

Variation of Inhibited Oxidation Parameters in Polyethylene Melting

Yury A. Shlyapnikov,* Natalya N. Kolesnikova

Institute of Biochemical Physics, Russia Academy of Sciences, 119991 Moscow, Russia

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ABSTRACT: The oxidation of low-density polyethylene by molecular oxygen was studied in the temperature range 80–210°C. In the curves of temperature dependence of several parameters of inhibited oxidation, breaks were observed at the melting temperature, near 110°C. At this temperature, the pre-exponential factor calculated from the temperature dependence of the rate constant of inhibitor consumption changed 105 times, sharply increasing at the transition from the polymer

melt to the solid polymer. This indicated that an essential difference existed between the properties of the intercrystalline amorphous polymeric substance and the completely molten one. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 978–981, 2006

Key words: polyethylene; melting point; antioxidants; phase behavior; crystallization

Polymeric substances differ from their low-molecular analogs in several ways, the most essential for the investigation of polymer oxidation processes are the virtual zero pressure of the polymer vapors and the combination of an extremely low transition mobility of their macromolecules and a high vibrational mobility. Polymer melting proceeds in relatively wide temperature range in which the amorphous substance coexists with the crystalline one. It was interesting to compare this intercrystalline amorphous substance with completely the molten polymeric one.

In this study, we used the simplest polymer, low-density polyethylene. As the method of investigation, we used the inhibited oxidation of the polymer in the temperature range 80–210°C, which included the melting temperature of this polymer (110°C). The antioxidant was 2,2'-methylene-bis(4-methyl-6-methylcyclohexylphenol) (MBP). A relatively high molecular mass of this antioxidant decreased the role of antioxidant evaporation in the course of oxidation. On the other hand, difficulties in the quantitative extraction of this heavy antioxidant caused us to use an indirect method to calculate the rate constants of antioxidant consumption from the concentration dependence of the induction period of inhibited oxidation.

In polymeric substances, there is a substantial increase in the role of the cage effect compared to that in their low-molecular analogs, which results in a decrease in the yield of hydroperoxides from approximately 100% in

hydrocarbons to 5–30% in polyolefins.^{1,2} The irregularities in polymer chain arrangement in the polymers are stable and may be considered the second component dissolved in the polymeric substance.³ In crystalline polymers below their melting temperatures, crystalline structures appear, whose contents increase with decreasing temperature. In some cases, these structures behave as free-radical traps (more correctly, traps for free valences). It was interesting to examine whether the intercrystalline amorphous substance differed in its properties from the same substance in a completely molten polymer.

The main steps of hydrocarbon polymer oxidation are analogous to those of low-molecular hydrocarbons:



However, in the second step, $RO_2\cdot + RH$, we see a marked difference. When the polymer is in the liquid state, molecular motion rapidly separates the primary products of this reaction, and nearly all of the hydroperoxide groups formed are preserved. In polymers, these products are either neighboring groups of the same macromolecule or are present on neighboring molecules. In both cases, these groups are for a long time situated aside and interact with high probability, for example, as



As a result, the yield of hydroperoxide per oxygen consumed decreases from 1 (100%) to a much smaller value and depends on oxygen concentration because the reaction with $R\cdot$ oxygen transforms these radicals into $RO_2\cdot$, which cannot decompose hydroperoxide

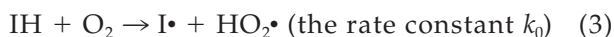
*Present address: 3612 Princeton Pike, Lawrenceville, NJ 08648

Correspondence to: Y. A. Shlyapnikov (yurysh30@yahoo.com).

groups.^{1,2} It is more convenient to describe the process by the following scheme:



The usual antioxidants, alkylated phenols and aromatic amines, more rapidly react with molecular oxygen than hydrocarbons and monomeric units of the polymer,^{1,4} and the initiating step in the oxidation process becomes the interaction of the antioxidant with oxygen. Because of the cage effect, most of the free radicals formed in this process disappear in reactions with the same antioxidant, and the process may be written as⁵



With subsequent interaction of $\text{HO}_2\cdot$ with the monomeric unit RH



Initiating the polymer oxidation and with the antioxidant IH



Thus, one elementary step of the reaction of the antioxidant with molecular oxygen results in the consumption of several antioxidant molecules ($f > 1$, where f is the number of antioxidant molecules consumed). A small number of the radicals involved in this process react with the monomeric units (RHs) initiating the polymer oxidation:



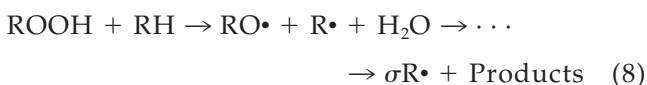
The kinetic chains initiated by these radicals are terminated by the same antioxidant:



where k_t is the rate constant of chain termination on antioxidant.

