rate of inhibitor consumption during PP oxidation in the same conditions. Thus, there are evident contradictions even on the level of experimental data, not speaking about their interpretation.

On one hand inhibitor is oxidized in the absence of oxidized substrate, so the substrates influence should not be observed. On the other hand, it is quite pronounced. Effective rate constants of the inhibitor consumption during oxidation appear noticeably higher, than maximally possible according to thermodynamical considerations. We will make an attempt to solve this contradiction later.

It should be pointed out, that because of the great number of probable and experimentally proved elementary stages of the inhibited oxidation,¹⁻⁴ it is very hard to estimate the efficiency of this compound—space-hindered phenol, amine or nitroxile radical—as an antioxidant. The reason of this lies in complexity of chemistry and kinetics of antioxidative action, their sensitivity to details of chemical construction of stabilizers, and especially the class of the compound.

At the same time parameters of efficiency should be clear enough by physical sense and easy to determine. This problem is being worked about in details in special literature.

The suggestion^{77,86,87} to divide antioxidants into strong and weak ones according to the form of concentration dependence of the induction period was one of the first. Weak inhibitors cause linear increase of the induction period with concentration. Strong ones show deviation from linearity—beginning from certain concentrations their efficiency being increased. After that the increase of the induction period appears according to the inhibitor consumption by first order law—semi-logarithmic plots of the concentration dependence gives the straight line.^{88,89}

Monophenols were attributed to weak inhibitors by the authors of this concept.^{2,p.154} Possible reasons of their low efficiency may lie either in low values of the rate constant of chain scissions, or in strong influence of inhibitors of this class on the probability of degenerated branching of kinetic chains. The first of reasons does not seem true. Numerous measurements of this value for different space-hindered phenols³ have shown, that functionality—unlike many other factors—does not practically influence the value of the rate constant of interaction with peroxide radicals. It is rather probable, that monophenols are not inferior by their chemical efficiency to bi- or polyfunctional compounds, and the problem lies in their increased volatility.

Estimation of the efficiency based on calculation of the influence of inhibitors on the degenerated branching does not seem adequate in sufficient degree to the real behavior of inhibitors. This method corresponds only with the value of inhibitor critical concentration. The main process of inhibitor consumption when its concentration exceeds the critical one, is regarded by the authors of the method as the reaction of direct oxidation by oxygen. It is autonomous, at least from the substrate and is defined just by the effective rate constant of this process.

The problem of inhibitor efficiency was investigated in details in Reference 90. The matter of the approach suggested consists of the fact that the kinetics of

inhibited oxidation is defined by the strength of just two bonds: R—H in polymer and C—H in inhibitor. With the help of these values correlational equations were received, from which rate constants of the most number of elementary steps (7 from 10) are being calculated. They are basic for different variants of the mechanism of the inhibited oxidation. Finally, for each given pair of polymer/inhibitor it is possible to calculate the factor of the inhibitory efficiency F , viz. decrease of the chain length during inhibited oxidation in comparison to uninhibited one.

$$F = (V_0/V)(1 - V^2/V_0^2) \quad (10)$$

where V_0 and V = the rates of uninhibited and inhibited oxidation, respectively.

So far as the bond energies for relatively small number of RH and InH are known, the equations were received in Reference 91 for estimation of the most part of rate constants of inhibited oxidation reactions on the basis of the values of rate constants of hydrogen scission from RH (K_2) and InH (K_7) by peroxide radical RO_2^{\cdot} at 60°C.

The important characteristics of inhibitor efficiency is the critical concentration, i.e. minimal affecting one. The phenomenology of critical phenomena goes up to gas phase branched chain reactions, where under certain conditions a very small change in the concentration of the agent, breaking kinetical chains, brings to the jump-like change of the reaction rate—from practically zero to explosion.⁹² Critical effects were also discovered during liquid phase oxidation of hydrocarbons.¹¹

Sharp increase of induction period at certain concentrations of inhibitor in oxidation of polyolephines was also interpreted as a critical phenomenon.^{2,93}

The theory of critical phenomena was worked out and described in details in References 1–4. The conditions of critical phenomena display during oxidation of polymers seem exhaustively formulated in Reference 1, p. 251. The matter is about possibility or impossibility to transform the regime unstationary by hydroperoxide accumulation to quasistationary one with the help of inhibitor. It occurs not far every time. If inhibitor radical is rather active, so that scissions of kinetic chains occur only through the reaction of In^{\cdot} with RO_2^{\cdot} , the stationary regime can be stated under any concentration of inhibitor. Corresponding quantitative calculations were made in Reference 94. It was defined, which concrete mechanisms of inhibition can cause critical phenomena and which cannot. In particular, even if the inhibitor radical is rather active in the reaction of chain propagation (high temperatures), there is a possibility of the appearance of the critical concentration of inhibitor only if In^{\cdot} reacts with $ROOH$.

