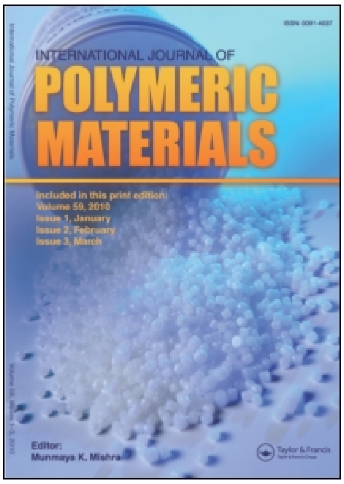

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Autooxidation of Oriented Polyolefins

L. S. Shibryaeva[a]; S. G. Kiryushkin[a]; G. E. Zaikov[a]
[a] Institute of Chemical Physics, the USSR Academy of Sciences, Moscow, USSR

To cite this Article Shibryaeva, L. S. , Kiryushkin, S. G. and Zaikov, G. E.(1992) 'Autooxidation of Oriented Polyolefins', International Journal of Polymeric Materials, 16: 1, 71 — 93
To link to this Article: DOI: 10.1080/00914039208035411
URL: http://dx.doi.org/10.1080/00914039208035411

Intern. J. Polymeric Mater., 1992, Vol. 16, pp. 71–93
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United Kingdom

Autooxidation of Oriented Polyolefins

L. S. SHIBRYAEVA, S. G. KIRYUSHKIN, G. E. ZAIKOV
Institute of Chemical Physics, the USSR Academy of Sciences, 117334 Moscow, USSR

The effect of the chemical structure of the polymer on its reactivity in the oriented state is studied, and causes of the effect of orientation drawing of polyolefins on the oxidation kinetics are identified.

The orientation drawing of the polymer is shown to be dependent on the nature of the latter which can either delay or accelerate the oxidation process. The effect of a delayed rate of oxidation for the samples of one drawing degree is determined by the nature of the side substitute in the monomeric link of the polymer.

The effect of the orientation drawing of the polymer on the change of parameters of oxidation ($k_2 k_6^{-0.5}$ [RH]), a decrease of the coefficients of solubility and diffusion of oxygen as well as the change in the polymer structure depending on its nature are considered.

Analysis of structural changes in the polymers due to orientation has shown that drawing of the polymer can result in localization of oxidation in defected zones of amorphous areas isolated from each other by transition chains in extremely straightened conformation. In this case, the oxidation kinetics of oriented polyolefins can be described with the use of postulates of the "zone" model developed by Yu. A. Shlyapnikov. Evaluation of the kinetic parameters of oxidation ($k_{2\mathrm{eff}}$, $k_{6\mathrm{eff}}$, θ) with the use of this model is made.

It is shown that the effect of the nature of the polymer is due to a change in activity of the C–H bonds participating in the oxidation process, peculiar features of changes in the structure and physical properties of the polymer in the process of orientation drawing, in terms of the "zone" model, to the rate of the expansion of the oxidation center, that is, the nature of the polymer determines the parameters $k_{2\mathrm{eff}}$, $k_{6\mathrm{eff}}$, θ in the oriented sample.

KEY WORDS Autooxidation, polyolefins, orientation

INTRODUCTION

As is known, chemical and physical structures of solid crystalline polymers are of great importance for the process of their oxidation.[1–3] The chemical structure, or the nature of the side substitute in the monomeric link of the polymer, determines the activity of the C—H bonds.[1,2] In its turn, the physical structure of the polymer or its morphology determine the reactivity affecting the physico-dynamic parameters of the polymeric matrix.[3] Herewith the polymer morphology and the nature of the side substitute in its monomeric link are interconnected.

It is important that the polymer oxidation rate can be changed by changing the morphology by means of orientation drawing.[4–6] In this case, changing of the polymeric matrix morphology and, consequently, the effect of orientation drawing could possibly depend on the chemical structure of the polymer. In this connection, it is necessary not only to find the reasons for the effect of orientation drawing of the polymers on the kinetics of their oxidation but also to determine the effect of the chemical structure of the polymer on its reactivity in the oriented state. An attempt is made in the present work to resolve these problems.

EXPERIMENTAL

Linear polyethylene (HDPE) (manufactured by "Montekatini Edison") is used with branching degree 20 CH_3 groups into 1000 at C, MM = 260,000, η = 2.4 cm^3/g at 135°C in *o*-dichlorobenzyl, 0.96 g/cm^3 density; polyethylene of low density (LDPE) manufactured in the USSR with branching degree 20 CH_3 groups per 1000 at C, MM = 120,000; isotactic poly-4-methylpentene-1 (PMP) manufactured by "Montekatini Edison" with η = 2.2 cm^3/g in tetralene at 135°C, 0.83 g/cm^3 density; isotactic polypropylene (PP) manufactured in Italy, named "ASSORENI" with MM = 34,000.

Oriented samples are prepared from tempered isotropic films by the technique of local heating under load.[5] The degrees of drawing (relative elongation) for HDPE, PP, PMP are equal to 0 + 900% ($\lambda = 0 + 9$), and for LDPE to −0 + 550% ($\lambda = 0 \div 5.5$).

Samples 15–50 mm thick are oxidized at 80°C and P_{O_2} = 600 torr in isometric conditions with the absorption of volatile products of KOH oxidation. The time corresponding to 0.1 mole/kg of absorbed oxygen is taken as the induction period of oxidation.

Structural characteristics of the samples are obtained by means of polarization infrared spectroscopy. The spectra are measured using an IR-20 spectrometer and two infrared "Hitachi" polarizers. One of them is placed in the comparison beam, the other in the working (operating) beam, which helps prevent the polarizing effect of the monochromator.

The intensity of the absorption bands is calculated with regard to the correction for polarization according to the following formula: $D^0 = D_\parallel + 2D_\perp/3$,[7] where $D_\parallel$ and $D_\perp$ are intensities of the bands in the polarization spectra whose vector of the beam polarization is parallel and perpendicular to the orientation axis.

The content of separate isomers of the macrochain is determined according to the intensity of the corresponding absorption band referred to the intensity of the reference peak. The bands with wavenumbers 1370, 1380, 900 and 920 cm^{-1} in HDPE, LDPE, PP and PMP are chosen as reference peaks, respectively.

The content of regular conformers are calculated according to the absorption bands at 720 and 730 cm^{-1}in PE,[8] 998 and 840 cm^{-1} in PP,[9] 848 cm^{-1} and 1000 cm^{-1} in PMP.[10] The content of irregular conformers is determined according to the absorption bands at 1303 cm^{-1}, 1352 cm^{-1} in PE,[8] 1155 cm^{-1} in PP[9] and 795 cm^{-1} in PMP.

The crystallinity degree of the polymers is determined using the following methods: X-ray (diffraction) analysis, differential thermal analysis, and by the use of infrared spectroscopy data.

The degree of infrared crystallinity of the polymers is obtained according to the optical density of the bands at 1220 and 1256 cm^{-1} in PP,[11] and using the expression given in 12 in PE, namely, $(D^0_{1895}/D^0_{1308})/(D^0_{1895}/D^0_{1308} + 0.25)$. The ratios of optical density of the absorption bands at 848 and 1170 cm^{-1} are given as characteristics of PMP crystallinity degrees.[13]

The values of the orientation factors are obtained from the ratios $(R - 1)/(R - 2)$ for the absorption bands at 1895 and 1303 cm^{-1} in PE and at 795 cm^{-1} in PMP, where R is the infrared dichroic ratio equal to $D_{\parallel}/D_{\perp}$.[14]

Analysis of nonvolatile products of the polymer oxidation is made using infrared spectroscopy.

The radio-thermo-luminescence scintillation curves (RTL) of preliminary irradiated polymers (at 77 K) are taken with a TLG-9 thermoluminograph at the rate of the sample heating equal to 15 degrees/min.

The value of error in determination of the structural characteristics of the polymer as well as the concentrations of the polymer oxidation products did not exceed 15%.

