External Effects on the Structure and Dynamics of Molecules in Oriented Polyolefins

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Oriented polyethylene samples are investigated mechanically, thermally and by oxidation. A complicated character of changes in mobility of molecules on static loading of oriented polyolefins is studied. The influence of deformation, stretching, molecular mass and its distribution on the value and sign of this change is found. The regularities of structural changes in the course of ozone oxidation are revealed. It is shown that the initial stage of oxidation is followed by a considerable improvement of mechanical properties. At a greater extent of oxidation the dependence of molecular mobility on reversible deformation of highly oriented samples of medium molecular weight (MW) and narrow molecular weight distribution (MWD) is reversed. A relaxational transition is observed over the temperature range of from 40°C to 60°C for polyethylene and from 60°C to 70°C for polypropylene. After ozone oxidation at a temperature above 90°C and oxidation under load and subsequent annealing (at the temperature of relaxational) transition the latter is not observed.

KEY WORDS Structure, molecular, dynamics, polyolefins.

INTRODUCTION

A study of the properties of oriented polymer fibers and films is an important task of applied physics of polymers since they find a wide application particularly at that state.

At present, particularly important are studies of the properties of oriented flexible chain polymers since they are most widely used commercially. Interest in these polymers is due to the fact that in recent years they have been used as source material for high-strength and high modular fibers and films. Since the polymer articles are subjected, as a rule, to mechanical stresses, temperature effects and oxidation, it is important to know the influence of these factors on the main properties of polymers. Physical and service properties of polymers, rates and mechanisms of chemical reactions are to a large degree functions of both relaxational properties of macromolecules and dynamics of low molecular weight additives. Therefore a comprehensive study of the dynamics of molecules in oriented polyolefins and determination of the main regularities of their changes as the polymers are subjected to different kinds of processing are important and urgent

problems of polymer physics and mechanics. Studies of this kind are necessary in developing theories for both degradation and stabilization of loaded polyolefins and in predicting their service life.

At present, there are two main techniques used for studying the dynamics of molecular motion: MMR and ESR spectroscopies. MMR spectroscopy permits the study of the dynamics of medium-scale motion of some areas of macromolecules at 10^4 Hz and above. ESR spectroscopy permits the study of small-scale motion of polymer chains (3–4 monomer links). Mobility of the polymer matrix and its alteration under various kinds of effects is closely associated with the polymer supermolecular structure. According to References 1–12 the polymer structure depends on the molecular weight, molecular weight distribution, amount of oriented stretching along with other factors. Investigations of polymer structure have demonstrated[13] that the highest share of ultimately straightened chains in polymers with relatively low molecular weight ($M_w \cong 40 \cdot 10^3$) accounts for approximately 10% of the number of chains proceeding from the crystals. The oriented stretching involves both an increase in the share of such chains[2–6,14] and a considerable change in the structure of the amorphous and crystalline areas that bring about a change in the physical, mechanical and dynamic properties of the polymer. While the structure and properties of oriented polyolefins have been studied extensively, the dynamics of molecular motion have not. Molecular motion in stressed polymers, has not been studied, nor have an influence of molecular weight, molecular weight distribution and amount and character of changes in mobility of molecules upon deformation been revealed. At present, NMR techniques have only been used to study the highly oriented polymer samples. As is shown in References 15–17 deformation of polypropylene samples is followed by an increase in molecular mobility, and deformation of polypropylene samples is followed by a decrease in molecular mobility. The studies of thermal effects and structural changes upon deformation have shown that the amount and sign of thermal effects and a decrease in density of amorphous areas depend on molecular weight parameters and degree of oriented stretching. Thus we may expect that the amount and character of changes in the mobility of molecules will be determined by molecular weight parameters and degree of oriented stretching.[18–19]

In the general case, the crystallites and amorphous areas in an oriented polymer are not in agreement with the minimum of free energy. The trend of the amorphous crystalline system toward the minimum of free energy is eased by annealing the polymer at a temperature below the melting point when macromolecules acquire sufficient mobility. Two conflicting processes influence the structure of amorphous areas on annealing: the trend of macromolecules in amorphous areas to chain conformation in a superchilled melt, generation of stresses in tie molecules and straightening of these as they are being drawn in a crystallite in the course of both crystallization of a partly molten compound and isothermic thickening of folded-chain crystals. According to Reference 20, quantitatively these two processes depend on the specific structure of amorphous areas and both on temperature and the state of annealing. For instance, in samples of narrow molecular weight distribution a partly molten compound is crystallized at the temperature of annealing. In these samples isothermic thickening is observed when the unstressed tie chains

and the molecules that have enriched the amorphous areas in the course of partial melting are being drawn in. In samples marked by a wide molecular weight distribution and containing numerous low molecular weight fractions there is no crystallization of a partly molten compound. The rate of isometric thickening is very small due to a high degree of tie chain straightening,[20] while in samples of narrow molecular weight distribution this rate is rather high since the tie chains are marked by a higher twist of conformation. Isometric changes in the longitudinal size of a crystallite in polyethylene[20] have indicated that at rather low annealing temperature the process of boundary melting prevails over the process of isometric thickening. At higher annealing temperature an increase in the crystallite longitudinal size noticeably exceeds a decrease in this size in the course of boundary melting. In isotropic samples of polyethylene and polypropylene a relaxational transition achieved by relaxational technique[21-28] is observed at 40–70°C. Some experiments[29-32] have indicated that in oriented polymers there is a relaxational transition within this temperature range. For example, within the temperature range of from −150°C to +50°C the highly oriented samples of polyethylene are characterized by high stability of structure (the polymer is marked by low negative linear thermal expansion coefficient and its only slightly depends on temperature). This coefficient is sharply increased over 50°C.[18] These regularities were also observed in high-modular fibers of polypropylene.[31-32] According to NMR data in oriented samples of polypropylene all amorphous phase chains are in highly elastic states at temperatures over 70°C. Within 40°–60°C there is a break of the curve showing the dependence of specific heat and parameters of the oriented polyethylene lattice on temperature which, according to Reference 30 is probably due to excitation of lateral flexural vibrations of molecules in the crystal. "Defreezing" of mobility in crystalline areas is also attested to by the results of structural studies of polyethylene.[28,29] Thus, the analysis of the reports show that annealing of both isotropic and oriented polyethylenes brings about a complex structural rearrangement followed by a change in the structural and dynamic states of the polymer matrix. Formation and crystallization of the partly molten compound, isothermic thickening of crystals and defreezing of mobility in the structures made up ultimately of tie straightened chains, all influence in a complicated way the dynamic state of a polymer matrix. Influences of this kind have not yet been studied.

No prediction of service life of polymer articles can be made and no optimal ways of polymer stabilization can be found without knowledge of the influence of oxidation on the structure and dynamics of a polymer matrix and mainly of the amorphous phase because oxidation takes place predominantly at these particular areas.[33] The rate and extent of polymer oxidation is largely determined by the mobility of molecules.[34] The structure also has a decisive effect on the oxidative properties of the polymer. Density of amorphous areas and a decrease in the molecule mobility as in the case of oriented stretching leads to significant changes in oxidation properties.[35] There is practically no information on the influence of ozone oxidation on the polymer properties.