It should be noted that experimental proofs of the existence of critical phenomena under high temperature oxidation of polymers were received with the help of such arbitrary parameters as the induction period, viz. the time of reaching of a certain determined rate or a reaction depth. It creates uncertainty in the interpretation of the results.

Lately the works have appeared on the change of kinetics of O_2 absorption in the range of induction periods,^{75,76,95–99} created in PE by different inhibitors. Different authors have observed practically similar regularities which permit to create non-contradictory model of the process.

As far as the initial concentration of inhibitor increases the rate of oxidation decreases gradually. Oxidation remains autoaccelerated (Figure 13). However, after reaching a certain concentration of inhibitor, in this case $2.5 \cdot 10^{-3}$ mole/kg

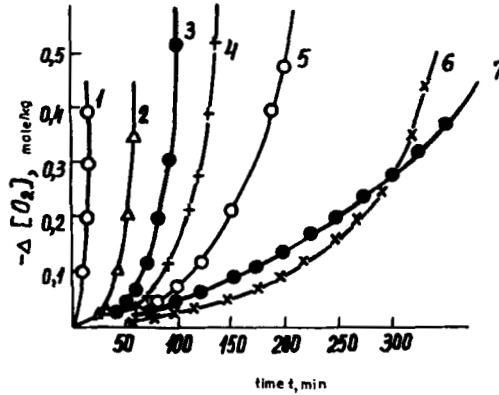


FIGURE 13 Kinetics of oxygen consumption at LDPE oxidation ($P_{O_2} = 300$ torr, $t^0 = 180^\circ\text{C}$, inhibitor Nonox WSP). $[\text{InH}]_0$, mole/kg $\cdot 10^{-3}$: 0 (1), 0.3 (2), 0.6 (3), 0.8 (4), 1.5 (5), 2.5 (6), 3 (7).

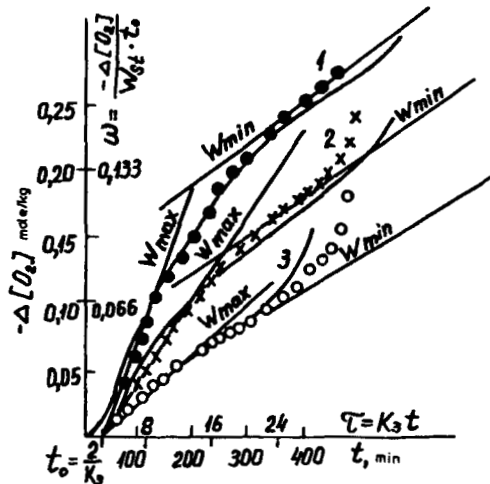
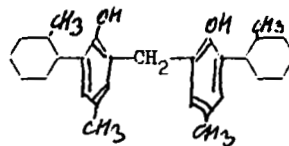


FIGURE 14 Kinetics of LDPE oxidation at $[\text{InH}]_0 > [\text{InH}]_{\text{char}}$ ($P_{O_2} = 300$ torr, $t^0 = 180^\circ\text{C}$, inhibitor Nonox WSP) $[\text{InH}]_0$, mole/kg: 0.08 (1), 0.05 (2), 0.02 (3).

NONOX WSP* (curve 6), oxidation rate begins to grow (for illustration see curve 7—for $[\text{InH}] = 3.0 \cdot 10^{-3}$ mole/kg). Such behavior of inhibitor during high-temperature oxidation is characteristic for high temperatures and does not depend on the class of inhibitor (phenol or amine) or the type of polymer. Evidently, that in this case the increase of inhibitor concentration over a certain one brings to decrease of its efficiency—the effect inverse to critical phenomenon.