RESULTS AND DISCUSSION

Kinetics of autooxidation of isotropic polyolefins

Oxidation of solid polymers can be described using the known scheme including the following stages of the process[1]:

Initiation of the kinetic chain:

$$\text{RH} + \text{O}_2 \xrightarrow{k_2} (\text{R}^{\cdot} + \text{HO}_2^{\cdot};\ \text{RH}) \longrightarrow f\text{R}^{\cdot} + \text{inactive products.}$$

Propagation of the chain:

$$\text{R}^{\cdot} + \text{O}_2 \xrightarrow{k_1} \text{RO}_2^{\cdot}$$

$$\text{RO}_2^{\cdot} + \text{RH} \xrightarrow{k_2} (\text{ROOH} + \text{RH}) \longrightarrow \alpha\text{ROOH} + \text{R}^{\cdot}$$

Branching of the chain:

$$\text{ROOH} + \text{RH} \xrightarrow{k_4} (\text{RO}^{\cdot} + \text{R}^{\cdot} + \text{H}_2\text{O};\ \text{RH}) \longrightarrow \delta P.$$

Termination of the chain:

$$\left.\begin{array}{l} \text{R}^{\cdot} + \text{R}^{\cdot} \xrightarrow{k_6'} \\ \text{RO}_2^{\cdot} + \text{RO}_2^{\cdot} \xrightarrow{k_6} \\ \text{R}^{\cdot} + \text{RO}_2^{\cdot} \xrightarrow{k_6''} \end{array}\right\} \text{inactive products}$$

where k_0, k_1, k_2, k_4, k_6 are rate constants of the respective reactions; f is the probability of the origin of the kinetic chains (formation); α is the yield of hydroperoxide per mole of absorbed oxygen; $\delta = (\alpha \cdot \sigma)$- is the probability of degenerated branching of kinetic chains; and σ- is the yield of free radicals. At high pressures of oxygen, the concentration of radicals $RO_2^{\bullet}$ is sufficiently high and that of $R^{\bullet}$ is negligibly low. At the initial stage of the oxidation reaction, the only way of hydroperoxide decay (decomposition) appears to be its reaction with hydrocarbon and the rate of the chain origin (formation) is low compared to the rate of its branching. In this case, at small transformation depths it is possible to neglect the RH consumption, decay of hydroperoxide in its balance and to consider the peroxides which are formed due to chain termination as stable ones. Then the equations of the balance of free radicals and hydroperoxide will have the form

$$d[RO_2^{\bullet}]/dt = W_0 + \sigma k_4[RH][ROOH] - 2k_6[RO_2^{\bullet}]^2 \tag{1}$$

$$d[ROOH]/dt = \alpha k_2[RO_2^{\bullet}][RH]. \tag{2}$$

Solving the system of equations (1) and (2) in quasistationary approximation (that is, $d[RO_2^{\bullet}]/dt = 0$, $d[ROOH]/dt \neq 0$), we get

$$[RO_2^{\bullet}] = (W_0 + \sigma k_4[RH][ROOH])^{0.5}/(2k_6)^{0.5}. \tag{3}$$

Taking into account that $W_0 = fk_0[RH][O_2]$, that is, the rate of the chain origin (formation) is negligibly small as compared with the rate of the chain branching at the early stage of the process, we substitute the value of radicals concentration $RO^{\bullet}$ (3) in equations (1) and (2), integrate the expression obtained and find the law for ROOH concentration changes with time

$$[ROOH] = \alpha NO_2 = \alpha^2\sigma k_2^2 k_4[RH]^3 t^2/8k_6 = At^2. \tag{4}$$

It is known that the reactivity of the polymer is determined by the relationship of the rate constants of the reactions of propagation k_2 and recombination of $RO_2^{\bullet}$-radicals k_6, i.e., $k_2k_6^{-0.5}[RH]$ or $k_2k_6^{-0.5}$. The observed difference in the oxidation rates of polyolefins in question can result from the difference in the values of parameter $k_2k_6^{-0.5}[RH]$ ($k_2k_6^{-0.5}$). The value of parameter k_2k_6 can be calculated using (4), by substituting the value $t = t - t_0$, where t_0 is the part of the axis intercepted on the t-axis of the linear anamorphous kinetic curve of oxygen absorption in the coordinates $(N_{O_2})^{0.5} - t$ (Figure 1).

The values for $k_2k_6^{-0.5}$ are determined on the basis of the values of the factors of oxidation reaction autoacceleration ("A") which are equal to $1.4 \cdot 10^{-7}$, $3.2 \cdot 10^{-7}$, $4.3 \cdot 10^{-6}$ and $7.4 \cdot 10^{-6}$ mole/kg·s)$^{0.5}$ in the case of isotropic samples of HDPE, LDPE, PMP and PP, respectively. The values k_4 of PP and PMP at 80° equal to 1.10^{-5} and $6.2 \cdot 10^{-6}$ s^{-1} were determined to evaluate $k_2k_6^{-0.5}$ from parameter "A," [RH] = 24 (mole/kg). For PE, the value $k_4 = 3.8 \cdot 10^{-6}$ s^{-1} [1] was used, [RH] = 36 (mole/kg). According to the data in the literature, the value of probability of degenerated branching of kinetic chains of oxidation (δ) can be taken to be 10^{-3}.[1] The values $k_2k_6^{-0.5}$ at 80°C determined from equation (4) were equal to $3 \cdot 10^{-5}$,

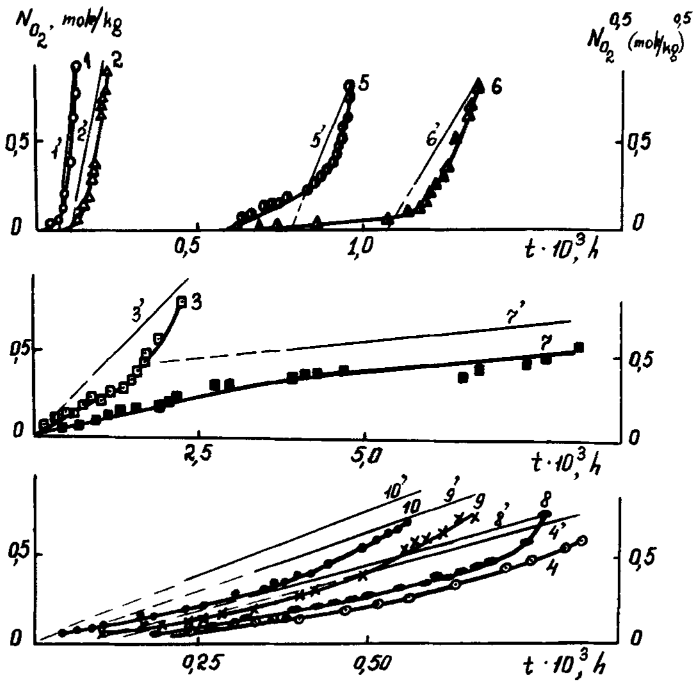

FIGURE 1 Kinetic curves of oxygen absorption by isotropic samples of PP (1), PMP (2) and LDPE (4), oriented samples of PP (5), PMP (6) and HDPE (7) with λ = 9, LDPE with λ = 2.5 (8), λ = 3.5 (9) with λ = 5.5 (10) at $t = 80°C$, $P_{O2} = 600$ torr linear anomorphous their kinetic curves in the coordinates $N_{O2}^{0.5} = f(t)$ 1′ − 10′.

$6.8 \cdot 10^{-5}$, $6.6 \cdot 10^{-4}$ and $1.0 \cdot 10^{-3}$ (kg/mole·s)$^{0.5}$ for HDPE, LDPE, PMP and PP, respectively. It is important that these values for PE and PP differ by 30 times.

The difference observed between $k_2k_6^{-0.5}$ of the polyolefins in question are due to the nature of the C–H bonds which localize the free valence leading the kinetic chains of oxidation: in HDPE these are peroxide radicals at the secondary carbon atom, in LDPE a contribution of the peroxide radical is observed at the ternary carbon atom of the side branch, in PMP and PP these are only radicals at the ternary carbon atom. Due to the above, not only the value $k_2k_6^{-0.5}$ but also each of the given constants separtely is less in the case of PE than in PP and PMP. Moreover, in PMP, the value $k_2k_6^{-0.5}$ is lower than in PP because of a higher value of k_6. At room temperature, $k_6 = 100$ and 10 (mole/kg·s), respectively.[15]

Nonvolatile oxidation products. As seen from Table I and Figure 2, the chemical structure of the polymer determines both the rate of its oxidation and the kinetics of accumulation of oxygen-containing oxidation products and their composition. In HDPE, the hydroxyl groups mainly contain single OH groups, while in LDPE OH groups appear that are bound by hydrogen bonds (Figure 2). (The single OH groups exhibit infrared absorption bands at 3600, 3640 and 3560 cm^{-1}[16] and bonded OH groups have a wide peak with the maximum at 3410 cm^{-1}).[16] This phenomenon is due to the contribution of ternary C–H bonds to HDPE oxidation. Hydroxyl

TABLE I

Nonvolatile products of oxidation of polyolefins (t = 80°C, P_{O_2} = 600 torr)

	Isotropic		Oriented		Isotropic		Oriented	
Sample	N_{O2} (mole/kg)	t_0 (h)	N_{O2} (mole/kg)	t_0 (h)	$[\rangle C{=}O]$ (mole/kg)	$[—OH]$	$[\rangle C{=}O]$ (mole/kg)	$[—OH]$
HDPE	0.82	2256	0.62	8529	0.53	0.01	0.08	0.10
LDPE	0.67	858	0.70	570	0.36	0.12	0.30	0.12
PMP	0.90	224	0.90	1340	0.26	0.20	0.03	0.06
PP	0.86	126	0.80	956	0.36	0.60	0.20	0.40

