

Inhibition of Polyketone Oxidation

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ABSTRACT: Oxidation of polyketones [poly(ethylene ketone) ($-\text{CH}_2-\text{CH}_2-\text{CO}-$)_n and poly(propylene ketone) ($-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CO}-$)_n] in the presence of antioxidant [2,2'-methylene-bis(4-methyl-6-*tert*-butylphenol)] was studied in the temperature range 120–190°C. The effectiveness of

the antioxidant in polyketones is much lower than that in polyolefins. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1182–1185, 2003

Key words: polyolefins; antioxidants

INTRODUCTION

Poly(ethylene ketone) and poly(propylene ketone) are the products of copolymerization of carbon monoxide with the corresponding olefin.^{1–3} As shown in our previous reports,^{4,5} when these polymers react with molecular oxygen at elevated temperatures, their oxidation is disrupted by structural irregularities [poly(ethylene ketone)], or by a negative temperature coefficient [amorphous poly(propylene ketone)], which results in a decrease in the rate of oxidation with increasing temperature.

In the present work we studied the oxidation of both of these polymers in the presence of 2,2'-methylene-bis(4-methyl-6-*tert*-butylphenol), which is an effective antioxidant for polyolefins. We will begin with poly(propylene ketone), although it is the more complex polymer, because it is amorphous and its oxidation is not complicated by phase transitions caused by temperature and the effect of reaction products.

In the very simplified form, the oxidation reaction may be described as follows:



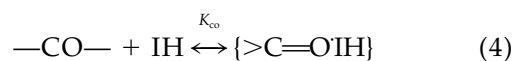
where RH is an aliphatic fragment of the polymer molecule containing a reactive hydrogen atom. These fragments possess extremely low translation mobility,

and reactions 1 and 2 proceed mainly inside the stable structure, the element of topological disorder.⁶ The polar carbonyl groups change the rate of reaction of hydrogen extraction (2) and decrease the concentration of the RH fragment in the vicinity of radicals (RO₂·) thereby decreasing the overall rate of the polymer oxidation.

Retardation of polymer oxidation is based on the reactions of antioxidants (A) with free macroradicals (mainly RO₂·), which terminate the reaction chains. If these antioxidants are aromatic amines or phenols, which contain a relatively mobile hydrogen atom (A = IH), the reaction may be written in the form

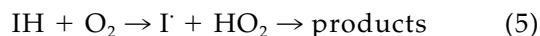


where I· is a mobile free radical of low activity that reacts either with other such radicals or with macroradicals (R·). Macroradicals of both RO₂· and R· types are virtually immobile, and to terminate the kinetic chain of the oxidation reactions, antioxidants must possess a certain mobility. Polar groups, such as $-\text{CO}-$ in polyketones; can form immobile complexes with mobile amines and phenols, thereby decreasing the ratio of mobile antioxidant molecules and their effectiveness;

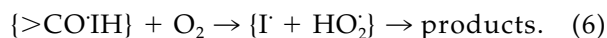


The main part of antioxidants is consumed not in reaction 3 of the kinetic chain termination, but in a side reaction with mobile oxygen molecules,⁷ which takes place both inside and outside the complexes (>COIH):

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and



The combination of these effect decreases the antioxidant effectiveness in polyketones compared with that in polyolefins.

EXPERIMENTAL

Poly(ethylene ketone) and poly(propylene ketone), prepared by copolymerization of the corresponding olefin with carbon monoxide and antioxidant 2,2'-methylene-bis(4-methyl-6-*tert*-butylphenol), were used. Oxidation was followed by measuring oxygen pressure, and volatile oxidation products were absorbed by solid KOH.

To study the complex formation between —CO— groups and antioxidants (IH), the sorption of antioxidant by polyketones was investigated. First, the polymer samples were immersed in alcohol solutions of 2,2'-methylene-bis(4-methyl-6-*tert*-butylphenol) for 30 days. Then, antioxidant was extracted with alcohol and analyzed by spectrophotometric methods. The authors realize that alcohol molecules may compete for the same sorption centers, because of the topological nature⁷ and the polar groups in alcohols, but nonpolar hydrocarbons dissolve some fractions of the polymers, forming nontransparent solutions.