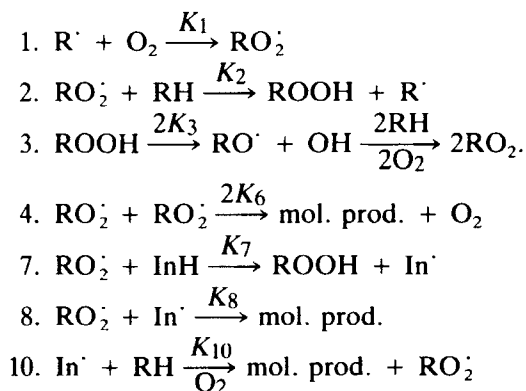
If the induction period τ had been registered at the concentration of absorbed

*Chemical formula of NONOX WSP.



oxygen lower than $2 \cdot 10^{-2}$ mole/kg, then τ should begin to decrease with the increase of inhibitor concentration. But at threshold value of $[O_2]_t > 2 \cdot 10^{-2}$ mole/kg τ will increase with the increase of inhibitor concentration. In accordance with these data, the conclusion is confirmed experimentally, that the induction period being the time of reaching of the defined degree (or rate) of oxidation is an arbitrary value and does not confirm any reliable information about inhibitor efficiency. So conclusions about critical phenomena based on the dependence of τ on $[InH]$, are also not proved enough.^{2,93,95,98} Following increase of $[InH]$ makes the kinetics of O_2 absorption during the induction period rather complicated (Figure 14). Autoacceleration is changed by retardation after the inflection point, after the second one—again by acceleration and the exit to the regime of uninhibited oxidation is observed. The rate of oxygen absorption at the primary step of oxidation keeps increasing with the increase of inhibitor concentration. The induction period, measured by a rather sensitive device should go on decreasing. Moreover, the time of reaching the regime of uninhibited oxidation, viz. the time of practically full consumption of inhibitor increases. Values of minimal rates of oxidation do not depend on $[InH]_0$, while maximal rates increase nearly proportional to $[InH]_0$.

In Reference 99 the calculation of kinetical scheme of inhibited oxidation was made, in which to the "inevitable" steps of peroxide radical RO_2^{\cdot} interaction with InH and In one more step was added. The latter is more than natural for high temperatures—it is the reaction of kinetic chain propagation by the inhibitor radical. Generally, the analysed scheme looks in the following way:



In dimensionless variables the rates of oxygen absorption, hydroperoxide accumulation and inhibitor consumption shall be described by equations:

$$d\omega/d\tau = (1 + i)p^{1/2}/(ai + 1)^{1/2} + p \quad (11)$$

$$dp/d\tau = (1 + i)p^{1/2}/(ai + 1)^{1/2} - p \quad (12)$$

$$-di/d\tau = bip^{1/2}/(ai + 1)^{1/2} \quad (13)$$

where $\omega = -\Delta[O_2]K_3K_6/K_2^2[RH]^2 =$ dimensionless concentration of absorbed oxygen; $p = [ROOH]K_3K_6/K_2^2[RH]^2 =$ dimensionless concentration of hydroper-

oxide; $i = K_7[\text{InH}]/K_2[\text{RH}]$ = dimensionless concentration of inhibitor; $\tau = K_3t$ = dimensionless time; $a = 2K_2K_8/K_6K_{10}$ = inhibiting parameter; $b = K_7K_2[\text{RH}]/K_3K_6$ = dimensionless rate constant of inhibitor consumption.

Attention is attracted by the analogy of the preceding equations to those describing the kinetics of uninhibited oxidation with quadratical scission. It has physical sense. According to present mechanism the scission happens in step (8)—of the interaction of RO_2^{\cdot} with In: The concentration of the latter is proportional to RO_2^{\cdot} if $K_8[\text{RO}_2^{\cdot}] < K_{10}[\text{RH}]$, viz. chains long enough by In \cdot radical. Then the rate of scission is proportional to $[\text{RO}_2^{\cdot}]^2$. The effective rate constant of this reaction increases in comparison with the usual constant K_6 by the parameter: $2K_7K_8[\text{InH}]/K_6K_{10}[\text{RH}]$, which exceed unity even at small values of $[\text{InH}]$, as