	Isotropic		Oriented		Isotropic	Oriented	Isotropic	Oriented
Sample	$\frac{D^0_{1745}}{D^0_{1720}}$	$\frac{D^0_{1780}}{D^0_{1720}}$	$\frac{D^0_{1745}}{D^0_{1720}}$	$\frac{D^0_{1780}}{D^0_{1720}}$	$\frac{D^0_{(max)}\rangle C{=}O}{D^0_{(max)} - OH}$	$\frac{D^0_{(max)}\rangle C{=}O}{D^0_{(max)} - OH}$	$\frac{D^0_{—OH(bound)}}{D^0_{—OH(single)}}$	$\frac{D^0_{—OH(bound)}}{D^0_{—OH(single)}}$
HDPE	0.40	0.10	0.30	0.10	146	2.2	0.001	0.40
LDPE	0.40	0.10	0.30	0.10	10	7.7	1.20	2.20
PMP	0.80	0.40	0.80	0.50	3.1	2.5	1.70	1.10
PP	0.60	0.40	0.80	0.60	1.7	1.5	3.10	3.40

*The drawing degree of oriented samples HDPE, PP and PMP is $\lambda = 9$, of LDPE is $\lambda = 5.5$. The concentration of $\rangle C{=}O$, —OH is determined by utilizing the coefficients extinction ($\Sigma_{-1}{}_{\rangle C=O} = 220$, $\Sigma_{—OH} = 70$ kg/mole.sm) in the maximum of absorption at $\nu = 1720\ cm^{-1}$ and $\nu = 3410\ cm^{-1}$, respectively.

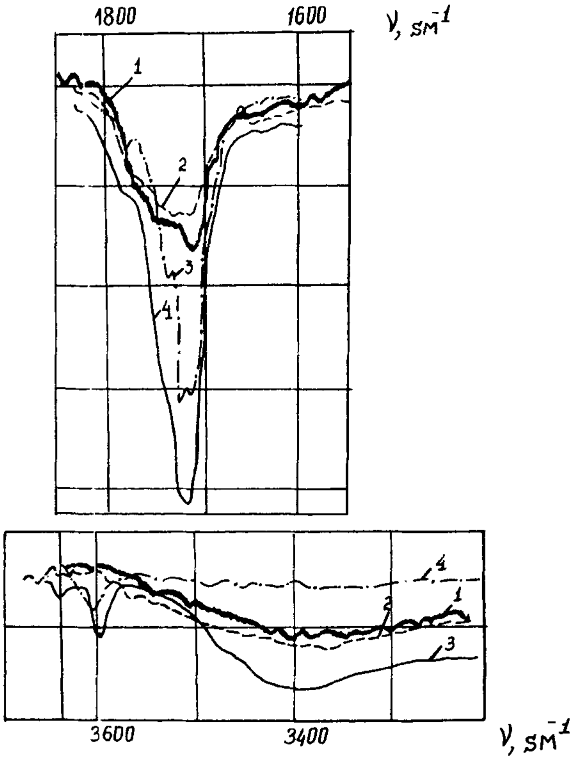

FIGURE 2 Infrared spectra of oxidized isotropic samples of PP (1), PMP (2), HDPE (3) and LDPE (4).

groups bonded by hydrogen bonds prevail in PP and PMP. In contrast to PP and PMP, nonvolatile oxidation products in PE predominantly contain $\overset{|}{\underset{|}{C}} = 0$ groups rather than OH groups, which can be due to the prevailing intermolecular transfer of kinetic chains of oxidation in PE and intramolecular one in PP and PMP.

Oxidation of oriented films

Figure 1 shows kinetic curves of oxygen absorption by oriented and isotropic samples of HDPE, LDPE, PMP, PP, and their linear anamorphoses in the coordinates $(N_{O_2})^{0.5} - t$. It follows from Figure 1 that orientation drawing of HDPE, PP and PMP results in a lower rate of the oxidation process and a longer induction period of oxidation, while an opposite affect is attained in LDPE, namely, the induction period is shorter and the oxidation rate increases with a higher degree of drawing. The increase of the induction period in the samples of HDPE, PP and PMP with the same drawing degree $(\lambda = 9)$ is different. The magnitude of the ratio of the oxidation induction period of the oriented sample to the isotropic one $\tau_{\lambda=9}/\tau_{\lambda=0}$ decreases in sequence as follows: PP > PMP > HDPE. A different mechanism of polymer oxidation is possible in oriented HDPE, in contrast to PP and PMP, at the observed depth of oxidation, which is confirmed by the practically linear dependence of the amount of absorbed oxygen on the time of oxidation.

The probable reasons for the changes in the oxygen absorption kinetics due to oriented polyolefins are the following: 1) a change in the ratio of kinetic rate constants of separate oxidation stages included in the parameter of reaction "A" (Equation (4)); 2) a decrease in solubility and diffusion coefficient of oxygen; 3) a change in the character of the oxidation process localization in the polymer due to structural transformations caused by orientation drawing. Now we will try to verify each of these hypotheses.

1) The ratio of the rate constants included in parameter "A" which is connected with the induction period of the polymer oxidation. These rate constants can be derived from equation (4); considering that N_{O_2} = 0.1 mole/kg, then $t - \tau_{ind}$.

The value of the ratio of the constants in oriented PP and PMP increases 6 and 3 times as compared with the isotropic samples, respectively, while at the same time the induction period increases by a greater degree (8 and 7 times). In contrast with PP and PMP, a change in the data of kinetic parameters well describes the observed changes of the induction period of oxidation. For the samples with the degree of drawing equal to 2.5, 3.5 and 5.5, it comes to 0.95, 0.69 and 0.60, respectively, which coincides with experimentally obtained values. Thus, an increase in the induction period of PP, PMP and HDPE oxidation cannot be explained only by a decreasing ratio of the above-mentioned rate constants. In the case of LDPE, a decrease in the induction period of oxidation is completely described by a change in these ratios. This can be due to a change in the contribution of the LDPE oriented samples of more reactive ternary C—H bonds to the oxidation process. We will return to this problem below.

2) Now we evaluate the contribution of decreasing solubility of oxygen to decreasing reactivity of oriented polymer using PP with $\lambda = 9$ as an example. For this purpose we employ the dependence $\tau_{ind} - P_{O_2}$ given in Figure 3. In this case we assume that the reaction proceeds homogeneously. Extrapolation of the data on oxygen solubility in the PP sample $\lambda = 0^{17}$ to 80°C at 600 torr gives a value of solubility equal to $2.2 \cdot 10^{-3}$ mole/kg. It is $1.0 \cdot 10^{-3}$ mole/kg for the oriented sample.

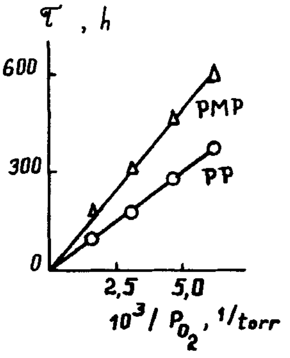

FIGURE 3 Dependence of the induction period of oxidationof isotropic samples of PP and PMP on the pressure of oxygen in the coordinates $\tau_{ind} = 10^3/P_{O2}$, 80°C.

This difference in oxygen solubility between the isotropic and oriented samples correlates with a decrease of P_{O_2} in isotropic PP from 600 to 270 torr and, consequently, to an increase of the value of the induction period from 90 h to 210 h. This decrease in oxygen solubility in oriented PP as compared with isotropic PP can result in a longer induction period (2.4 times), while an eightfold increase of the induction period is observed. In PMP the solubility of oxygen in the oriented sample $\lambda = 9$ is practically near the solubility of the isotropic sample.[17] Thus a decrease in the solubility of oxygen in oriented samples cannot completely explain the observed increase of the induction period in the case where the reaction proceeds homogeneously.

A decrease of the diffusion coefficient of oxygen in the polymer may result in a decreasing rate of oxidation[1] due to transformation of the oxidation process which exchanges the kinetic regime for the diffusion one. To determine the maximum thickness of the sample L_k at which oxidation proceeds in the kinetic regime we use the Frank–Kamenetskii equation[18]:

$$L_k = (D[O_2]/W_{O_2})^{0.5} \tag{5}$$

where D, O_2 are the diffusion coefficient and the solubility of oxygen and W_{O_2} is the oxidation rate. Taking into account that the concentration of oxygen in the film of oriented PP at 80°C and $P_{O_2} = 600$ torr is equal to $1.0 \cdot 10^{-3}$ mole/kg, the maximum rate $W_{O_2} = 1.7 \cdot 10^{-6}$ mole/kg·s and the diffusion coefficient of oxygen determined by extrapolation of the data in reference 17 to 80°C is equal to $4.9 \cdot 10^{-7}$ cm^2/s, we obtain $L_k = 1.7 \cdot 10^{-2}$ cm, which substantially exceeds the experimental value of the film thickness. Calculations made for PMP with $\lambda = 9$ give the same results.