Dynamics of molecules in variously stretched samples as a function of molecular weight and molecular weight distribution.

Polymers have the following molecular characteristics:

	PE-1	PE-2	PE-3	PE-4	PP-1	PP-2
$M_w \cdot 10^5$	1.47	3.00	0.40	70.00	1.30	3.00
M_w/M_n	2	10	2	2	2	10

Let us consider the influence of MW and MWD on the dynamics of a slightly stretched molecule λ. As is seen in Figure 1 the largest values τ_c that are characteristic of rotary mobility of spines (which in turn provides information about molecular mobility in amorphous parts of the polymer) are observed in samples with a relatively high share of low molecular weight fractions (PE-2, PE-3, PP-2) that is evidence of the highest retardation of macromolecules in these samples. A distinctive feature of these polymers is that in the course of oriented stretching, we can observe a slight change in such structural and dynamic parameters as density ρ_a, orientation Δn, crystallinity æ, modulus of elasticity E, and correlation time τ_c, while the oriented stretching of samples with medium MW and narrow MWD (PE-1, PP-1) leads to a significant increase in parameters reported elsewhere in this paper. Based on these data a conclusion may be drawn that samples of PE-2, PE-3 and PP-2 with small values of stretching λ, assume a fairly perfect form of fibrillar structure with very good mechanical properties and further oriented stretching does not bring much improvement to it, which is probably due to the presence of low molecular weight fractions. In samples of PE-1, PE-4 and PP-1, the fibrillar structure is improved in the course of oriented stretching (Figures 1, 2) (see Table I). Thus, the investigation into various types of PE and PP has shown that different supermolecular structures determined largely by molecular parameters (MW, MWD) are responsible for different behavior in the course of oriented stretching. So we
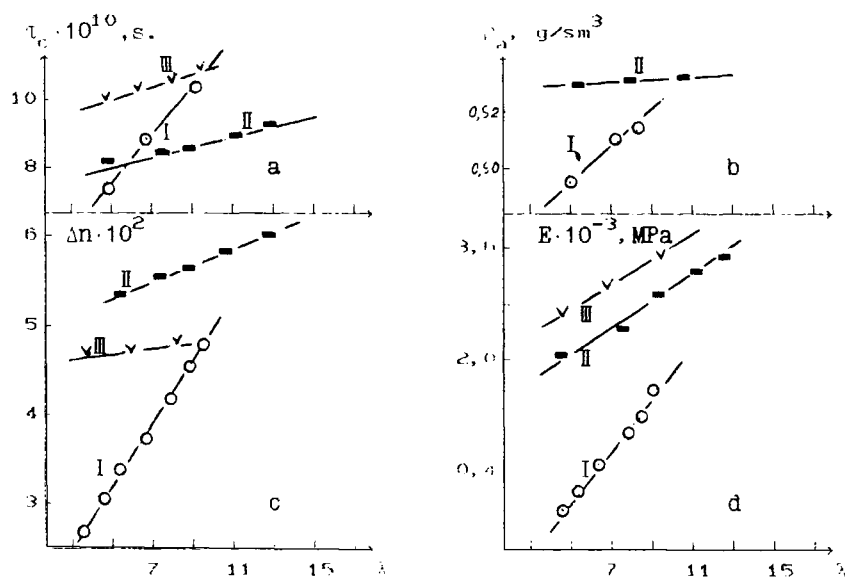

FIGURE 1   Dependence of (a) τ_c, (b) ρ_a, (c) Δn, and (d) E on λ for (I) PE-1, (II) PE-2, and (III) PE-3.
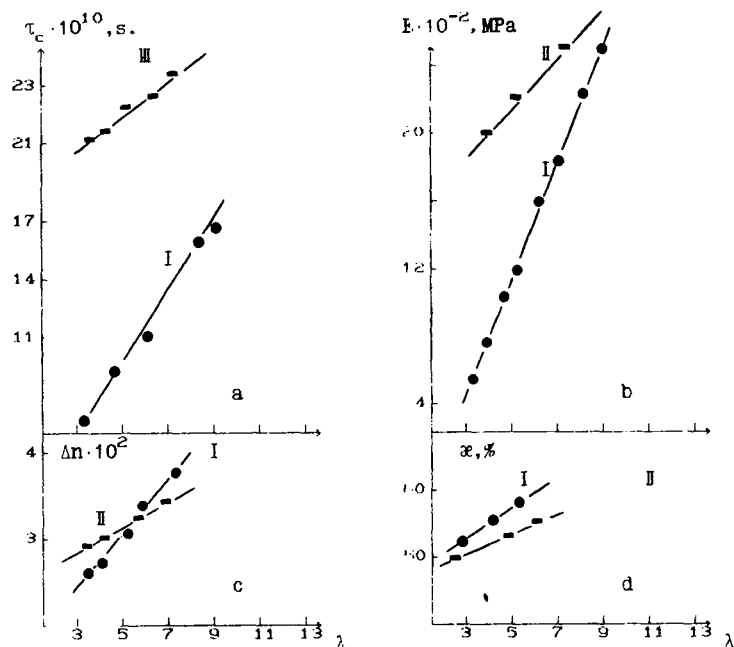
FIGURE 2 Dependence of (a) τ_c, (b) E, (c) Δn, and (d) æ on λ for (I) PP-1 and (II) PP-2.

TABLE I

Structure and dynamic parameters of polyolefins

Polymer	λ	Δn	ρ g/sm^3	ρ_a g/sm^3	τ_c 10^{10} s	E kg/mm^2	æ
PE-1	5	3.3	0.954	0.900	7.3	55	0.648
	7.5	3.9	0.955	0.904	8.8	95	0.656
	10	4.8	0.956	0.914	10.5	145	0.670
PE-2	6	5.2	0.963	0.926	8.6	280	0.670
	13	5.3	0.963	0.927	9.0	400	0.680
PE-3	5	4.0	0.966	0.862	10.0	310	0.720
	10	4.0	0.966	0.863	10.6	390	0.720
PE-4	3.5	3.1	0.937	0.857	9.5	40	0.480
	5	3.1	0.937	0.857	9.5	40	0.480
PP-1	4	2.8			8.8	75	0.600
	7	3.1			12.0	120	0.680
	14	3.8			127.0	300	0.750
PP-2	5	3.0			22.5	220	0.650
	7	3.1			23.5	290	0.740
	10	3.3			24.8		0.740

may expect that reversible deformation of the reported polymers will be marked by different regularities.

Investigation of the molecular structure and molecular motion dynamics in oriented polymers under load

Let us consider some changes in the mobility of molecules in polymers under deformation. We shall consider a relationship between τ_c and ε for PE-1 (with

narrow MWD and medium MW) with different stretching values λ. In this case we can observe the following regularities (Figure 3a). Reversible deformation of samples with low stretching value λ is followed by an increase in molecular mobility. When the stretching value is equal to eight the inversion and deformation takes place and if it is greater than eight mobility will be restrained. Similar regularities can be ascribed to PP-1 (Figure 3b).

