Variation of Inhibited Oxidation Parameters in the Range of Phase Transition

I. G. Kalinina,[1] K. Z. Gumargalieva,[1] Yu. A. Shlyapnikov[2]

[1]Institute of Chemical Physics, Russian Academy of Sciences, Moscow 119991, Russia
[2]Institute of Biochemical Physics, Russian Academy of Sciences, Moscow 119991, Russia

ABSTRACT: Parameters of inhibited oxidation of isotactic propylene containing antioxidant 2,2′-methylene-bis(4-methyl-6-tertbutylphenol) have been studied in the temperature range 140–210°C. Unlike polyethylene, the dependencies of inhibited oxidation parameters of critical antioxidant concentration and of rate constant of antioxidant consumption change with temperature do not obey Arrhenius law both below and above the melting temperature. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2711–2713, 2007

Key words: crystalline polymers; polypropylene; antioxidant effectivity; thermal dependence

INTRODUCTION

Polypropylene is sensitive to oxidation of atmospheric oxygen and needs stabilization against this process. As most polymers, materials based on polypropylene are designed for longer use, but investigations of the antioxidative stability of these polymers are usually performed at elevated temperatures, because the experiments at the temperatures of service may need many years. Thus to apply the data obtained at accelerated testing to the service conditions we must know how these data change in the range dividing the temperatures of testing and the temperatures of service.

In this study we investigated oxidation of isotactic polypropylene (IPP) prepared on metallocene catalysts in the range of 140–210°C and oxygen pressure 300 mmHg. Antioxidant was 2,2′-methylene-bis(4-methyl-6-tertbutylphenol (MBP)), often used as standard antioxidant.

IPP is a crystalline polymer. Crystalline polymer IPP does not completely crystallize at any temperature, although over a certain *melting temperature* the crystalline substance in it disappears completely. Some processes in the polymer proceed mainly or completely in amorphous phase, but the elements of the crystalline phase, even when they are small, link several polymer chains, preventing their translational mobility and, in the same time, only slightly affect the vibrational one. Thus, the intercrystalline amorphous substance in the polymer must resemble gel in which mobility of the polymer chains needed for formation of centers of the additive sorption is restricted. It is interesting to understand how these elements of crystalline phase affect the oxidation processes in polymer.

In this work we studied dependencies of two parameters of inhibited oxidation: the critical antioxidant concentration, below which antioxidant only slightly affects the oxidation rate, and apparent rate constant of the antioxidant consumption on the temperature oxidation.

EXPERIMENTAL

IPP ($M_w = 690,000$, $M_w/M_n = 3.5$, and isotacticity 96%) prepared by polymerization on metallocene catalyst[1] has been used. Antioxidant MBP has been purified by vacuum sublimation. Antioxidant was added to the polymer powder from alcohol solution with subsequent drying at room temperature. The samples of 0.050 g of IPP were oxidized in the vacuum equipment described in Ref. 2, and volatile products of oxidation were absorbed by solid KOH.

To calculate the parameters of inhibited oxidation the formula (1) has been used[2,3]

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

where τ is the induction period of oxidation of the sample containing antioxidant at concentration of $[\text{IH}]_0$, $[\text{IH}]_{\text{cr}}$ is the critical, i.e., the minimal effective concentration, τ_0 is the induction period at this concentration (i.e., when $[\text{IH}]_0 = [\text{IH}]_{\text{cr}}$), and k_{eff} is the apparent rate constant of antioxidant consumption, describing the complex process initiated by direct oxidation of antioxidant.[2]
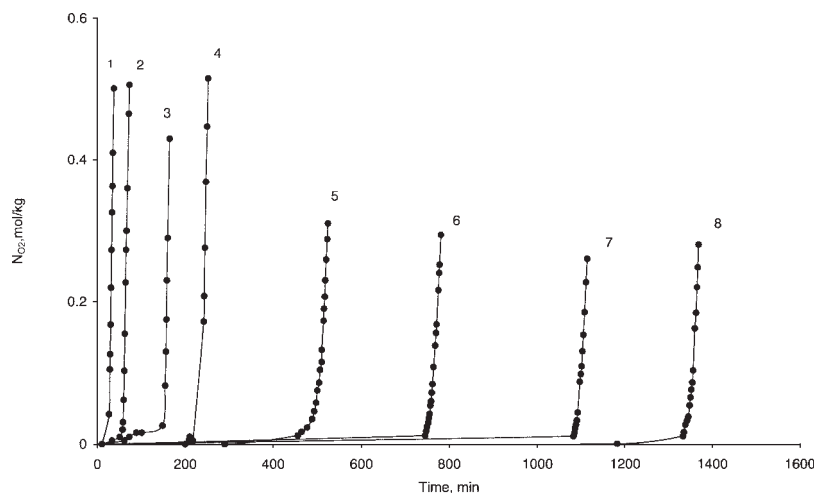
Figure 1 Oxygen consumption at oxidation of polypropylene: 210°C, MBP concentrations are 0.002 (1), 0.003 (2), 0.005 (3), 0.006 (4); 160°C, MBP concentrations are 0.0003 (5), 0.0004 (6), 0.0006 (7), 0.00075 (8) mol/kg; oxygen pressure 300 mmHg.