3) Peculiar features of the effect of orientation drawing of PP, PMP, HDPE and LDPE on the oxidation rate can be explained in terms of localization of oxidation in defected zones of amorphous areas. These zones constitute only part of the area oxidized in the isotropic sample.

This localization of oxidation is predetermined by structural transformation of amorphous areas of polymers due to the effect of plastic deformation.

Structure of oriented polyolefins

The data given in Table II indicate that the degree of polymers crystallinity determined by DTA and X-ray methods does not change with the changes in the degree of drawing, while the application of infrared spectroscopy shows an increase in the degree of crystallinity. This means that the amount of regular conformers in amorphous areas of the polymer increases, i.e., the orientation drawing of the polymer does not change the crystallinity degree of polyolefins but at the same time changes the conformation set of amorphous areas. The data given herein are confirmed by the data obtained by other authors.[19]

Analysis of the experimental results for the polyolefins in question shows that increasing the degree of drawing substantially increases the concentration of regular conformers and insignificantly decreases the concentration of irregular conformers in HDPE and LDPE (Figure 4). Thus it is important to note that in a case of

TABLE II

The degree of polymer crystallinity

Polymer	λ	Degree of crystallinity, X, %		
		SAKS	DTA	IR spectroscopy
HDPE	0	70	—	55
	4	70	—	68
	5.5	—	—	72
	9	—	—	78
LDPE	0	36	—	36
	2.5	—	—	44
	3.5	—	—	46
	5.5	—	—	48
PP	0	60	68	66
	4.5	60	66	72
	6.0	60	66	72
	9.0	63	68	78
PMP	0	50	50	0.25*
	4.5	50	50	0.25*
	9.0	50	53	0.23*

*The degree of crystallinity of PMP is the ratio of optical density of the absorption bands at 848 and 1170 cm^{-1}.

similar character of changes in the conformation set in these polymers, the changes in reactivity of oriented samples is quite the opposite. An increase in the concentration of regular conformers in oriented PP is much less and a decrease in the concentration of irregular conformers is slightly higher than in PE (Figure 4). No clearly defined changes in conformation composition of the PMP amorphous area were observed (Figure 4).

Peculiarities of changes in conformation composition of polyolefins appear to be due to the peculiarities of their microstructure, namely, the type of conformation macrochains (regular conformation in PE: trans-zigzag (I_1)), spiral 3_1 consisting of alternating trans- and guache-isomers in PP, spiral 7_2 in PMP (Figure 5); various isomeric composition of macrochains in amorphous areas: irregular chains in PE are representedby a wide range of trans- and gauche-conformations (TGT, GTG and GG), collisions of parts of levo- and dextrorotatory spirals (GTG-TTG$^-$TG$^-$, GTGG$^-$TG$^-$) i.e., a set which differs from PE.[20] Consequently, the mechanisms of changes as well as the rates of change in isomeric composition of macrochains in these polymers can be different from each other.

The value of the factors of orientation in amorphous and crystalline areas of the polymer, or to be more precise the orientation of irregular and regular conformers, increases with an increase in the drawing degree (Figure 6). Moreover, if the orientation of regular conformers reaches the limiting value (the orientation factor is equal to unity) even at low drawing degrees and does not change further, then the orientation of irregular conformers gradually increases at the same time remaining low even in highly oriented samples.

The average density of the amorphous phase increases with an increase in the

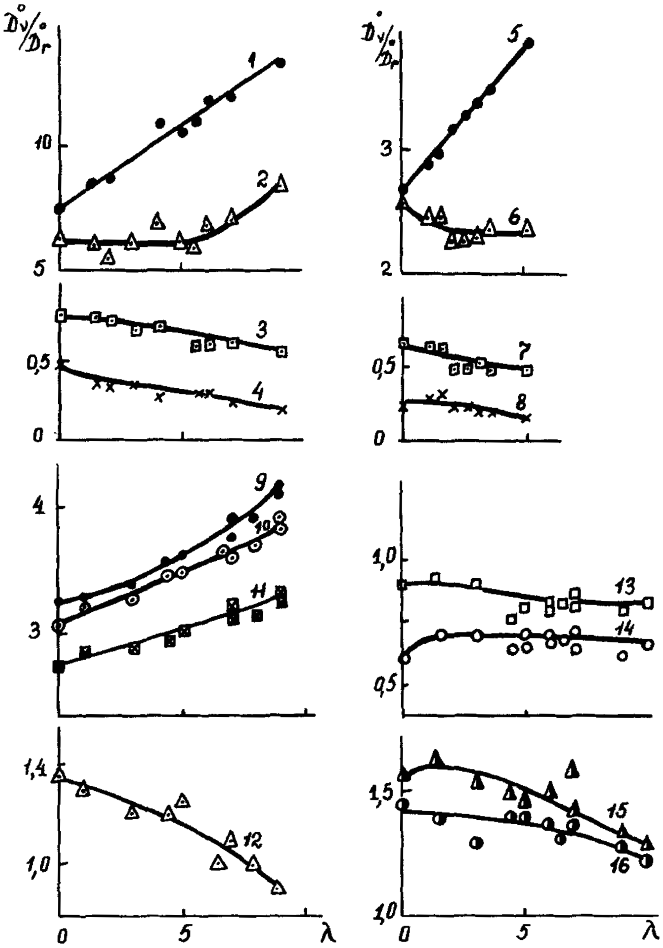

FIGURE 4 Dependence of intensity values of the absorption band referred to the intensity of the reference peak of HDPE (1–4), LDPE (5–8), PP (9–12), and PMP (13–16), corresponding to the content of regular conformers: 720 (1,5), 730 (2,6) cm^{-1} in PE, 975 (9), 998 (10), 840 cm^{-1} (11) in PP, 997 (13), 848 cm^{-1} (14) in PMP; and of irregular conformers: 1352 (3,7), 1303 cm^{-1} (4,8) in PE, 1155 cm^{-1} (12) in PP, 1155 (15), 795 cm^{-1} (16) in PMP on the degree of samples.

drawing degree in the sample, which is indicated by a lower solubility of phenylbenzoate (Figure 7). In this case, increasing density of amorphous areas may be due to a decrease of the concentration in defected zones with less dense patching, which, according to references 21 and 22, is indicated by a decreasing intensity of γ-maximum of the RTL curve corresponding to the temperature interval (70–170 K) (Figure 8). Besides, analysis of the curves of lumination of isotropic and oriented polyolefins shows a decrease of the segmental mobility of the latter (which is confirmed by increasing T_c in oriented polyolefins, a shift by 10–20° in PP and HDPE (Figure 8a)) and decreasing intensity of RTL as well as a shift of all maxima of lumination curves toward higher temperatures (Figure 8). References 21 and 22 show that the observed effects in RTL of oriented samples result from changes in

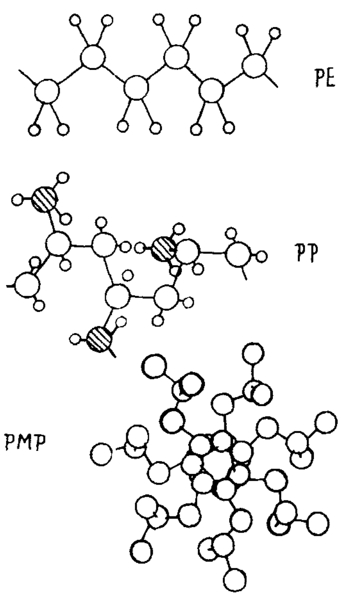

FIGURE 5 The type of regular conformation of macrochains PE, PP and PMP.

conformation composition of amorphous areas, a lack of irregular conformers. This is in agreement with the data obtained by infrared spectroscopy.

Structural transformations observed in oriented polyolefins and the existing structural models of fibrilla (Figure 9)[23-26] allow localization of irregular conformers in small parts of intrafibrillar amorphous areas and their isolation from each other by extremely straightened chains. According to References 3, 27 and 28, irregular conformers exhibit a higher reactivity and, consequently, localization of the oxidation process can be observed in defected parts of amorphous areas of the oriented polymer. Localization of the process should affect the composition of nonvolatile oxidation products.

Comparison of the infrared spectra in the regions of 1700–1800 and 3200–3700 cm^{-1} in oriented and isotropic samples has shown that at near depth of oxidation the total concentration of —OH and $-\overset{|}{C}$ groups is higher in the latter regions (Table I). Carbonyl-containing products consist of a greater amount of ester (ν = 1745 cm^{-1}) and lactone (ν = 1770–1780 cm^{-1}) in oriented HDPE and PP samples as compared with isotropic ones. On the contrry, in LDPE the share of acid-ketone $-\overset{|}{C}{=}O$ groups (ν = 1720 cm^{-1}) increases with an increase in the drawing degree, and also increases the value of the ratio of the concentration of bound OH groups to the concentration of single groups. The latter correlates with the induction period (Figure 10). In LDPE with λ = 5.5, the concentration of single OH groups is low. It is important to note that bound OH groups in oriented LDPE do not exhibit dichronism (R_{3410} = 1), while at the same time single OH groups are characterized by a high magnitude of this parameter (R_{3600} = 0.05).