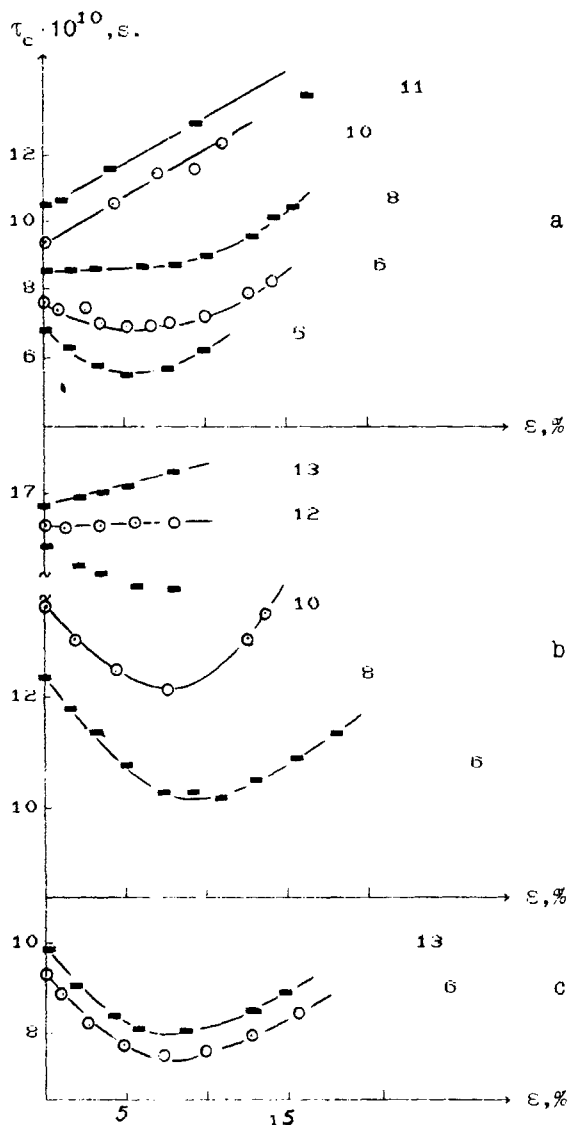The presence of low molecular weight fractions in samples of PE-2, PE-3 and

FIGURE 3 Dependence of τ_c on ε for (a) PE-1, (b) PP-1, and (c) PE-2 (figures at the curves show a degree of stretching).

PP-2 is responsible for their following behavior under load. Regardless of the extent of oriented stretching, the reversible deformation is followed by an increase in molecular mobility. When ε is greater than 5–6%, the inversion occurs and further stretching leads to an increase in τ_c, which points to a reduction in mobility (Figure 3b). In samples of PP the inversion is ensured by ε greater than 10–11%.

The experiments on film stretching in three states of loading (σ, ε-const., and stepwise loading) have demonstrated that a decisive factor that affects molecular mobility is deformation, and consequently the structural changes in amorphous areas. The information on structural changes is based on X-ray analysis data. From these data it follows that the density of amorphous areas decreases in the course of reversible stretching (Figure 4). The relationship between τ_c and ε, on the one hand, and ρ_a and ε, on the other, reveals first of all a symbatic of τ_c and ρ_a which indicates that a decrease in density of amorphous areas has a decisive effect on molecular dynamics. This conclusion is confirmed by calculation of changes in free volumes, ΔV_{τ_c} and ΔV_{ρ_a}, from the data on τ_c and ρ_a and the results are presented in Table II. The values of ΔV_Q calculated from data derived by using the deformation calorimetry technique are also presented in Table II. This technique was employed for better understanding of the processes that take place in the course of deformation. The investigations have indicated[18] that elastic deformations of slightly stretched polyolefins produce endoeffects due to a decrease in density of amorphous areas. Deformation of highly oriented samples is followed by exoeffects. Changes in free volume were estimated on the basis of data on Q by the following formula[36]:

$$Q = \frac{\Delta V \alpha_v}{V_0 B_v} T \varepsilon$$

where B_v is an isothermic modulus of compression and α_v is a coefficient of thermal expansion.

The estimation of changes in free volume by data on τ_c is conducted by using a free volume equation $\tau_c = A_{\exp}(\Delta V^*/V)$, where A is constant, ΔV^* is the activation volume and V is the free fluctuation volume.

The values ΔV_{τ_c}, ΔV_{ρ_a} and ΔV_Q, which are only slightly different, indicate that an increase in intensities of molecular motion are basically due to an increase in free fluctuation volume in amorphous areas. It is significant that the activation of molecular mobility decreases in density and endoeffects are observed in PE only at 5–6% and in PP at 10–11% irrespective of MW, MWD and λ. The following regularities have also been noted. An increase in MW and oriented stretching leads to a decrease in the effect of molecular mobility on elastic deformation (Table III).

The calculations reported in Reference 20 make it possible to estimate the share of straightened chains in amorphous areas upon elastic deformations. They have made it possible to discover that the elastic deformation is followed by an increase in the mass of amorphous areas. These processes are intensified with an increase in λ and MW which reduces the effect of the decrease in density of the amorphous areas, and consequently the dependence of molecular mobility on ε. In this case an increase in mass is a result of an increase in the share of tightly packed chains.
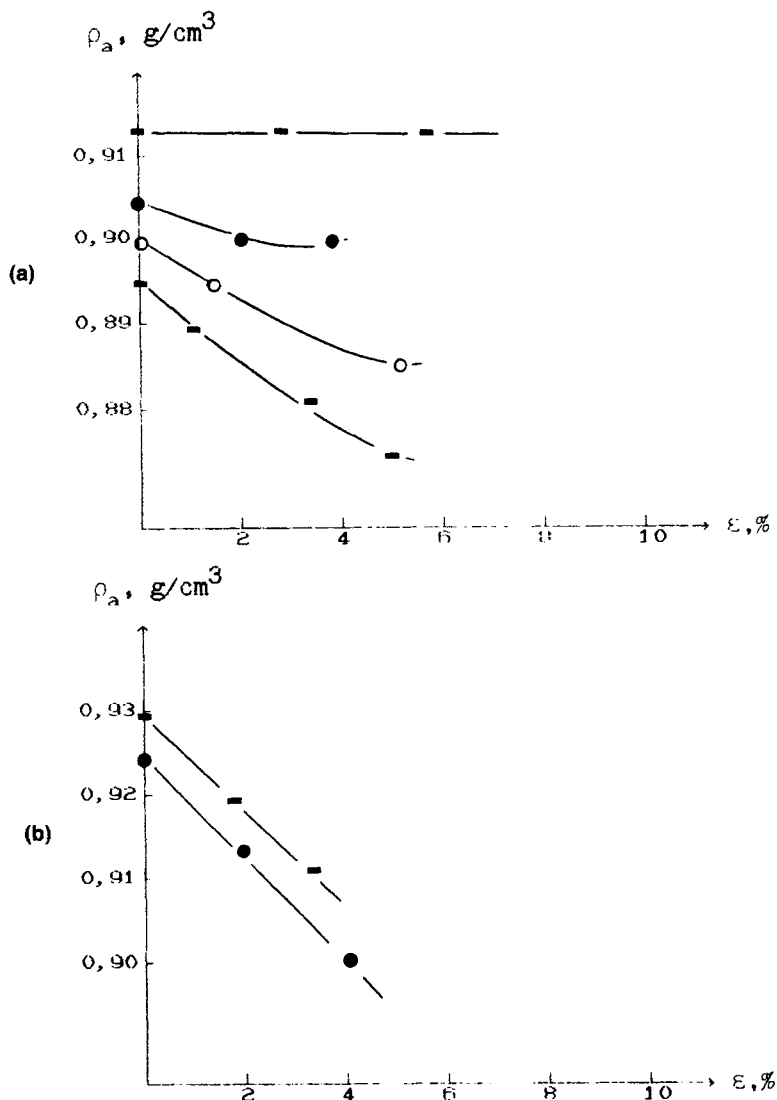
FIGURE 4   Dependence of ρ_a on ε for (a) PE-1 and (b) PE-2.