According formula (1), the experimentally found dependence of induction period on initial antioxidant concentration must be a straight line beginning from the horizontal line corresponding to induction period of noninhibited polymer at $[IH]_0 = [IH]_{cr}$ in the coordinates $\tau - \log[IH]_0$. The slope of this line is connected with the rate constant k_{eff} by the formula:

$$k_{eff} = \frac{\Delta \ln[IH]_0}{\Delta \tau} \qquad (2)$$

Studying the polymer by method of differential scanning calorimetry we found its melting temperature 163°C.

RESULTS AND DISCUSSION

Figure 1 shows the examples of curves of oxygen consumption during IPP oxidation on the presence of MBP. It is seen that the curves are characterized with very distinct induction periods. Figure 2 shows that the experimental data plotted in coordinates $\tau - \log[IH]_0$ are reliable straight lines, i.e., obey the formula (1). It is also seen that the data obtained from slopes of these lines are reliable when the meanings of abscissas of the intersection points corresponding to critical antioxidant concentrations are less reliable.

Figure 3 shows the dependencies of critical concentration of MBP and Figure 4 the logarithm of the
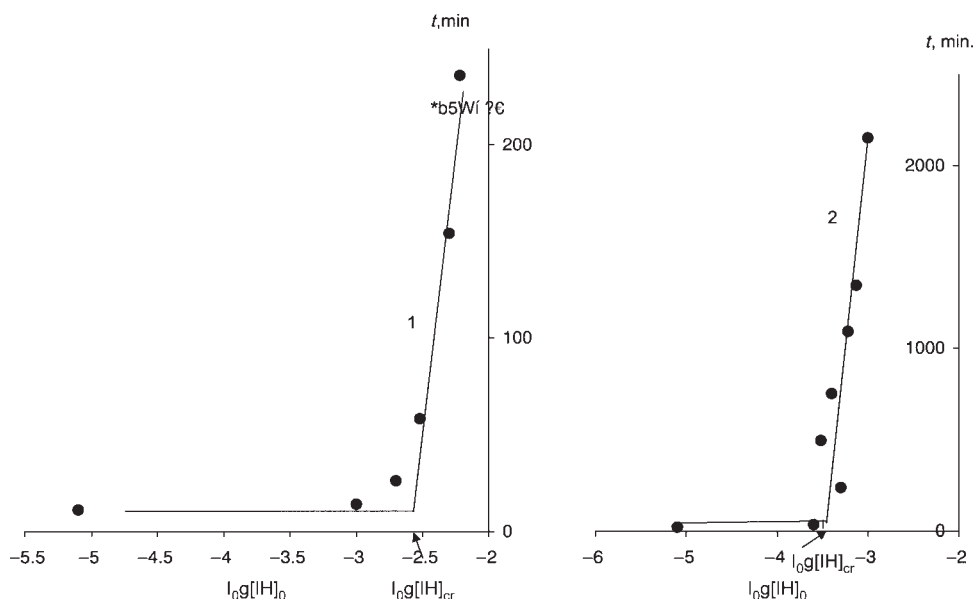

Figure 2 Dependencies of induction period of IPP oxidation on logarithm of initial antioxidant concentration. Temperatures: 210°C (1) and 160°C (2).