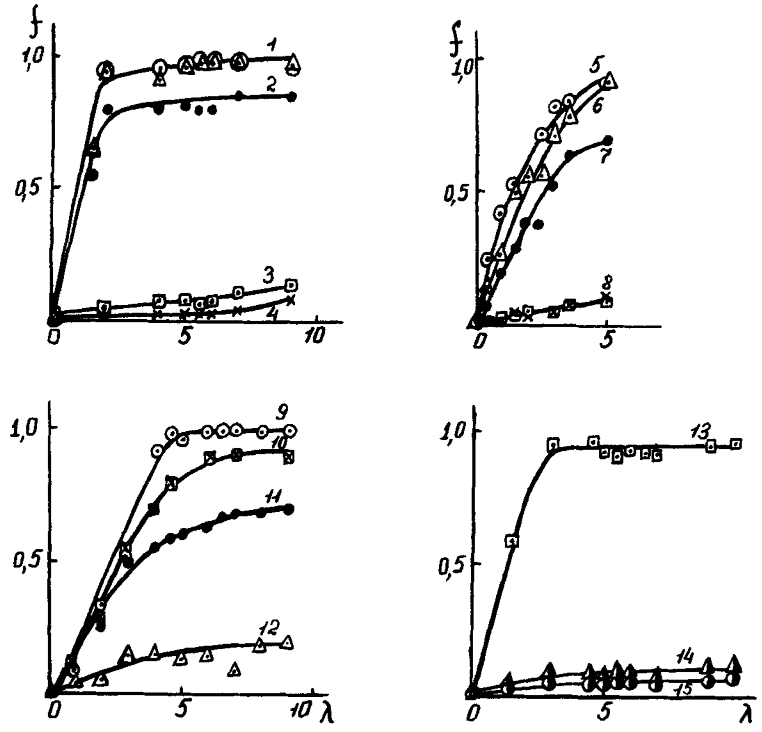

FIGURE 6 Dependence of values of macrochains orientation factors of HDPE (1 – 4), LDPE (5 – 8), PP (9 – 12), and PMP (13 – 15) on the degree of the sample drawing. The orientation factors of chains in regular conformation (1895 cm^{-1}) are equal to 1,5 (720 cm^{-1}) to 2,6 in PE (998 (9), 840 (10); 975 cm^{-1} (11) in PP; 997 cm^{-1} (13) in PMP; those of the chains in coiled conformation (1303 (3, 8 (☐)), 1352) (4,8(x)) in PE; 1155 cm^{-1} (12) in PP; 1155 (14), 795 cm^{-1} (15) in PMP.

This can be explained by the fact that bound OH groups in PE are localized in defected parts where chain orientation is slight.

The peculiarities of oxidation in oriented LDPE samples can be explained in terms of the localization process in defected zones as follows. In the case of orientation, the chain parts containing branchings, and consequently ternary carbon atoms, are shifted toward these defected zones of amorphous areas.[29] Localization of ternary C—H bonds, which are more active than the secondary ones, increases in defected zones with an increase of the degree of LDPE drawing. This seems to be due to a change in the composition and activity of peroxide radicals leading the kinetic chains of oxidation, i.e., it changes parameter $k_2k_6^{-0.5}$. In addition, the initiating ability of hydroperoxides thus formed can also change and k_4 can increase. A change in the composition of oxidation products also indicates this fact, i.e., the formation of bound OH groups is typical of polymers with ternary C—H bonds.

The appearance of ester and lactone groups in PP and HDPE can be due to intracellular recombination of alcoxyl radicals resulting from ROOH degradation or $RO_2^{\bullet}$ recombination. The share of intracellular reaction will increase with a decreasing molecular mobility in the reaction preceding in the microreactor. Moreover, the appearance of these groups can be considered as a result of the reaction between the conjugated functional groups, these reactions being involved in ab-

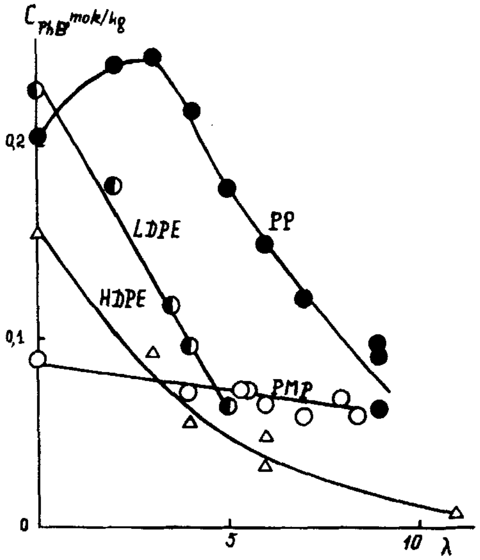

FIGURE 7 Dependence of the solubility of phenylbenzoate in the amorphous areas of polymers on the degree of the sample drawing.

sorption of oxygen and leading to increasing concentration of volatile oxidation products.

When localization of oxidation takes place in intrafibrillar amorphous layers, the reaction of oxidation will spread from one "microreactor" to another. In this case the kinetics of oxygen absorption can be described in terms of the "zone" model developed by Yu. A. Shlyapnikov.[1,30]

According to this model, the chain reaction originates at the moment it comes to the defected zone of free valence; the reaction terminates if the $RO_2^{\bullet}$ radical leaves the "zone" or another radical enters the "zone."

The concentration of $RO_2^{\bullet}$ radicals in the "zone" is equal to one particle on the volume of "zone" (particle/cm^3)

$$[RO_2^{\bullet}] = 1/V_Z \tag{6}$$

where V_Z is the "zone" volume.

The flow rate of reactive RH groups in the "zone" proceeds according to the exponential law

$$[RH]_Z = [RH]_{Z_0} \exp(-K_2 V_Z^{-1} \cdot t), \tag{7}$$

where $[RH]_Z$ is the concentration of reactive groups in the zone (mole/kg).

The oxidation rate is determined by the amount of the substance in a separate "zone" and by the rate of transition of free valence from one "zone" to another:

$$W_{O_2} = V_Z[RH]_Z\, \theta^{-1}[RO_2^{\bullet}] \cdot N_{Ab} \cdot 10^{-3}, \tag{8}$$

where $[RO_2^{\bullet}]$ is the average concentration of peroxide radicals taking into account

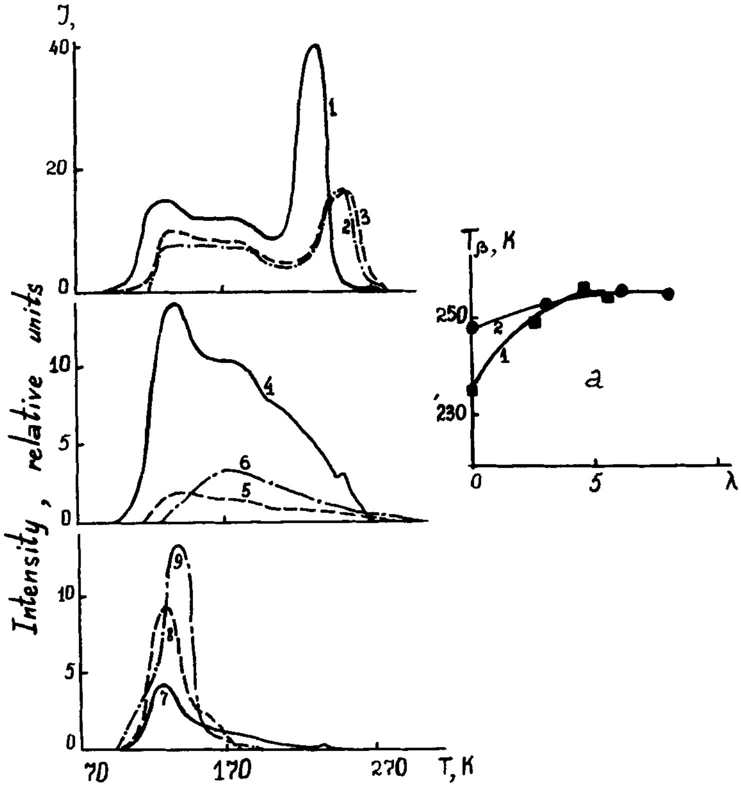

FIGURE 8 Curves of lumination of isotropic and oriented samples of polyolefins: LDPE $\lambda = 0$ (1), $\lambda = 2{,}5$ (2), $\lambda = 5{,}5$ (3); PP $\lambda = 0$ (4), $\lambda = 6$ (5), $\lambda = 8$ (6); PMP $\lambda = 0$ (7), $\lambda = 4{,}5$ (8), $\lambda = 9$ (9).

(a) Dependence of the glass-transition temperature of LDPE (1) and PP (2) on the drawing degree.

the whole polymer (mole/kg), and θ is the duration of the stay of the free valence in a separate zone.