Therefore, the results can be interpreted as follows. As the value of λ in samples of PE-1, PE-4 and PP-1 is increased, the share of ultimately straightened chains is also increased which is confirmed by an increase in the crystallite skewness angle.[1] The presence of these particular chains is responsible for the fact that elastic deformations involve not only drawing apart the crystallites and decrease in density in the interfibrillar amorphous areas, but also reversible shear deformations of the crystals and penetration of crystalline areas into amorphous areas. An increase in λ and MW brings about intensification of these processes due to an increase in the share of ultimately straightened chains. The following factors make one believe that elastic shear deformations of crystals limit the area of elastic deformation. The

TABLE II

The values ΔV_{τ_c}, ΔV_{ρ_a} and ΔV_Q corresponds to ε greater than 2%.

	ΔV_{τ_c} cm³/mol			ΔV_{ρ_a} cm³/mol			ΔV_Q cm³/mol		
λ	PE-1	PE-1	PP-1	PE-1	PE-2	PP-1	PE-1	PE-2	PP-1
6	0.25	0.38	0.13	0.27	0.40	0.17	0.24	0.50	0.20
8	0	0.17	0.12	0.17	0.30	0.12	0	—	—
10	−0.06	—	—	0.10	—	—	—	—	—
13	—	0.12	0.10	—	0.20	0	−0.88	—	—

TABLE III

Parameters of $\Delta\tau_c/\Delta\varepsilon$ (ε is greater than 2%) $\Delta\tau_c/\Delta\varepsilon \cdot 10^{10}$ c

Polymer λ	PE-3	PE-2	PE-1	PE-4	PP-1	PP-2
7	75.5	70.0	50.0	0	30.0	130.0
8	50.0	55.0	0	—	15.0	100.0
10	35.0	35.0	−0.02	—	—	60.0
13	—	—	—	—	−10.0	42.0

period of identity in PP is 1.5 times as large as it is in PE and the same relationship is noted between these polymers in respect to the area of elastic deformation. It is also noted that inversion takes place when ε is approximately 5–6% in PE and 10–11% in PP irrespective of MW, MWD and λ.

Thus, in contrast to oriented stretching the elastic deformation in most cases results in an increase in the mobility of molecules and is determined by MW, MWD and λ.

The effect of ozone oxidation on the structure and dynamics of the molecules in oriented polyolefins

The oriented samples are subjected to ozone-oxygen action where the concentration of ozone [O_3] is $7 \cdot 10^{-4}$ mol/l. The investigation of molecule dynamics of ozonated samples demonstrates that the stiffness of amorphous areas is significantly increased in the course of ozonation, and when D (reduced optical density of carbonyl groups) is approximately 0.12 ($t = 2h$) there is a break on the τ_c versus D curve. It is significant that within the first two hours of oxidation the modulus of elasticity grows and orientation improves (Figure 5). It is known that the polar oxygen-containing groups are accumulated in the course of oxidation and the stiffness of the polymer matrix is increased. On the other hand, the degradation that takes place upon oxidation gives rise to greater mobility of degradated chains. Therefore, it can be supposed that at the first stage of oxidation the stronger intermolecular interactions in the form of mechanical "sewing" prevail, while after two hours of the oxidation process the degradative processes become predominant. The mechanical properties are probably affected by further spontaneous orientation (Figure 5). According to Reference 38 chemical "sewing" is almost not observed. The intensive degradation after two hours of the oxidation process is confirmed by a
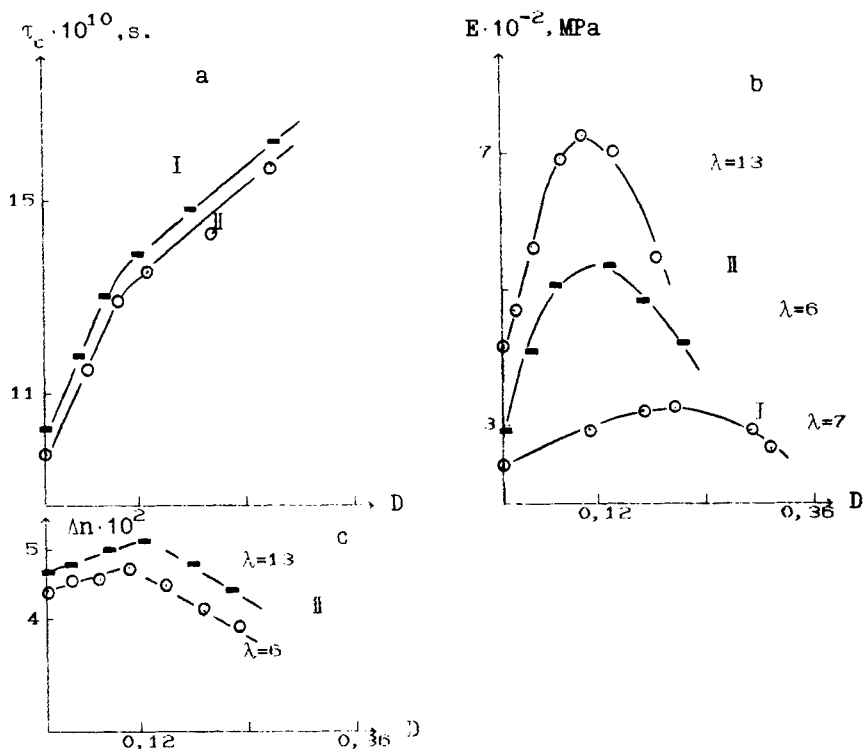
FIGURE 5   Dependence of (a) τ_c, (b) E, and (c) Δn on degree of oxidation of D for (I) PE-1 and (II) PE-2.

sharp decrease in orientation and in the modulus of elasticity E. It should be mentioned that the effect produced by an increase in the modulus of elasticity is most conspicuous in PE-2 and PP-2 (with broad MWD). These results can be explained as follows. The thermodynamic analysis of crystallization and segregation of molecules shows[39] that highly straightened chains are segregated or crystallized through the mechanism of the straightening of macromolecules. While polymers are being prepared, certain parts of the chains are in thermodynamically non-equilibrium states. A reduction of steric obstacles and an increase in mobility of destroyed molecules in the course of ozone oxidation favor transition of the polymer system into a better equilibrium thermodynamic state. In this case the structure consisting of straightened chains becomes more perfect. In PE-2 and PP-2 the share of straightened chains is very high according to the data about their modulus of elasticity, orientation, amorphous area density, and correlation time. In this case the structure improvement is more conspicuous.