$$K_7K_8/K_{10}K_6 \gg 1.$$

It is important to point out, that with increased inhibitor concentration the initiation also increases simultaneously with the termination. It occurs due to decay of that hydroperoxide, that is generated in stage (7) of the InH interaction with RO_2^{\cdot} . Initiation is proportional to $[\text{InH}]$, and terminations—to $[\text{InH}]^{1/2}$. Until $i \ll 1$, the initiation on InH is unnoticeable ($i + 1 \approx 1$), and the termination increases because of a large value of parameter $a - (ai + 1) \gg 1$. But if the inhibitor concentration becomes large, so that $i \geq 1$, the initiation will grow faster, than the termination because of the difference in the value of power index. When i crosses the value $i = 1$ during $[\text{InH}]$ increase, the inhibitor begins to accelerate the oxidation instead of its retardation. Approximative analytical solutions of the equations and the exact solution by computer¹⁰⁰ lead to the state, that these equations quantitatively describe the kinetics of oxidation during the induction period.

The mechanism of inhibited oxidation looks as follows: the first stage of inhibited oxidation is nonstationary by hydroperoxides at all the inhibitor concentrations. At small concentrations of inhibitor stationary state by hydroperoxides has no time to be achieved. The process transits into nonstationary uninhibited oxidation. When the initial concentration of inhibitor is large enough, the stationary regime of oxidation is being achieved. It happens after the kinetic curve passes the inflection point. Quasi-stationary states for hydroperoxides do not mean the constancy of $[\text{ROOH}]$. In this regime the concentration of hydroperoxide follows the concentration of its predecessor—in the case of the initial stage of inhibited oxidation with large inhibitor concentration— $[\text{InH}]$.

Inhibitor is being consumed from the very beginning. But only at the period of quasi-stationary states for hydroperoxides the rate of oxidation and concentration of hydroperoxides become proportional to its concentration.

Figures 15 and 16 show the kinetics of $[\text{ROOH}]$ change and the dependence of the rate of oxidation on $[\text{ROOH}]$. It is seen, that the curve of hydroperoxide accumulation (Figure 15), calculated from the corresponding equation with use of parameters, defined from the kinetics of oxygen absorption, describes the experimental data well enough. In the coordinate axes both real values and their dimensionless meanings are shown. The curve (Figure 15) has the maximum and minimum. After reaching the maximum ($d[\text{ROOH}]/dt = 0$) the oxidation regime

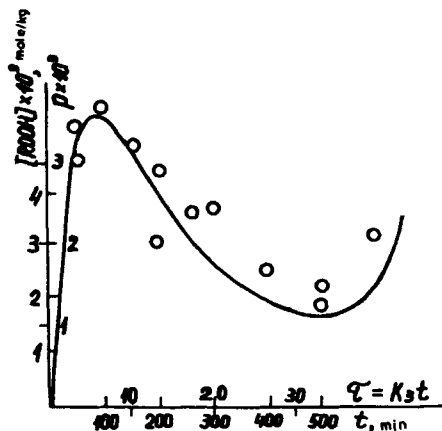


FIGURE 15 Kinetic curve of hydroperoxide accumulation during the period of induction of LDPE oxidation ($P_{O_2} = 300$ torr, $t^0 = 200^\circ\text{C}$, Nonox WSP, $[\text{InH}]_0 = 0.08$ mole/kg).

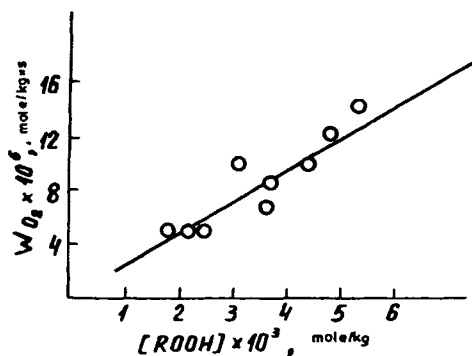


FIGURE 16 The dependence of oxidation rate on $[\text{ROOH}]$ during inhibited oxidation of LDPE (200°C , 300 torr, Nonox WSP, $[\text{InH}]_0 = 0.08$ mole/kg).

becomes quasi-stationary with respect to hydroperoxides. The rate of oxidation in these conditions is described by the following expression:

$$d\omega/d\tau = (1 + i)^2/(ai + 1) = p_{st} \quad (14)$$

or in a dimensional form:

$$W(\text{O}_2) = 2K_3[\text{ROOH}]_{st} \quad (15)$$

The last one is proved experimentally by the data in Figure 16. At large $[\text{InH}]_0$ $i > 1$

$$p_{st} = d\omega/d\tau \approx (i + 2)/a \quad (16)$$

The rate of oxidation depends linearly on $[\text{InH}]$ and has a component, independent on $[\text{InH}]$.