The rate constant of the reaction of the oxidation kinetic chain transfer is equal to

$$k_{2\text{eff}} = V_Z[\text{RH}]_Z \cdot [\text{RH}]^{-1}\theta^{-1}\text{N}_A \cdot 10^{-3}, \qquad (9)$$

where [RH] is the average concentration of RH groups in the polymer (mole/kg).

The rate of the kinetic chain termination is determined by the frequency of the entering of two free valences into one "zone."

The rate constant of these radicals recombination is equal to

$$k_{6\text{eff}} = 2[Z]^{-1}\theta^{-1}. \qquad (10)$$

It follows from this model that the oxidation process of polymers is expected to localize in defected parts consisting of the chains in coiled conformation (Figure 9). In this case, isolation of these parts or microreactors by highly oriented chains

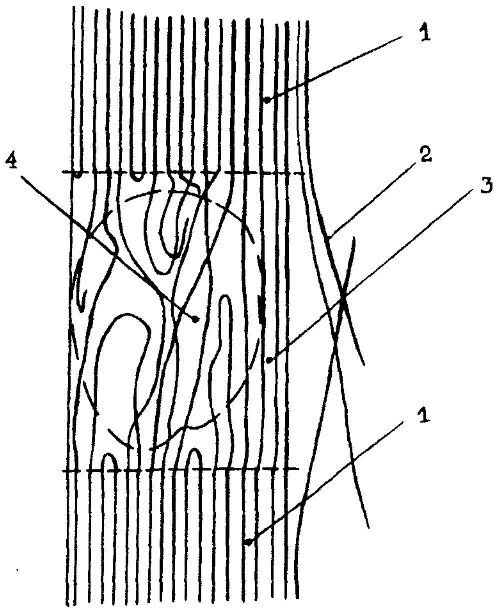

FIGURE 9 The structure model of drawing polymers. Indicated are the defected parts, consisting of the chains in coiled conformation, where the oxidation process may be localized. crystallites (1); interfibrillar transition chains (2); extremely straightened intrafibrillar transition chains (3); irregular chains (4).

FIGURE 10 (a) A change in the ratio between the content of bonded and unbonded hydrogen bonds of OH groups in oxidized LDPE depending on the drawing degree ($D^\circ_{3410}/D^\circ_{3600} = f(\lambda)$, (80°C, P_{O_2} = 600 torr). (b) Dependence of the induction period of oxidation on this ratio ($\tau_{ind} = f(D^\circ_{3410}/D^\circ_{3600})$).

in extremely straightened conformation with low reactivity should complicate the transition of free valence from one microreactor into another; it is the factor that slows down the oxidation process.

We have derived the expression describing the dependence of the induction period of oxidation on the concentration of "zones" ([Z]) to verify the application of the "zone" model for description of polyolefins oxidation. Equation (4) earlier employed in the work was used

$$\mathrm{N}_{\mathrm{O}_2} = k_2^2 k_4 \delta [\mathrm{RH}]^3 t^2 / 8 k_6.$$

In terms of the zone model, the kinetic parameter of oxidation $k_{2\mathrm{eff}}^2$, k_{eff}^{-1} can be expressed as follows:

$$k_{2\mathrm{eff}}^2, k_{6\mathrm{eff}}^{-1} = V_Z^2 [\mathrm{RH}]_Z^2 [Z] \cdot \mathrm{N}_{Ab} \cdot 10^{-6} / 2 [\mathrm{RH}]^2 \theta. \tag{11}$$

Hence

$$\theta = V_Z [\mathrm{RH}]_Z [\mathrm{RO}]_2^{\cdot} \cdot \mathrm{N}_{Ab} \cdot 10^{-3} / W_{\mathrm{O}_2}. \tag{12}$$

Substituting (10) into (9), we get

$$k_{2\mathrm{eff}}^2, k_{6\mathrm{eff}}^{-1} = V_Z [\mathrm{RH}]_Z \cdot W_{\mathrm{O}_2} \cdot \mathrm{N}_{Ab} \cdot 10^{-6} \cdot 2^{-1} [\mathrm{RH}]^{-2} [\mathrm{RO}_2^{\cdot}]^{-1} \cdot [Z]. \tag{13}$$

Substituting this expression into (4), we find

$$\mathrm{N}_{\mathrm{O}_2} = \delta k_4 [\mathrm{RH}] \cdot V_Z [\mathrm{RH}]_z \cdot \mathrm{N}_{Ab} \cdot 10^{-6} W_{\mathrm{O}_2} (16)^{-1} [\mathrm{RO}_2]^{-1} \cdot [Z] \cdot t^2. \tag{14}$$

According to the postulate of the zone model, $[\mathrm{RO}_2^{\cdot}] \equiv 1/V_Z$, which allows us to assume that $[\mathrm{RO}_2^{\cdot}] \cdot V_Z = \text{const.}$, hence it is possible to obtain the following relationship:

$$\mathrm{N}_{\mathrm{O}_2} = B \cdot W_{\mathrm{O}_2} \cdot [Z] \cdot t^2,$$

where

$$B = \delta k_4 [\mathrm{RH}]\ V_Z [\mathrm{RH}]_Z \cdot \mathrm{N}_{Ab} \cdot 10^{-3} (16)^{-1} [\mathrm{RO}_2^{\cdot}]^{-1}. \tag{15}$$

At the initial stage of oxidation

$$W_{\mathrm{O}_2} = N_{\mathrm{O}_2} \tau_{\mathrm{ind}}^{-1} \tag{16}$$

Substituting equation (4) into (13), we get

$$\mathrm{N}_{\mathrm{O}_2} = B \cdot \mathrm{N}_{\mathrm{O}_2} \tau_{\mathrm{ind}}^{-1} [Z] \cdot t^2 \tag{17}$$

Simplifying this equation, we find the dependence to be determined:

$$B \cdot [Z] \cdot \tau_{\mathrm{ind}} t^2 = 1 \quad \text{or} \quad t = (\tau_{\mathrm{ind}} \cdot B \cdot [Z]^{-1})^{0.5}. \tag{18}$$

The expression obtained was used to describe the dependencies $\tau_{\mathrm{ind}} = f([Z])$

exemplified by the kinetics of oxidation of PP samples with different degrees of drawing at 130°C and $P_{O_2} = 600$ torr. In this case the concentration of defected zones was considered to be equal to the solubility of phenylbenzoate in the polymer as was previously shown in reference 31.

The data obtained are given in Table III and Figure 11. These data show that the dependence $\tau_{ind} = f([Z])$ is practically linear, which allows the "zone" model to be used for evaluation of kinetic parameters of the oxidation process of isotropic and oriented polymer samples. The values of $k_{2\,eff}$, $k_{6\,eff}$, θ are determined.

Determination of the $k_{2\,eff}$, $k_{6\,eff}$, values

To obtain these parameters it is necessary to determine the following: volumes of the "zones," their concentration in polymers (V_Z and $[Z]$), the concentration of reactive RH groups in the zone (RH_Z), the average concentation of $RO_2^{\cdot}$ radicals in the polymer.

Determination of the V_Z, $[Z]$ values

It should be taken into account that the polymer contains microreactors that differ in volume. To simplify the calculation we will assume that "zones" are distributed evenly; the minimal volumes are almost similar in isotropic and oriented samples. The minimal volume of zones (microreactors) being comparable with volume of phenylbenzoate molecule, is equal to $9 \cdot 10^{-21}$ cm^3. The concentration of microreactors is equal to the solubility of phenylbenzoate in the polymer, [PhB]. The maximum volume of the microreactor in the isotropic sample is equal to $V_{PhB} \times n$ and that in the oriented sample is equal to $V_{PhB} \times m$, $m \neq n$ so as the orientation drawing of the polymer changes both the concentration and the volume of maximal defected "zones." The concentration of zones is equal to $[PhB]_{\lambda=0}/n$ in the isotropic sample and to $[PhB]_{\lambda=9}/m$ in the oriented sample.

For calculation it is necessary to consider two extreme situations: n and m are equal to 1 and m,n equal maximum size. For this purpose the data of X-ray structural analysis are employed. For example, we describe the calculation made for PP samples.

We consider an oriented PP sample with $\lambda = 9$. The volume of the sample in question is equal to $2 \cdot 10^{-2}$ (g)/0.85 (cm^3/g) $= 2.4 \cdot 10^{-2}$ cm^3 (the sample mass/density). The total volume of amorphous layers is equal to $1 \cdot 10^{-2}$ cm^3, with degree of crystallinity being taken into account (the latter is equal to 60%). The total volume of intrafibrillar amorphous layers with defected structure is equal to $9.5 \cdot 10^{-3}$ cm^3 (at MM = 34,000, the share of interfibrillar amorphous parts does not exceed 5%, according to reference 32). Volume I of intrafibrillar layer does not exceed $8 \cdot 10^{-19}$ cm^3 (80 × 100 × 100 Å^3). These data show that this PP sample contains $9.5 \cdot 10^{-3}/8 \cdot 10^{-19} = 10^{+16}$ intrafibrillar amorphous layers. If we assume that each amorphous layer contains one zone ($m = 1$) with minimal volume, we obtain that the concentration of the latter in polymer is equal to $10^{16}/6 \cdot 10^{23} \cdot 2 \cdot 10^{-5} \cong 10^{-3}$ mole/kg.