Molecular dynamics in oxidized polymers in the course of stretching

It has been demonstrated earlier that elastic deformation of the parent nonoxidized samples supplies more mobility to molecules in all samples except relatively low-stretched PE-1 and PP-1 in which stretching is followed by a decrease in mobility.

Figure 6 shows a plot where τ_c is a function of deformation of preoxidized PE-1 where the values of λ are 6 and 10. It can be seen that ozone oxidation leads to greater dependence of molecular mobility on deformation at $\lambda = 6$. Ozonation of samples where λ is equal to 10 leads to a change in relationship, and deformation results in an increase in mobility instead of its decrease. Similar regularities are observed in PP-1. It is remarkable that in samples with broad MWD there is no noticeable increase in dependence of τ_c on deformation after ozonation. In Figure 7 the plot of relative change in the τ_c/τ_{c_0} ratio is shown where the value of τ_c is normalized to τ_{c_0} at $\varepsilon = 0\%$ on deformation by 1%. It is notable that irrespective of oxidation in all cases molecular mobility increases only up to $\varepsilon = 6-7\%$ in PE and 10-11% in PP, which is an additional argument for the assumption that the elastic shear deformation of crystallites by the amount of elastic macrodeformation of the polymer is a decisive factor.

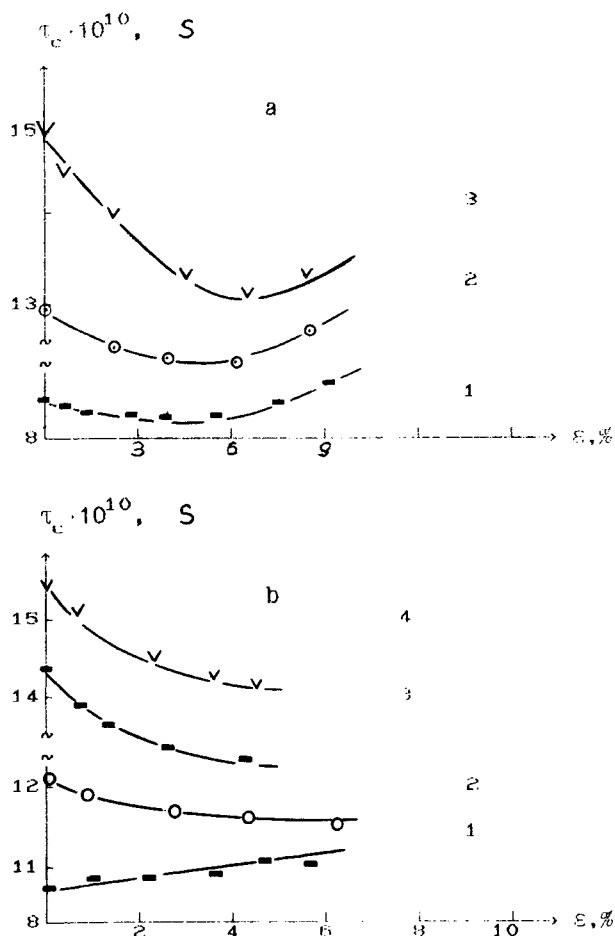As has already been shown, an increase in molecular mobility in the course of

FIGURE 6   Dependence of τ_c on E for (a) PE-1 $\lambda \approx 6$, (1) initial, (2) after 1.5 hours of oxidation, (3) after 2.5 hours of oxidation and (4) after 3 hours of oxidation.
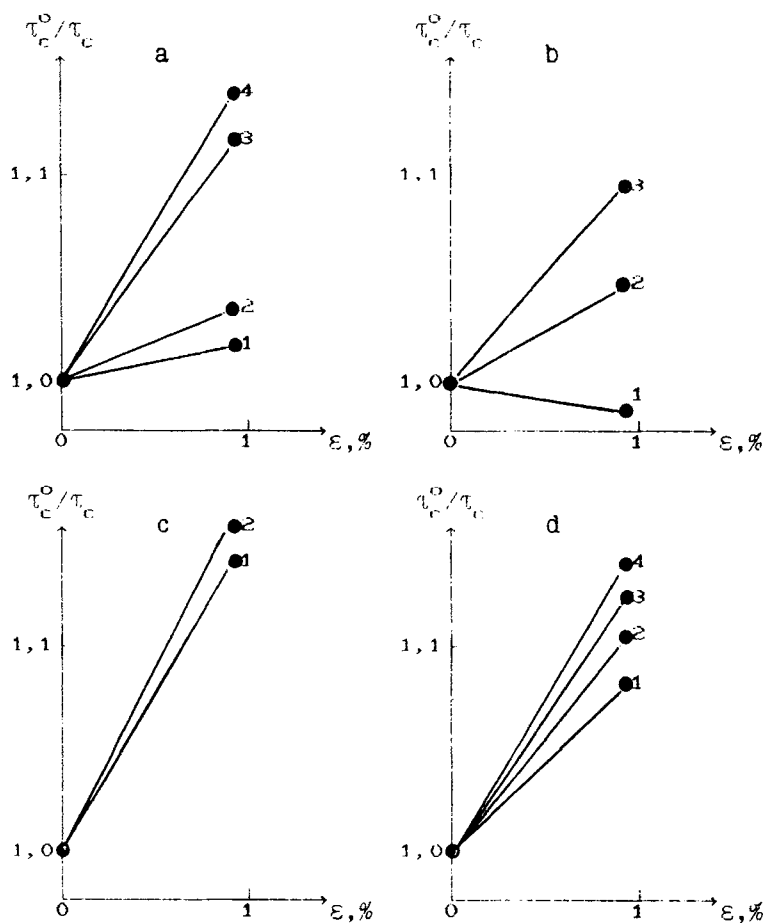
FIGURE 7   Dependence of τ_c^o/τ_c on ε for oxidized samples of (a), (b) PE-1 and (c), (d) PE-2. (The degree of oxidation is increased from one to four.)

elastic deformation of nonoxidized samples is largely due to a decrease in density of amorphous areas. In this case deformation is followed by an increase in the mass of amorphous areas which is responsible for a smaller change in density and consequently in mobility as compared with theoretical data calculated by formula where the mass of amorphous areas is assumed to be constant upon deformation. Recall that the greatest change in the mass of amorphous areas is observed in PE-1 and PP-1. It has been suggested that ultimately straightened chains favor the penetration of crystallite areas into amorphous areas and it makes for an increase in the mass of amorphous areas. As is known from Reference 40, it is the stressed chains that are the first to be oxidized and destroyed by ozone. It leads to weakening of the processes that involve penetration of crystalline areas into amorphous areas, and consequently to amplification of the effect of a decrease in density of amorphous areas as well as to an increase in mobility in the course of elastic deformation of polymers (Figure 6).