Thus, eq. (6) does not change the value of f . Most of the radicals of antioxidant $\text{I}\cdot$ transform into the product of their condensation, which can retard oxidation in the absence of the initial form of the antioxidant.^{1,6}

Chain branching proceeds at the interaction of hydroperoxide groups with adjacent monomeric units:



where σ is the average yield of active free radicals.

In the developed chain reaction, the main source of free radicals is not chain initiation but chain branching. If the rate of chain branching exceeds that of chain termination, the process remains self-accelerated, or

$-\Delta P_{\text{O}_2}$, mm Hg

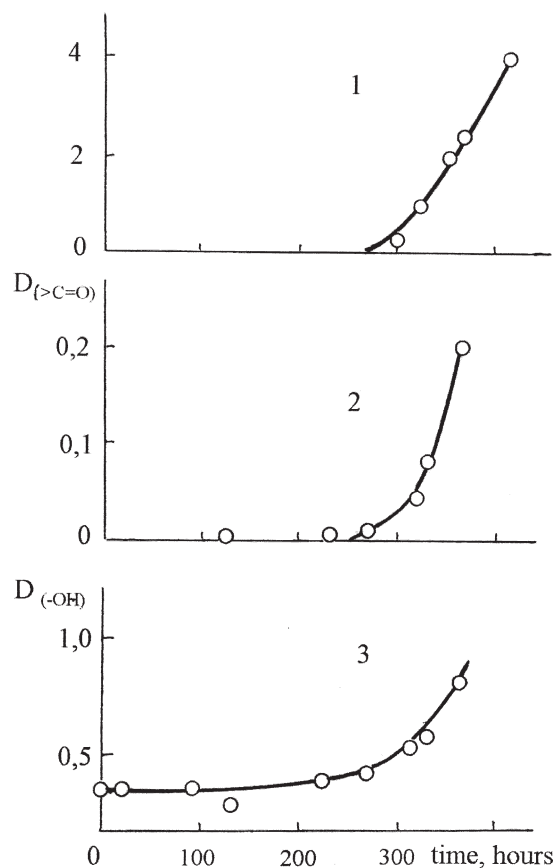


Figure 1 (1) Oxygen consumption, (2) accumulation of carbonyl, and (3) hydroxyl groups in units of optical density at 1700 cm^{-1} for =CO and 3600 cm^{-1} for -OH during the oxidation of polyethylene containing MCHP ($1.25 \times 10^{-4} \text{ mol/kg}$; 100°C , oxygen, 150 mmHg).

nonstationary. If the rate of chain termination is equal to or greater than that of chain branching, the process remains stationary, and its rate after an initial period is a unique function of the reaction conditions, including the concentrations of antioxidant, oxygen, and monomeric units. The border between nonstationary and stationary oxidation corresponds to the critical antioxidant concentration ($[\text{IH}]_{\text{cr}}$). According to refs. 1 and 7, its meaning is equal to

$$[\text{IH}]_{\text{cr}} = \frac{\alpha \sigma k_2 [\text{RH}]}{(1 - \sigma) k_t} \quad (9)$$

where α defines the average yield of hydroperoxide groups at reaction of $\text{RO}_2\cdot$.

As shown by eq. (9), the expression for $[\text{IH}]_{\text{cr}}$ contains the ratio of two rate constants and the product of two coefficients, each of which may depend on temperature.