This value is approximately 90 times less than the concentration of phenylbenzoate dissolved in the amorphous regions of this polymer sample, $[PhB] = 9 \times$

TABLE III

Dependence of the induction period on concentration of defected zones (130°C, 600 torr)

λ	τ (min)	τ_λ/τ_0	$[Z]$ = [PhB] (oll polym.) (mol/kg)	$(\tau/Z)^{0.5}$ ((min·kg/mole)$^{0.5}$)	$[Z]$ = [~TGG⁻T] + [~GTTG⁻~] (mol/kg)	$(\tau/Z)^{0.5}$ ((min·kg/mole)$^{0.5}$)
0	40	1.00	8×10^{-2}	22.4	5.00	2.8
3	85	2.12	1×10^{-1}	29.0	5.05	4.1
4	100	2.50	6.3×10^{-2}	40.0	4.40	4.8
6	120	3.00	6.0×10^{-2}	44.7	3.60	5.8
9	150	3.75	3.6×10^{-2}	61.2	3.00	7.1

TABLE IV

The values of kinetic constants and parameters of autooxidation isotropic and oriented samples of PP obtained using the zone model

Sample	m ore n	V_Z (cm^3)	$[Z]$ (amorp. fase) (mole/kg)	$[Z]$ (oll polym.)	$[RH]_e$ (oll polym.) (mole/kg)	$[RH]_z$ (mole/kg)
PP	$n = 1$	9×10^{-21}	2×10^{-1}	8×10^{-2}	5.6	13.0
$\lambda = 0$	$n = 125$	1×10^{-18}	1.6×10^{-3}	6.4×10^{-4}	5.6	13.0
PP	$m = 1$	9×10^{-21}	9×10^{-2}	3.6×10^{-2}	5.6	28.0
$\lambda = 9$	$m = 70$	6×10^{-19}	1.3×10^{-3}	5.2×10^{-4}	5.6	28.0

Sample	W_{O2} (oll polym.) (mol/kg·s)	$[RO_2^{\cdot}]$ (oll polym.) (mole/kg)	θ (s)	$k_{2,eff}$ (kg/mole·s)	$k_{6,eff}$ (kg/mole·s)
PP	6×10^{-6}	2.8×10^{-7}	3.3	9×10^{-1}	7.6
$\lambda = 0$	6×10^{-6}	2.8×10^{-7}	3.6×10^{2}	9×10^{-1}	8.6
PP	2×10^{-6}	1.4×10^{-7}	10.6	6×10^{-1}	5.2
$\lambda = 9$	2×10^{-6}	1.4×10^{-7}	7.1×10^{2}	6×10^{-1}	5.4

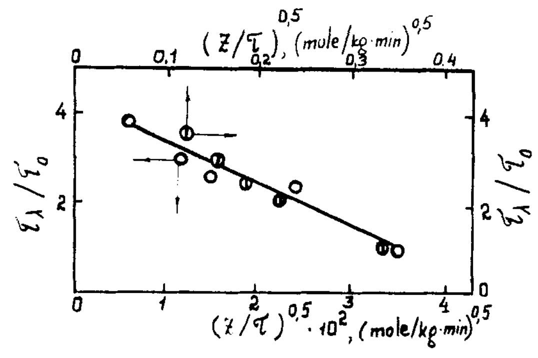

FIGURE 11 A change in the ratio between the induction period of oxidation of the isotropic and oriented PP samples ($\tau\lambda/\tau_0$) depending on the value of $(Z/\tau)^{0.5}$ for the case where the concentration of zones ($[Z]$) = [PhB] (○), where $[Z]$ is the concentration of irregular chains [~TGG⁻T~] + [~GTTG⁻~] (⦶).

10^{-2} mole/kg. Thus it follows that $m \cong 90$, i.e., each amorphous layer of the oriented PP sample can contain up to 90 minimum defected zones with the volume equal to $9{\cdot}10^{-21}$ cm^3, or 1 maximum defected zone with the volume equal to $\sim 8{\cdot}10^{-19}$ cm^3.

We now consider the isotropic sample. The volume of PP $\lambda = 0$ is equal to $2.4{\cdot}10^{-2}$ cm^3. The total volume of its amorphous regions is equal to $1.0{\cdot}10^{-2}$ cm^3, the volume of a single amorphous layer is 10^{-18} cm^3 [(100 Å)^3], and the number of these layers is 10^{16}. In the case where only one defected zone (volume is equal to $9{\cdot}10^{-21}$ cm^3) is localized in each amorphous layer, the concentration of the zones is equal to $10^{16}/6{\cdot}10^{23}{\cdot}2{\cdot}10^{-5} \cong 10^{-3}$ (mole/kg). This value is 200 times less than that obtained experimentally considering $[Z] = [\mathrm{PhB}] = 0.2$ mole/kg. Hence, the amorphous layer can contain up to 200 zones, i.e., $n \cong 200$.

To verify the results thus obtained, we evaluate the content of monomeric links entering into the chain parts in coil conformation, i.e., their share in the total content of monomeric links in the amorphous layer when $n = 200$ and $m = 90$. Then we compare these data with those obtained by the method of polarization infrared spectroscopy.

The defected zones consist of elementary defects. According to the data obtained from the Stewart–Brigleb model, each of these defects contain up to 10 monomeric units united into the chain part with the GTGTGG⁻TG⁻TG⁻ or TGTGTTG⁻TG⁻T coiled conformation.[20] The volume occupied by each of these elementary defects is approximately equal to $2{\cdot}10^{-21}$ cm^3. Consequently, the defected zone with the minimal volume contains up to approximately 5 microdefects of this kind.

The total content of defected zones with $V_Z = 9{\cdot}10^{-21}$ cm^3 in the amorphous layer of the oriented sample is equal to 90. The total number of monomeric links in the layer with coiled conformation is equal to $10 \times 5 \times 90 = 4.5{\cdot}10^3$. The total content of monomeric units in the amorphous layer is equal to $8{\cdot}10^{-19} \times 0.85 \times 6{\cdot}10^{23}/42 = 10^4$. Hence the share of monomeric links with coiled conformation with respect to the total amount of these links in the amorphous layer of the oriented sample is equal to 40%.

The total content of monomeric links in the isotropic sample is $0.83{\cdot}10^{-18}{\cdot}6{\cdot}10^{23}/42$

$\cong 1.2 \cdot 10^4$. The content of monomeric units in the chains with coiled conformation is equal to $200 \cdot 5 \cdot 10 = 10^4$, which is 80% of their total amount.

The content of irregular conformers was determined by the same method of polarization infrared spectroscopy. In this case, optical densities of the band at 1155 cm^{-1} were used, the extinction coefficient for this band taken equal to $2.8 \cdot 10^{21}$ CH_2/cm^3 similar to PE,[33] and these data were used to acknowldge receipt of linear dependence $\tau_{ind} = f([Z])$ (Table III, Figure 11). It is found that the content of monomeric links in the chains consisting of coiled conformers in the oriented and isotropic sample is equal to 3.0 and 5.0 mole/kg, respectively. The total content of monomeric links in the polymer is 24 mole/kg. The crystallinity degree is equal to 60% in both cases. We believe that all monomeric links with coiled conformation are accumulated in amorphous regions of polymers. Consequently, their total amount is equal to 9.6 mole/kg. Whence we obtain that the shares of irregular conformers in the total content of conformers are equal to 31% and 52% in oriented and isotropic samples. These values are near those given in reference 32, and they are used to increase the accuracy of the quantity of n and m: $n = 125$, $m = 70$ and $V_{z(\max)\lambda=0} = 1.0 \cdot 10^{-18}$, $V_{z(\max)\lambda=9} = 6.0 \cdot 10^{-19}$ cm^3, respectively.

Determination of [RH]$_Z$

The following relationship was used to determine $[RH]_Z$:

$$[RH]_e = V_z \cdot [Z]^{\circ} [RH]_Z \cdot N_{Ab} \cdot 10^{-3} \tag{19}$$

where $[RH]_e$ is the concentration of the polymer participating in the reaction of oxidation (mole/kg).

This value was determined experimentally using the dependence $W_{O_2} = f(N_{O_2})$ (Figure 12) by extrapolating the rate of oxidation to the concentration of absorbed oxygen equal to zero. This value is similar for both isotropic and oriented PP samples and is equal to $N_{O_2} = 5.6$ mole/kg. Taking into account that each absorbed molecule of oxygen leads to consumption of one RH group, we obtain $[RH]_e =$ 5.6 mole/kg. Substituting $[RH]_e$ into expression (19) and taking into consideration the values of $[Z]$ and V_Z for both isotropic and oriented samples, we obtain $[RH]_{Z(\lambda=9)} = 28$ mole/kg and $[RH]_{Z(\lambda=0)} = 13$ mole/kg.