Ozone oxidation of stressed polymers

Figure 8 shows the relationship between crystallinity æ and oxidation D in loaded (1) and unloaded (2) oxidized samples in which λ is equal to six. It is seen from the figure that in samples (1), crystallinity is increased over the whole D range while in samples (2), crystallinity is increased only at the initial stage of oxidation. Orientation also varies in a similar way, which points to structural rearrangements in the polymer. In rather highly stretched samples ($\lambda = 11$) the regularities show up differently (Figure 9). Crystallinity in samples (1) and (2) is increased only at the initial stage of oxidation, while at deeper stages crystallinity is decreased. Additional information on structural changes in the course of ozone oxidation are supplied by melting curves (Figure 10). There are two tendencies in the process: changes in the peak intensity and in the shape of the melting curve at its low-temperature part. An increase in the peak shows that the newly formed crystal phase resembles the previous one while the shoulder that appears on the curve points to the presence of the phase whose properties are different. To analyze changes in melting curves their heights were superimposed in each particular case. In samples where λ is equal to six an increase in melting intensity peak is observed over the whole range of oxidation time. Melting intensity in samples where λ is equal to 11 (Figure 10b, curves 6–11) is only slightly changed in a complicated way. Oxidation of films where λ is equal to six is followed by the appearance of a shoulder and its intensity grows to merge with the basic peak to form a broadened line (curve 5). An opposite picture is observed in samples where λ is equal to 11. The shoulder intensity is decreased in the course of oxidation and it is broadened with temperature. In this case the basic melting peak is narrowed. These results and regularities can be explained as follows. One of the factors that brings about a growth of crystallinity of loaded and unloaded samples during their oxidation by
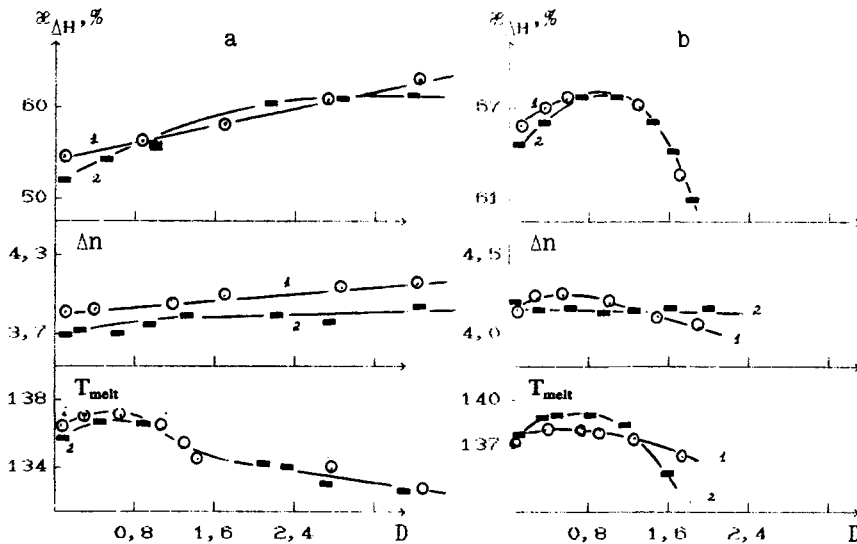

FIGURE 8 Dependence of $æ_{\Delta H}$, Δn, T_{melt} on the degree of oxidation of D for samples of PE-1 with (a) $\lambda = 6$ and (b) $= \lambda$; (1) oxidized under load, (2) oxidized under no load.
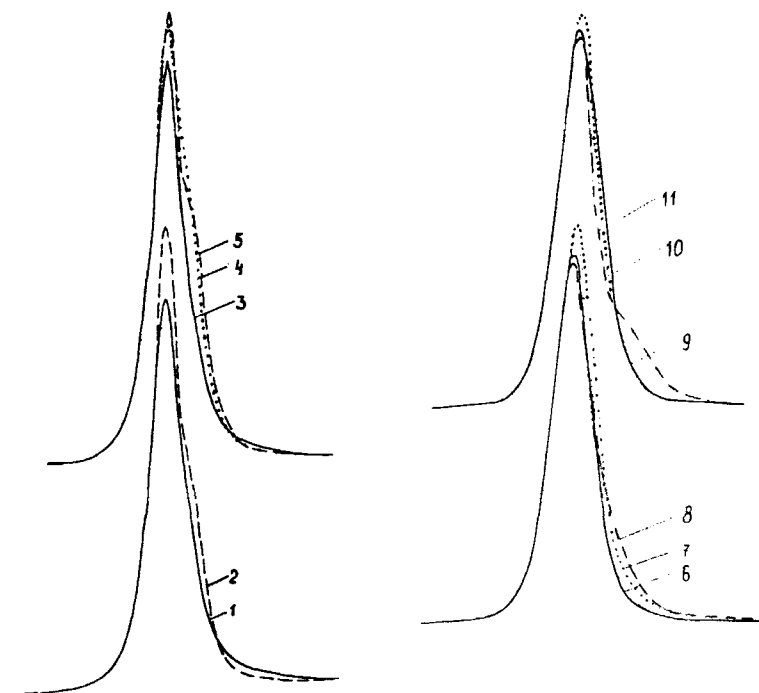
FIGURE 9   Melting curves for samples at various oxidation times. $\lambda \approx 6$ (1.22, 3, 4.5), $\lambda \approx 11$ (6–11), $\varepsilon \approx 0\%$ (1, 2, 6–8), $\varepsilon \approx 10\%$ (3–5, 9–11), oxidation time (hours) - 0 (1, 3, 6, 9), 2 (10), 5 (7), 10 (2, 4, 8, 11), 11 (5).