Under the same conditions ($i > 1$, $\tau \gg 1$) the time of full inhibitor consumption, that could be taken for the induction period independent on the sensitivity of measuring device, will be equal:

$$\tau_{\text{ind}} = (a/b)\ln(i_0 + 1) \quad (17)$$

It corresponds approximately to the inhibitor consumption, usually observed in the first order reactions. The effective reverse rate constant of this process has a clear kinetic sense:

$$a/b = 2K_3K_8/K_{10}[\text{RH}]K_7$$

or in dimensional form

$$K_{\text{eff}} = 2K_8/K_7K_{10}[\text{RH}] \quad (18)$$

It is important to point out, that for rather effective spatial-hindered phenols the values of K_8 and K_7 are approximately equal, and the difference in the rate of consumption will be defined by the parameter $K_{10} \cdot [\text{RH}]$ only.

The influence of the rate constant of inhibitor interaction InH with peroxide radical RO_2^- – K_7 will be of two kinds. On one hand, the larger K_7 is, the smaller is the characteristic $[\text{InH}]_{\text{char}}$

$$[\text{InH}]_{\text{char}} = K_2[\text{RH}]/K_7 \quad (19)$$

and the higher inhibitor efficiency will be. On the other hand, the effective rate constant of inhibitor consumption increases with K_7 increase (Equation 18). The induction period is reduced correspondingly and inhibitor efficiency decreases. The K_7 value should have a certain optimal value for the guarantee of maximal inhibitor efficiency. Analogous conclusion was made in Reference 94. However, in this work the upper limitation of the K_7 constant was connected with the fact, that parallel to this constant the rate constants of side reactions of inhibitor consumption—namely its interaction with hydroperoxides and oxygen—increase. In Reference 99 the initiating function K_7 corresponds to hydroperoxide, generated during the act of inhibiting.

The scheme with chain propagation over inhibitor radical In \cdot describes quantitatively both the kinetics of oxygen absorption and inhibitor consumption, and hydroperoxide accumulation with the help of the same set of kinetic parameters. In the mechanism, suggested in Reference 99, there is no sharp border between inhibited and uninhibited oxidation. In the first case just an additional source of scission and initiation of kinetic chain exists, both phenomena being linear connected with inhibitor concentration.

The dignity of such a description of kinetics is in the possibility of determination of kinetic parameters, connected with constants of the elementary steps of inhibited oxidation, studied well in other conditions. The comparison shows, that the deviation of absolute values from those received by extrapolation of literature data,

are not large for K_7 . However, the temperature coefficient of the constant K_7 was found close to zero, while its usual value is expected about 3–5 kcal/mole.

One of possible reasons of this deviation consists in nonconsidered reaction of In' interaction with ROOH. This contribution appears rather small for distortion of oxidation kinetics, but rather large for inducing small changes of defined kinetic parameters.

The most considerable deviation appeared for the constant K_{10} , manifesting in increase by three orders. It testifies to the benefit, that the stage of chain transition does not run in such a simple way, as written in the scheme. Moreover, it is not quite clear how this reaction can be realized in the written form, i.e. without inhibitor regeneration.

Inhibitor regeneration contradicts the experiment, because in the frames of the accepted scheme inhibitor consumption will not practically occur. Moreover, in the primary form the scheme does not foresee the influence of oxygen concentration on the kinetics of inhibited oxidation. In reality such influence is rather essential.

In the main, the reaction of direct (molecular) oxidation of inhibitor being not taken into account because of its low thermodynamical probability, only two steps of oxidation should be sensitive to oxygen concentration: the transformation of alkyl radicals R' into peroxide RO_2 and possible interaction of In' radical with oxygen resulting in InO_2 radical formation. The last one, in its turn, will be more intensive in cutting off H' from RH , then In' . It will affect the increase of the rate constant of chain propagation (K_{10}) by inhibitor radical.