Determination of the concentration of [RO$_2^{\cdot}$] radicals

The concentration of radicals was determined with the use of the relationship $W_{O_2} = k_2 k_6^{-0.5} [RH] [RO_2^{\cdot}]$. In this case we assume that initiation of kinetic chains of oxidation is due to the presence of traces of hydroperoxide. Now we consider the data on PP oxidation at 80°C, $P_{O_2} = 600$ torr. In these conditions the rate of oxidation in PP $\lambda = 9$ and $\lambda = 0$ is equal to $2 \cdot 10^{-6}$ and $6 \cdot 10^{-6}$ (mole/kg), respectively. The k_2 value was obtained using the data from Table 2.3 in reference 1. At 80°C, this value is equal to 0.9 and 0.6 kg/mole·s for PP, $\lambda = 0$ and $\lambda = 9$, respectively. Hence the value of $[RO_2^{\cdot}] = 2.8 \cdot 10^{-7}$ and $1.4 \cdot 10^{-7}$ (mole/kg) shows that the orientation drawing does change the volume of the defected zone and its concentration; a consequence of this is a change in the values k_{2eff}, k_{6eff}, θ. The

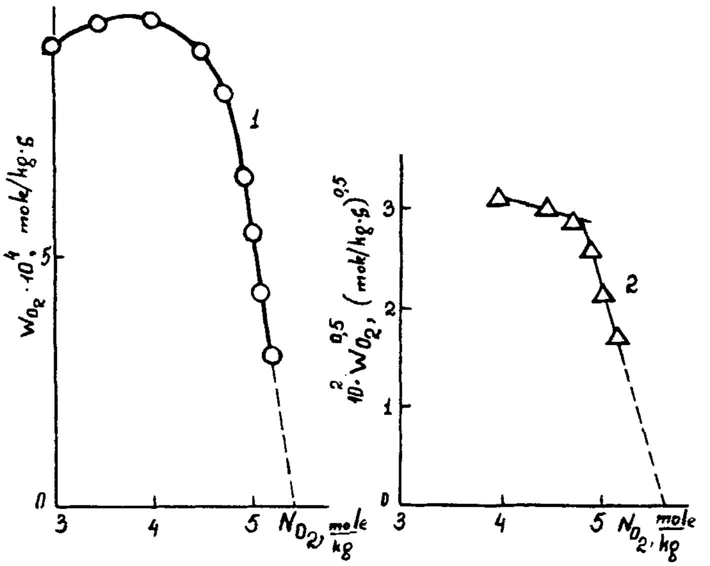

FIGURE 12 Dependence of the oxidation rate in the isotropic sample of PP on oxygen absorption (1), and linear anomorphous of this curve in coordinates $W_{O_2}^{0.5} = f(N_{O_2})$ (2).

values $k_{2\text{eff}}$, $k_{6\text{eff}}$ are reduced and θ is increased. Defected "zones" of the volume less than $9 \cdot 10^{-21}$ cm^3 is not taken into account in determining the above-mentioned constants, which substantially changes the relationship between certain parameters of oriented and isotropic samples.

In terms of the model described in this work the role of oriented drawing of the polymer is reduced to increasing isolation of reactive zones of the polymer from each other. This isolation is implemented by the chains in extremely straightened conformation, namely, interfibrillar transition chains, chains of possible "linear" systems,[25,26] extremely straightened intrafibrillar transition chains. Isolation of microreactors by these chains makes difficult the transition of free valance from one microreactor to another and increases the time of the presence of free valence in the zone. In this case extremely straightened chains play the role of membranes, preventing the transfer of free valence. At the stage of deep oxidation these chains involved in the oxidation process cease to play the role of semipermeable membranes for free valence and the effect of orientation is offset.

The role of the side substitute nature is that it determines the reactivity of the C – H bonds and, consequently, also determines the rate at which these membranes are destroyed. Besides, the nature of the side substitute determines the share of these membranes in the polymer and their permeability.

References

1. Yu, A. Shlyapnikov, S. G. Kiryushkin and A. P. Mar'in, Antioxidative Stabilization of Polymers, Chemistry, Moscow, pp. 50 – 99 (1986).
2. J. C. W. Chien and D. S. T. Wang, *Macromolecules*, **8**, 920 (1975).

3. N. Ya. Rapoport and G. Ye. Zaikov, *Uspehi Chemistry*, **52**, 1568 (1983).
4. A. A. Popov, N. Ya. Rapoport and G. Ye. Zaikov, Oxidation of Oriented and Strained Polymers, Chemistry, Moscow, pp. 86 - 130 (1987).
5. N. Ya. Rapoport, L. S. Shibryaeva and V. B. Miller, *Vysokomolek. Soed.*, **A25**, 831 (1983).
6. A. A. Popov, N. N. Blinov, B. E. Krisyuk, S. G. Korpova, A. N. Neverov and G. Ye. Zaikov, *Vysokomolek. Soed.*, **A23**, 1510 (1981).
7. R. J. Samuels, *J. Polymer. Sci. Part A*, **3**, 1741 (1965).
8. P. M. Pakhomov, M. Shermatov, V. B. Korsukov and V. S. Kuksenko, *Vysokomolek. Soed.*, **A18**, 132 (1976).
9. Yu. V. Kissin, *J. Polymer. Sci. A-2*, **21**, 2085 (1983).
10. Yu. V. Kissin, *Europ. Polymer. J.*, **8**, 487 (1972).
11. Yu. V. Kissin, *J. Polymer. Sci. A-2*, **21**, 2085 (1983).
12. O. V. Starzev, Yu. Vapirov, S. G. Kiryushkin and E. S. Torsueva, *Doklady Akad. Sci. USSR*, **280** 4), 946 (1985).
13. S. Yamada, Y. Konakahara and S. Kitahara, *Kobunci Kagaku*, **23**, 521 (1966).
14. J. Dechant, R. Danz, W. Kimmer and R. Schmolke, Ultrarotspektroskopische Untersuchungen an Polymeren, Akademie Verlag Berlin, pp. 127 - 233 (1972).
15. L. S. Shibryaeva, N. Ya. Rapoport and G. Ye. Zaikov, *Vysokomolek. Soed.*, **A28**, 1230 (1986).
16. V. L. Antonovskiy and M. M. Buzlanova, Analytical Chemistry of Organic Peroxy Compounds, Moscow, p. 254 (1978).
17. L. S. Shibryaeva and S. G. Kiryushkin, *Vysokomolek. Soed.*, **B29**, 113 (1987).
18. D. A. Frank-Kamenezkiy, Diffusion and Heat Transfer in the Chemical Kinetics, Moscow (1987).
19. I. I. Novak, V. I. Vettegren and S. P. Petrova, *Vysokomolek. Soed.*, **B9**, 403 (1967).
20. T. M. Birshtein and O. B. Ptizin, Conformations of Macromolecules, Moscow, p. 391 (1964).
21. V. A. Bershtein and V. M. Yegorov, *Vysokomolek. Soed.*, **A27**, 2440 (1985).
22. V. A. Bershtein, V. M. Yegorov and Yu. A. Yemel'yanov, *Vysokomolek. Soed.*, **A27**, 2451 (1985).
23. A. Peterlin, *J. Mater. Sci.*, **6**, 490 (1971).
24. V. A. Marikhin and L. P. Myasnikova, Overmolecular Structure of Polymers, Leningrad (1977).
25. Yu. A. Zubov, S. N. Chvalun, A. N. Ozerin, V. S. Shchirets, V. I. Selikhova, L. A. Ozerina, A. V. Chichagov, V. A. Aulov and N. F. Bakeev, *Vysokomolek. Soed.*, **A26**, 1766 (1984).
26. V. A. Aulov, Yu. A. Zubov and N. F. Bakeev, *Vysokomolek. Soed.*, **A27**, 1166 (1985).
27. N. Ya. Rapoport and V. B. Miller, *Vysokomolek. Soed.*, **A19**, 1534 (1977).
28. N. Ya. Rapoport and V. B. Miller, *Doklady Acad. Sci. USSR*, **227**(4), 911 (1976).
29. A. G. Sirota, Modification of Structure and Properties of Polyolefins, *Chemie*, Leningrad, p. 5 (1984).
30. Yu. A. Shlyapnikov, *Kinetics and Catalysis*, **19**, 503 (1978).
31. N. M. Livanova, A. P. Mar'in and Yu. A. Ershov, *Vysokomolek. Soed.*, **B18**, 410 (1976).
32. V. A. Marikhin, L. P. Myasnikova and N. L. Viktorova, *Vysokomolek. Soed.*, **A18**, 1302 (1976).
33. Yu. V. Kissin, Isospecific Polymerization of Olefins (with Heterogeneous Ziegler - Natta Catalysts), Springer-Verlag (1985).