ozone is further crystallization of crystallite end faces due to the break of folds as probably the most overstressed parts of the chain.[41] Oxidation in unloaded samples occurs mainly at the areas where a decrease in density is the greatest and therefore it results in no increase in crystallinity in the course of relatively deep oxidation, while among loaded samples there is a fairly great number of stressed chains with high oxidation rates.[40] In this case the structure consisting of straightened and stressed chains improve the order of their arrangement due to partial chain destruction, moderation of steric obstacles, and strengthening of intermolecular interactions that provide further contribution into crystallization. The nonequilibrium state of the structure is more and more increased with an increase in oriented stretching (the case mostly typical for PE-1 and PE-4). It is indicated by an increase in the crystallite angle skewness.[1] Therefore, ozone oxidation is a kind of chemical annealing when the structure passes into a higher equilibrium state with a lower value of λ. It is also indicated by a decrease in the range of from 300 Å to 275 Å that corresponds to samples with $\lambda = 7$. In this case crystallinity also decreases but at the initial stage of oxidation when the share of the destroyed chains is small the process of further crystallization is dominant. It should also be noted that in all cases the crystallite melting temperature increased at the initial stage of oxidation, which points to the improvement of three-dimensional crystals in the course of weak oxidation.
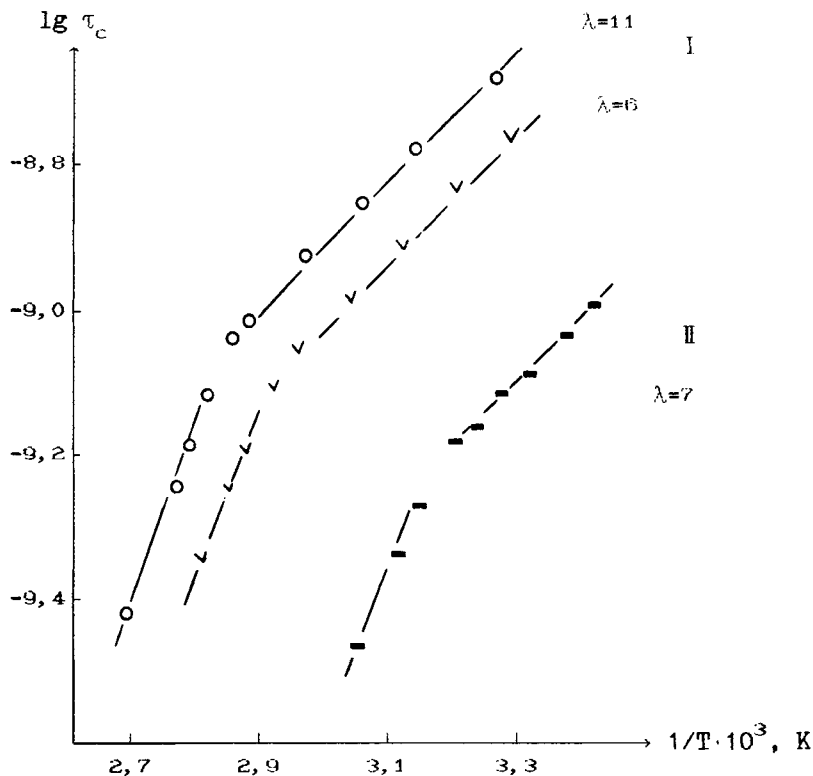
FIGURE 10 Temperature dependence of τ_c for (I) PP-1 and (II) PE-1.

Thermal effects on physical and mechanical properties and molecular dynamics

Figure 11 shows the relationship between temperature and τ_c in PE-1 and PP-1. The curves show the breaks over the range of from 40°C to 60°C for PE and 60°C to 70°C for PP. The activation temperature U over the lower temperature range in both PE and PP with λ equal to 6 and 10 amounts to approximately 20–21 kJ/mol and it is approximately 41–42 kJ/mol over the higher temperature range, which is in good agreement with References 42 and 43. "Normal" values of pre-exponential factor τ_0 before break are 10^{-12}–10^{-13} c, while at higher temperatures τ_0 is greater than 10^{-12} c and it sharply differs from the "normal" values. Besides, the value τ_0, is in linear relationship with activation energy, i.e., there is a sort of compensation. It points to the fact that after the break in τ_0 the activation energies become effective. A distinctive feature of these polymers is that there is a break of the curve showing the dependence of the modulus of elasticity on temperature over the same temperature range (Figure 12).

The observed peculiarities can be explained by taking into account a change in the activation barrier with an increase in temperature. Without going into detail, we will only point to the fact that both activation energy U and the value τ_0 depend
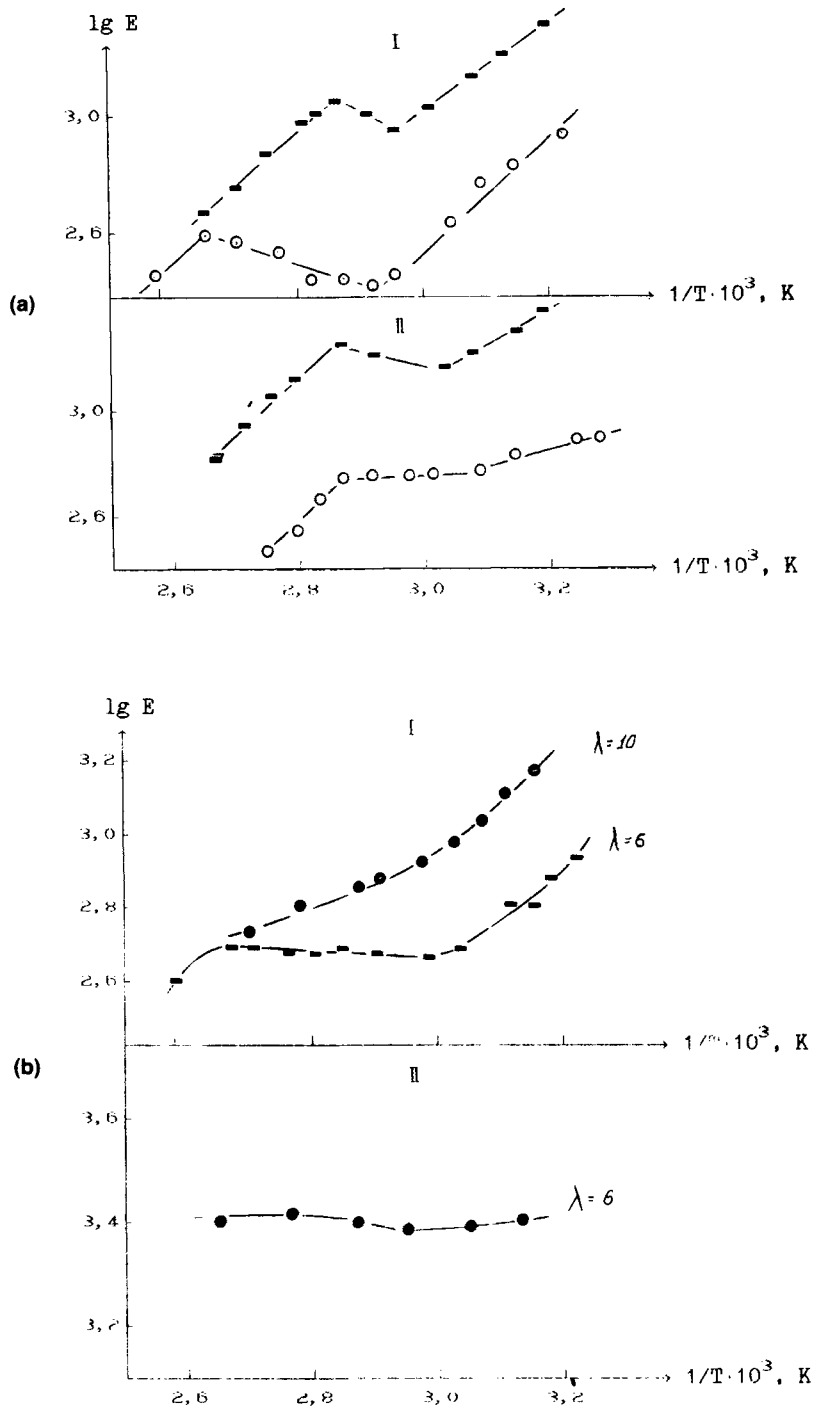
FIGURE 11   Temperature dependence of the modulus of elasticity E for (a) (I) PP-1, (II) PP-2 and (b) (I) PE-1, (II) PE-2.
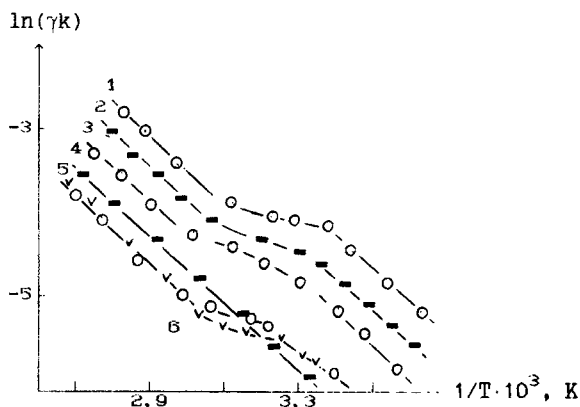
FIGURE 12   Temperature dependence of γk for high-density PE (1) $\lambda \approx 1$, (2) 10, (3) $\lambda \approx 10$ after annealing at 96°C, (4) $\lambda \approx 10$ after ozonation at 50°C, (5) $\lambda = 10$ after ozonation at 30°C.