The calculation of two alternative kinetic schemes [101] has shown, that the dependences of induction period on oxygen pressure should have different forms in these two cases. Experimental data of LDPE oxidation in the presence of Nonox WSP antioxidant simply show, that the second mechanism of peroxide radical

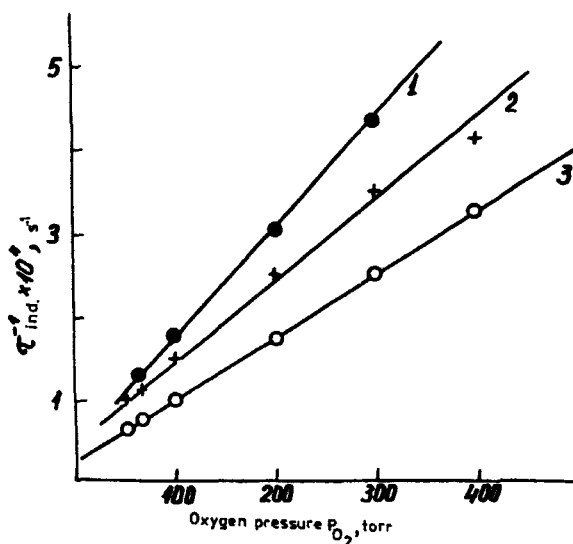


FIGURE 17 The dependence of inverse period of induction of LDPE oxidation on oxygen pressure (210°C, Nonox WSP, $[\text{InH}]_0 = 3$ (1), 5 (2), 8 (3)).

InO_2 formation is realized (Figure 17). The dependence of induction period on oxygen concentration is described by the following formula:

$$t_{\text{ind}} = 2K_8/K_7(K_{10} + K'_{10}[\text{O}_2])[\text{RH}] \quad (20)$$

where K'_{10} = the rate constant of InO_2 interaction with [RH].

It is important to note, that practically the same experimental data on inhibitor oxidation are interpreted by different authors in absolutely different ways. Direct inhibitor oxidation by oxygen as the main source of its consumption and critical phenomena are used for interpretation in works^{75,76,95-99} and the absence of these, but realization of step of kinetic chain transmission by InO_2 radical—in others.⁹⁹⁻¹⁰¹

Independence of the rate constant of phenol consumption on the presence of polymer system⁸⁵ appeared to be the strong argument for the benefit of inhibitor oxidation by oxygen. However, if radicals InO_2 can be formed in the inhibitor, its oxidation will occur in that very way of degenerative-branched chain reaction as in hydrocarbons or polymers. But it does not mean that the molecular reaction between phenol and oxygen occurs.

In Reference 99 both inhibited oxidation of PE and that of PP were studied.

In equal conditions Nonox WSP consumption in PP occurs nearly 7 times faster, than in PE ($P_{\text{O}_2} = 300$ torr, $t^0 = 200^\circ\text{C}$, $[\text{InH}]_0 = 0.08$ mole/kg). The main mass of inhibitor being oxidated by oxygen, this difference could not be observed. It is interesting, that relative parameters of the efficiency of one and the same inhibitor are nearly equal in PE and PP. It means, that the effect of retardation of the oxidation rate in comparison with the maximal one—without inhibitor W_∞ do not differ much in PE and PP. However, the values of W_∞ for PE and PP do differ, that is why in PP the time of inhibitor consumption is essentially shorter.

In the framework of known experimental data it seems senseless to speak about critical phenomena and use of the corresponding mathematical apparatus for interpretation of experiment, when there is a part nonstationary by ROOH at all the concentrations of inhibitor. Really, at high $[\text{InH}]_0$ the stationary state for ROOH is reached. It happens while the oxidation rate increases, i.e. during decrease of inhibitor efficiency. Initial parts of kinetic curves according to the scheme⁹⁹ are described by quadratic parabolas, starting from the origin of coordinates. It means, that at the beginning of reaction the rate of initiation is negligibly small and does not play any role in development of oxidation reaction. It being so, the reaction will never leave the induction period in conditions stationary for ROOH, when the coefficient of autoacceleration is negative. Direct inhibitor oxidation being the source of radicals, the rate should be maximal at the beginning, but this fact is not observed in the experiment. That is why we are to make the choice for the benefit of inhibitor action mechanism in melt through the transmission of the chain by inhibitor radical.