RESULTS AND DISCUSSION

The sorption isotherms of poly(propylene ketone) (curve 1) and poly(ethylene ketone) in 2,2'-methylene-bis(4-methyl-6-*tert*-butylphenol) are shown in Figure 1. Both curves possess Langmuir-type shapes, which may be described by⁸

$$[\text{IH}]_p = a[\text{IH}]_m \cdot (1 + b [\text{IH}]_m)^{-1}$$

where $[\text{IH}]_p$ is the additive concentration in polymer and $[\text{IH}]_m$ is that in the surrounding medium. The limit to which $[\text{IH}]_p$ varies with increasing $[\text{IH}]_m$ is the total concentration of sorption centers, which is equal to

$$[Z_a] = a/b$$

According to the data in Figure 1, for poly(propylene ketone), $[Z_a] = 6.8 \cdot 10^{-4}$ mol/kg, and the constant of equilibrium ($\gamma_a K_a$) = 0.74 L/kg; and for poly(ethylene ketone), $[Z_a] = 3.5 \cdot 10$ mol/kg, and $\gamma_a K_a = 6.5$ L/kg.

Because the properties and stability of poly(ethylene ketone) and poly(propylene ketone) differ sub-

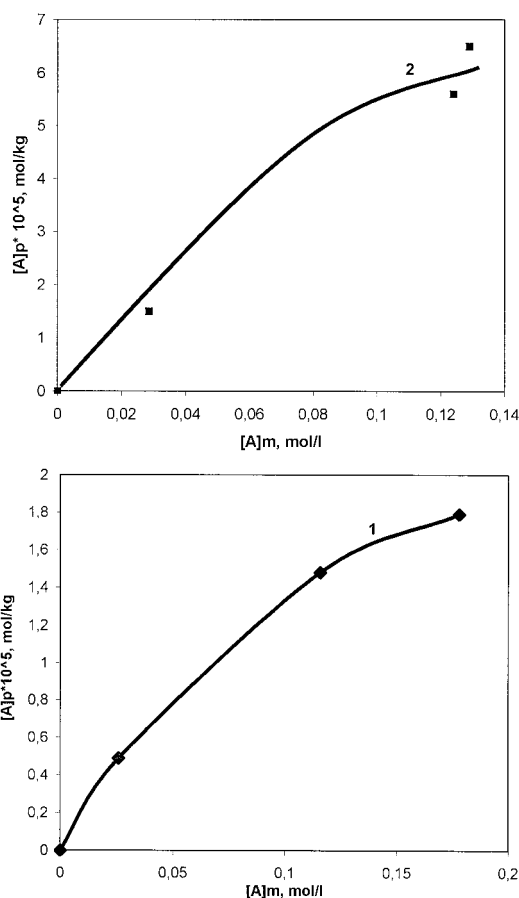


Figure 1 Sorption isotherms of 2,2-methylene-bis(4-methyl-6-*tert*-butylphenol) with poly(ethylene ketone) (1) and poly(propylene ketone) (2), from ethanol at 40°C.

stantially, we had to study their oxidation in different temperature ranges.

The concentrations of antioxidant used in this study (up to 0.10 mol/kg) substantially exceed the sorption limits. According to the previously considered theory,^{6,7} this result may be explained by the assumption that the antioxidant rearranges the structure of the polymer at high temperatures.

The curves of oxygen consumption by poly(propylene ketone) at various temperatures and antioxidant concentrations are presented in Figures 2 and 3, respectively.

Because of the low melting temperature of poly(propylene ketone), its oxidation is not complicated with phase transitions, but the regularities of the process remain complicated. As seen from Figures 2 and 3, kinetic curves of poly(propylene ketone) oxidation consist of two parts: an initial stage of rapid oxygen consumption, and a subsequent phase in which the rate rapidly decreases and then remains nearly constant. As shown earlier,⁴ the rate of non-inhibited oxidation of poly(propylene ketone) changes with temperature over a maximum of 130–140°C. As seen from Figure 3, the slopes and shapes of the curves of