on the thermal expansion coefficient α in the following way[44]:

$$U_{exp.} = U_{true} (1 + \alpha T_{vitr.}),$$

$$\tau_{0\ exp.} = \tau_{true} + \frac{U_{true}}{R} \alpha$$

where U_{true} and τ_{true} are the values of vitrification temperature, $T_{vitr.}$, and $U_{exp.}$ and $\tau_{0\ exp.}$ are experimental values. Calorimetric and X-ray structural investigations show[18-32] that it is above the temperature range of from 40°C to 60°C that the net capacity and coefficient α suffers a jump which probably is reflected by a jump on the curve constructed as a function of temperature. Some authors believe that this jump is caused by "defreezing" of bending vibrations in crystalline areas.[30] There is an opinion that chain mobility is defrozen on the crystal surface just at these temperatures.[27] It should be noted that thermal annealing gives rise to structural rearrangements. In the general case crystallites and amorphous areas tend to relax into the state of overchilled melt, while the crystallites tend to the minimum of free energy by changing their size (chiefly the longitudinal one). At sufficiently low annealing temperatures, the process of boundary melting dominates over the process of crystal thickening. It is also known[20] that in the course of crystallite refinement the chains may be drawn from the amorphous areas into the crystallites, which results in an increase in the share of straightened chains in amorphous areas. It is possible that these processes are responsible for an increase in the modulus of elasticity at the areas of elevated temperature (Figure 11).

Thermal annealing under ozone

The rate of interaction between high-density PE and ozone V_{O_3} is measured against adsorption of ozone whose concentration is 10^{-5} mol/l. Parameter γk is determined from the reaction rate

$$V_{O_3} = \gamma k\ [O_3][PH]$$

where γ is the coefficient of ozone solubility in polymer, k is the reaction rate constant, $[O_3]$ is the concentration of ozone in the gas phase, and PH is the concentration of monomer chains in polymer.

Figure 12 shows the plot for isotropic (1) and oriented ($\lambda = 10$) samples where γk parameter is presented as a function of temperature. Maximum oxidation of these samples is $9.42 \cdot 10^{-2}$ mol/kg or 0.13%. The following regularities are observed. For both isotropic and oriented samples the Arrhenius curve shows a break over the range of from 40°C to 60°C. Numerous facts cited previously point to the fact that in this temperature range there is a relaxational transition, and complicated structural rearrangement takes place probably due to defreezing of both end face surfaces of crystallites and dense areas in amorphous phase.

Let us consider the influence of preliminary thermal annealing on the rate of ozone oxidation and the character of its dependence on temperature. The samples were annealed at approximately 96°C (curve 3). The data that follow show that the oxidation rate decreases both in low-temperature and high-temperature fields but the temperature-dependent curve remains the same; the break of the curve occurs in the range of from 40°C to 60°C.

The rate of reaction between high-density PE and ozone.

$$V_{O_3} \cdot 10^{-5} \text{ mol/sec}$$

T	1	2	3	4	5	6
35°C	0.79	0.53	0.37	0.14	0.19	0.14
97°C	5.60	3.60	2.36	1.92	1.45	1.92

The samples were previously oxidized at 30°C and 50°C and the degree of oxidation D was approximately 0.2. As is seen from Figure 12, curves 5 and 6 show the character of temperature dependence as it looked previously. The oxidation rate was reduced by 2–3 times as compared to the initial rate (2).

Let us consider the influence of preliminary chemical annealing at relatively high temperatures 95°C (curve 4) with $D \approx 0.2$. In this case the curve constructed as a function of temperature has changed over the entire temperature range and is linear without breaks.

These results can be explained as follows. We assume that relaxational transition in the range of from 40°C to 60°C is due to "defreezing" of both end face surfaces of crystallites and most dense areas in the amorphous phase because of their being highly defective. Observing the process of "defreezing," we might expect that the structure of the crystallite surface will pass into a more equilibrium and ordered state and the "defreezing" temperature will be higher. But experimentally this is not corroborated. It looks as if the structure of the end face crystallite surfaces is not ordered since it is prevented by the tie straightened chains. The oxidation rate and destruction of such chains at relatively low temperatures is small and therefore the chemical annealing does not lead to a substantial change in the structure. It is known[45] that at 95°C the mobility of the crystalline areas is "defrozen." Based on this information, we might suppose that at 95°C the crystallites are rearranged and the chains are partly drawn from the amorphous areas into the crystallites. The tie

straightened chains are getting stressed, which increases by several times the destruction rate of these chains. In this case the obstacles that preclude ordered and regular layout of the crystallite end face surfaces are eliminated and the "defreezing" temperature at these areas is increased with no relaxational transition over the range of from 40°C to 60°C (Figure 12, curve 4). The following experiment was carried out in support of this hypothesis. The samples were ozonized under load to accelerate destruction of tie straightened chains. Then the samples were annealed at the temperature of relaxational transition in order that the structure be brought to equilibrium. As a result the oxidation rate versus the temperature curve becomes linear without breaks.

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