An important feature of inhibition mechanism is the possibility of multiple chain terminations—a peculiar negative catalysis of radical recombination, when chains are being terminated, but inhibitor is not consumed. Unfortunately, such practically

tempting idea could be successfully realized only in rather specific conditions. Thus, during oxidation of PP nitroxile radicals NO^\cdot are consumed and regenerated from the products, i.e. multiple chain termination take place.^{102,103} Aromatic amines display analogous properties.¹⁰⁴ Possible explanations of this phenomenon are based on the fact, that the primary act of interaction of $>\text{NO}^\cdot$ with R^\cdot is followed by formation of hydroxame ester $>\text{NOR}$, or hydroxylamine $>\text{NOH}$ (due to disproportion). Both of these compounds can be oxidated by peroxide radical RO_2^\cdot with regeneration of $>\text{NO}^\cdot$.

During inhibition of phenols regeneration of inhibitor and multiple chain termination may also happen. It was stated, that the regeneration occurs by the way of quinone reduction by the interaction with HO_2^\cdot radicals and oxygen elimination. Hydrogen peroxide H_2O_2 is the source of HO_2^\cdot . It is created during degradation of blocked hydroperoxides in PP. Because of it multiple chain termination are not observed in PE, where hydroperoxides are isolated. The same takes place in PP, when it has just single peroxides.¹⁰⁵⁻¹⁰⁷

All these observations were made at rather low temperatures -100 – 130°C . Temperature being increased up to 200°C (the usual temperatures of the processing) the reactions of multiple termination do not seem play essential role in the general balance of chemical transformations.

Synergism is being used for quite a long time in practice of polymer stabilization and is studied rather well. The use of sulphites and phosphites as admixtures for degradation (reduction) of hydroperoxides without radical formation seems the most wide-spread method of increase of antioxidant efficiencies. The possible result of that is evident—the stationary concentration of hydroperoxide will decrease according to increase in degradation constant. The rate of initiation is also decreased by the part of radical less degradation of hydroperoxide. Moreover, the products of transformation of synergetic admixtures can also react with the hydroperoxide. There are some more directions of possible positive action of such admixtures: radicalless degradation of quinolide peroxides, reduction of In^\cdot up to InH .^{108,109} As a result, the summary effect of synergetic mixtures is very high. For example, the time period of preceding cracking in *i*-PP samples during aging in air at 130°C increases from 72 hours, at either phenol or sulphite concentration of 0.5%, up to 1350 hours under their joint use at the same concentrations.

The theory of induction period when synergists of such type are used^{2,p.173} was worked out in details. The theory was based on critical phenomena. Theoretical dependences of induction period on inhibiting mixture composition are bell-like curves and curves with sharp maximum. They conform qualitatively with experimental data, received during PP oxidation (220°C , 300 torr) with two different mixtures containing dilauryltiodipropionate, both phenyl- β -naphthylamine¹¹⁰ and 1,6-diisobornyl-4-methylphenol.¹¹¹

In Reference 48 the behavior of synergetic mixture of Irganox 1010—Irgafos 168 was studied during multiple processing of HDPE. (See chemical formulae on p. 35.)

Phosphite was found to prevent inhibitor consumption. However, phosphite is consumed simultaneously. After the processing the induction period of oxidation t_{ind} in the oxygen flow was measured for every sample by the method of DSC as a measure of antioxidation potential. Figure 18 shows the dependence of t_{ind} on