If above critical concentration, the antioxidant is consumed mainly in reactions of direct oxidation as in

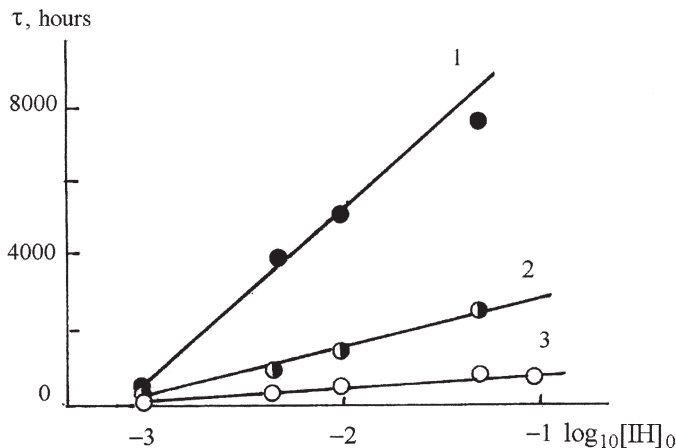


Figure 2 Induction period of polyethylene oxidation as function of the logarithm of $[IH]_0$ at (1) 80, (2) 90, and (3) 100°C.

equations (3)–(5), which follow the first kinetic order according to antioxidant; then, we may write

$$-\frac{d[IH]}{dt} = k_{\text{eff}}[IH] \quad (10)$$

where the rate constant k_{eff} is equal to the rate constant of the reaction $IH + O_2$ (k_0) multiplied by f in eqs. (4)–(6), following eq. (3).^{1,3}

When in the course of oxidation the current antioxidant concentration decreases to its critical meaning, the reaction rate rapidly increases, and the remaining antioxidant is consumed in a short time period equal to $[IH]_{\text{cr}}$. Calculated according to this assumption, the dependence of the induction period on the initial antioxidant concentration ($[IH]_0$) will be^{1,7}

$$\tau = \tau_0 + \frac{1}{k_{\text{eff}}} \ln \frac{[IH]_0}{[IH]_{\text{cr}}} \quad (11)$$

where τ is the induction period and τ_0 is the absence of antioxidant.

Equation (11) may be used to calculate the oxidation parameters of inhibited oxidation, namely $[IH]_{\text{cr}}$ and the apparent (effective) rate constant of antioxidant consumption. So k_{eff} is

$$k_{\text{eff}} = \frac{\Delta \ln [IH]_0}{\Delta \tau} \quad (12)$$

and the critical concentration corresponds to the sharp bend in the curve of the induction period as a function of $[IH]_0$.

Considering that the specific structure of the polymeric compound above and below the range of the polymer melting essentially differ, the goal of our work was to study the changes in the inhibited oxidation parameters at the transition from the completely molten polymer to the partially crystallized one. It was espe-

cially interesting to elucidate the changes in the rate of oxidation of the antioxidant dissolved in the polymer.

EXPERIMENTAL

Low-density industrial polyethylene (weight-average molecular weight = 55700) and antioxidant nonox WSP-MCHP were used. Polyethylene was precipitated from *m*-xylene and washed with alcohol. MCHP was precipitated from an alcohol solution (mp = 140°C). We prepared the samples by mixing the powders with subsequent additions of small amounts of alcohol, which was then evaporated. The samples (0.05 g by weight) were oxidized in a static vacuum device¹ at an oxygen pres-

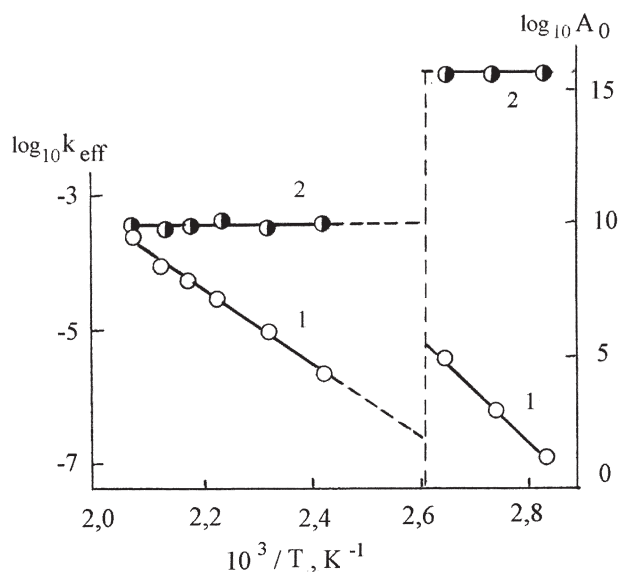


Figure 3 Dependence of (1) the apparent rate constant of antioxidant consumption and (2) the preexponential factor of this constant on the temperature (T) in coordinates of the Arrhenius equation $\log_{10} k_{\text{eff}}$ versus $1/T$. The dotted line shows the polymer melting temperature.