rate constant of its consumption on inverse temperature ($1/T$). The dependence of critical concentration is presented by the curved line with maximum, when the rate constant in these (Arrhenius) coordinates consists of two wings meeting in the point corresponding to the melting temperature of IPP (163°C). Opposite to polyethylene[4] both wings are curved lines, which does not make possible to calculate the activation energies of the process responsible for antioxidant consumption. It must be specially noted that below the melting point of the polymer the rate constant increases with decreasing temperature. Aforementioned details explain this phenomenon and we must assume that the polypropylene melt contains complicated structures,[5] the ratios of which change with temperature. Below the melting point the elements of disorder[6] present in the polymer are displaced by growing crystallites into noncrystallized elements of amorphous phase, the composition of which is varying with the temperature. The compounds dissolved in the polymer are present mainly in the sorption centers formed around these elements of disorder, and compression of these effects the rates
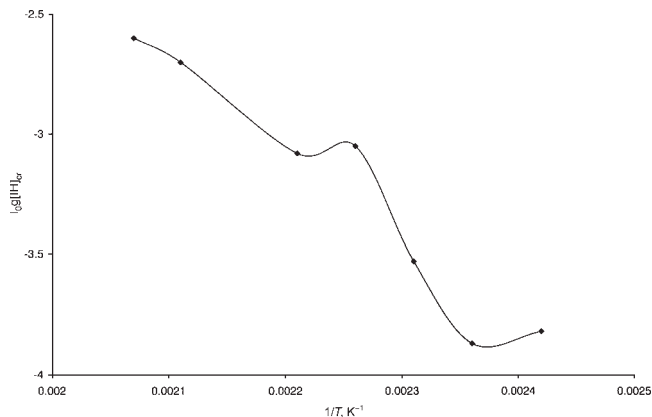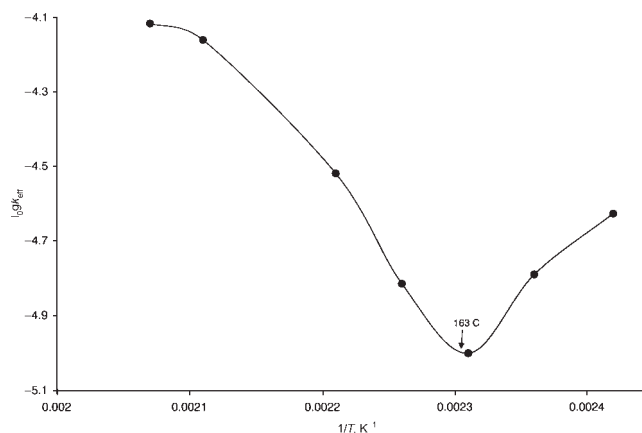

Figure 4 Dependencies of logarithm of apparent rate constant on oxidation temperature in the coordinates of Arrhenius law.

of their interaction. As the result the rate constant increases 2.3 times at transition from 163 to 140°C. Another conclusion from our data is as follows: the use of the simple Arrhenius formula for extrapolation over the melting temperature is incorrect.

Figure 3 Dependencies of logarithm of critical antioxidant concentration on oxidation temperature in the coordinates of Arrhenius law.

References

1. Nedorezova, P. M.; Aladyshev, A. M.; Savinov, D. V.; Klyamkina, A. N.; Optov, V. A.; Lementovskiy D. A. Vysokomolecular Soedin (Russian Polym Sci) 1991, 43, 595.
2. Shlyapnikov, Yu. A.; Kiryushkin, S. G.; Mar'in, A. P. Antioxidative Stabilization of Polymers; Taylor & Francis: London, 1996.
3. Shlyapnikov, Yu. A. In Developments in Polymer Stabilisation-5; Scott G., Ed.; Applied Science: London, 1978; p 1.
4. Shlyapnikov, Yu. A.; Kolesnikova N. N. In Chemical Physics of Pyrolysis, Combustion and Oxidation; Berlin, A. A. Novakov, I. A., Khalturinskiy, N. A., Zaikov, G. E., Eds.; Nova Science Publishers, 2004; p 111.
5. Varga, J.; Menzel, J.; Sholti A. Vysokomolek Soedin (Russian Polym Sci) 1984, 26, 2467.
6. Shlyapnikov, Yu. A. Russian Chem Rev 1997, 66, 963.