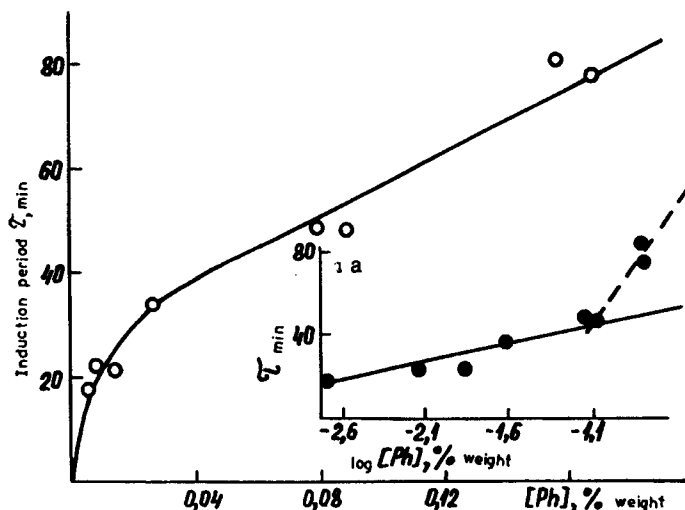


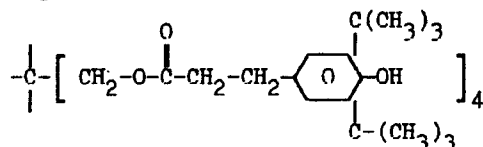
FIGURE 18 The dependence of induction period of HDPE samples on concentration of Irgafos 168 phosphite after multiple processing at 220°C and 260°C. a) Semilogarithmic anamorphosis of data from Figure 18.

the phosphite concentration $[Ph]_0$. The value of it differed by 35 times from minimum up to its maximum. The induction period for control and with phosphite only was as short as 1 minute.

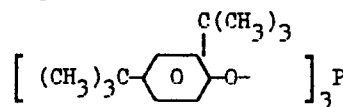
It should be noted, that points on the curve at Figure 18 correspond to different conditions of the processing. They are: temperature and multiplicity of the processing—and slightly different concentrations of the main inhibitor also. Meanwhile, different concentrations of InH and equal ones of $[Ph]$ give close induction periods. Close $[InH]$ and different $[Ph]$ bring to different t_{ind} , t_{ind} is seen to increase as $[Ph]$ increases. However, the efficiency of Ph in t_{ind} increasing is decreased, analogous to the action of inhibitor without synergist.

³Chemical formulae:

Irganox 1010



Irgafos 168



Semilogarithmic transformation of the curve from Figure 18—at Figure 18a—shows, that 6 of 8 experimental points are described by linear dependence. Two points, appropriated to the single processing with high $[Ph]$, are falling out in the direction of t_{ind} increase. It means, that during 4 processings in samples with high $[Ph]$ it was being consumed slower, than under analogous influence on PE with low $[Ph]$. The reason of this may be in the decrease of stationary concentration of hydroperoxide. When concentrations of Ph are rather small, this effect does not

appear. It may be, because the rate of thermal decay of hydroperoxide in these conditions is considerable.

6. DEGRADATION OF POLYURETHANES

This part is devoted to the study of degradation of polymers with more complicated chemical structure, than that of polyolefines. In the work¹¹² the analysis of changes in thermoplastic polyurethanes of different molecular weight and structure was made. In all the samples "soft" segments were created by polytetramethyleneglycol (PTMG). Single molecules of 4,4-diphenylmethandiisocyanate (PMD) served as "hard" segments in one series of samples (polyurethanes PU with non-elongated chain) and 2 molecules of PMD separated by $-(CH_2)_4-O-$ group (PU with elongated chain) in another one. The samples were exposed to γ -irradiation.

The investigations by the method of gel-penetrating chromatography have shown, that PU with elongated and non-elongated chain behave in different ways. Crosslinking prevails in non-elongated PU, and degradation—in elongated one. Authors of Reference 112 investigated in details the possibility of appropriate reactions occurrence by "hard" segments. It was namely their structure that differ in the series of samples. However, the contribution of "hard" segments was found to be comparatively small. In degradation, which occurs rather deep, it does not exceed 20%, and in crosslinking—not more than 10%. The conclusion was made, that chemical transformations occur through the reactions in polytetramethyleneglycol soft segments. It is confirmed by the fact, that at equal molecular weights of PU the degree of crosslinkage increases linearly with the increase of M_w of soft PTMG blocks. GPC-chromatograms of PU with non-elongated chain being linked, as a result of γ -irradiation show, that simultaneously with crosslinking the degradation occurs. The mechanism of degradation and crosslinking in PU seems not quite clear. It is unclear, for example, why elongation of hard segments with comparatively short segments of $-CH_2-$ groups changes the balance between appropriate reactions, occurring in soft segments to such a considerable degree. It is possible, that the mechanism of this process will become more clear in comparison with PE degradation during the processing, where analogous phenomena are observed—simultaneous degradation and linking by $-CH_2-$ groups. Thus, in polymers with methylene groups, the latter are, as a rule, the most vulnerable ones to oxidation degradation. The vast amount of data on thermooxidation of carbochain compounds may be used for an understanding of regularities of this reaction.

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