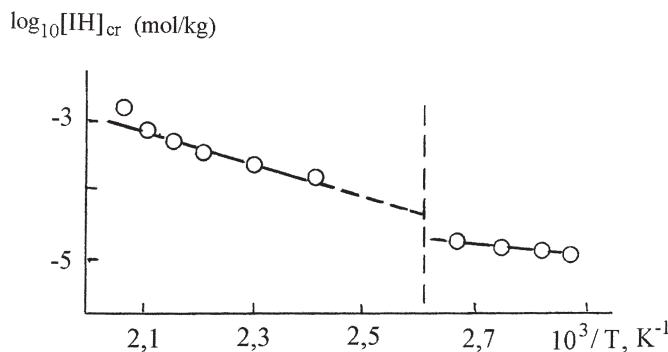


Figure 4 Temperature dependence of $[\text{IH}]_{\text{cr}}$ on polyethylene in coordinates of the Arrhenius equation.

sure of 150 mmHg (which approximately corresponds to its partial pressure in atmosphere).

RESULTS AND DISCUSSION

In Figure 1, the curves of oxygen consumption and accumulation of $-\text{OH}$ and $-\text{CO}$ groups at the oxidation of the sample containing 1.25×10^{-4} mol/kg of MCHP at 100°C are shown. The oxidation of this sample proceeded with a marked induction period, and the time corresponding to the increase of all of these values coincided. According to theory,^{1,7} this time corresponds to the moment at which the antioxidant concentration, decreasing in the course of oxidation, reaches its critical meaning.

According to eq. (11), the induction periods of polyethylene oxidation vary with $[\text{IH}]_0$ according to logarithmic law (Fig. 2). This enabled us to calculate the dependence of k_{eff} on the oxidation temperature. As shown in Figure 3, in both ranges, below and above the polyethylene melting point (XXX), with the activation energy 36.5 kcal/mol (153 kJ/mol) below and 30.0 kcal/mol (126 kJ/mol) above the melting point. Most interesting was a considerable variation in the preexponent, the decimal logarithm, which decreased from 15.6 to 10.0 (c^{-1}) at polymer melting.

Similar to the changes at the transition over the melting temperature were those in the critical concentration of the antioxidant, which we determined from the transformation of the curves of the dependence of the induction period on $[\text{IH}]_0$. Opposite to k_{eff} , the apparent activation energy calculated for $[\text{IH}]_{\text{cr}}$ in the solid polymer was lower than that in the polymer melt; the values were 3.0 kcal/mol (12.6 kJ/mol) and 11.5 kcal/mol (48.2 kJ/mol), respectively (Fig. 4). The expression for $[\text{IH}]_{\text{cr}}$ contains several rate constants, and we could not attribute the observed changes to any of these.

According to eqs. (3)–(6), the reaction of the antioxidant with oxygen was followed by several secondary reactions. Considering these reaction, we had to write eq. (12) with f as the number of antioxidant molecules consumed in the primary and secondary reactions. Accord-

ing to eqs. (3)–(6), $f = 3$. The change in the local IH concentration at transition over the melting temperature could not change k_{eff} , which was first order in antioxidant concentration. The value of f also could not have markedly changed, even if the consequence of secondary reactions differed from our assumption.

It is not difficult to explain the greater activation energy below the melting temperature. According to theory proposed in refs. 3 and 8, the mechanism of additive sorption, the molecules of compound A dissolved in a polymer are present mainly in the sorption centers, the zones of short-order violation, the volumes of which are by their size and shape close to that of dissolved molecules of A (in our case, MCHP). Below the upper border of the melting zone in the polymer exists a crystalline formation preventing free movement of macromolecules and their segments, and the rearrangement of the sorption center necessary for the formation of the reaction complex needs additional energy. It is much more difficult to explain the increase in the preexponential factor of five decimal orders. We do not discuss this effect, as any conclusions would be premature.

From the previous discussion, it follows that the structure and properties of the amorphous part of the crystalline polymer in which the low-molecular additives dissolved in it were present markedly differed from the structure of the polymer melt above the melting point.

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