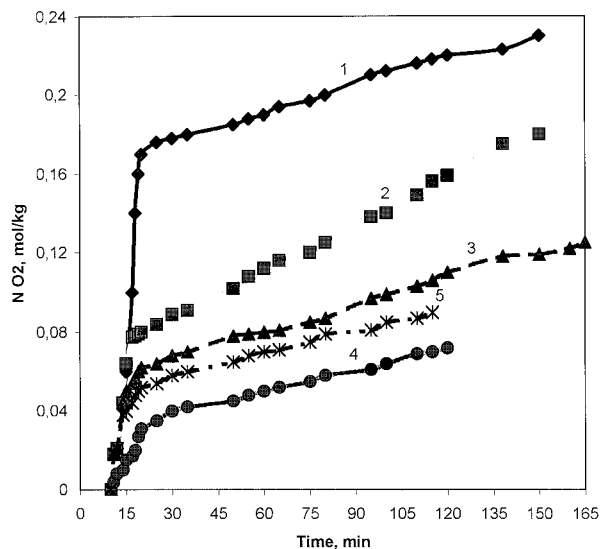


Figure 2 Oxygen consumption during oxidation of poly(propylene ketone) at 120°C, under an oxygen pressure of 300 mmHg. Initial antioxidant concentrations were (1) 0.00125, (2) 0.005, (3) 0.01, (4) 0.03, and (5) 0.06 mol/kg.

oxygen consumption also change with temperature. At 130 and 140°C, reactions begin with rapid oxygen consumption, even during the period of the sample heating, and then the rates decrease and became nearly the same at 160 and 180°C. This process is self-accelerated in the initial period, and then the rate becomes nearly constant.

The most interesting observation is the dependence of the oxidation rate on initial antioxidant concentrations (Fig. 4): the rate first increases, passing over maximum at $[IH] = 0.007$ mol/kg, then rapidly decreases, and then slowly increases again at high antioxidant concentrations. It must be noted that the direct antioxidant oxidation ($IH + O_2$) reaction, participating in oxygen consumption, partially compensates for the

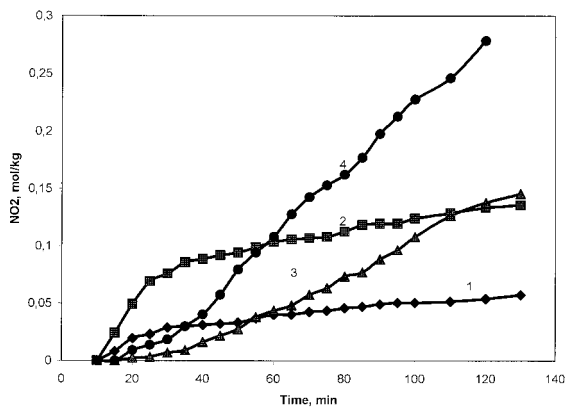


Figure 3 Oxygen consumption during oxidation of poly(propylene ketone) at an initial antioxidant concentration of 0.01 mol/kg, under an oxygen pressure of 300 mmHg, and temperatures of (1) 120, (2) 140, (3) 160, and (4) 180°C.

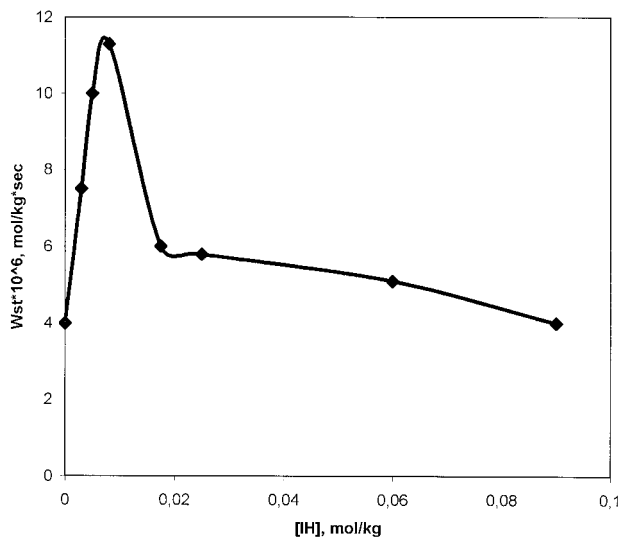


Figure 4 The rate of poly(propylene ketone) oxidation during the second (stationary) stage of oxidation as function of initial antioxidant concentration (120°C; oxygen pressure, 300 mmHg).

decrease of the rate of the polymer oxidation with the increase of $[IH]$.⁹

The activation energy at the first stage of poly(propylene ketone) oxidation in the presence of 2,2'-methylene-bis(4-methyl-6-*tert*-butylphenol), 0.1 mol/kg, cannot be reliably determined. At deep stage, the activation energy is 64 kJ/mol (15.3 kcal/mol).

The kinetic curves of oxygen consumption in the course of poly(ethylene ketone) oxidation at $[IH] = 0.01$ mol/kg are shown in Figure 5. After a short delay in the beginning, which may be attributed to sample heating, the curves are close to straight lines, with scarcely detectable bends, corresponding to 0.08 mol/kg of oxygen consumed. The activation energies calculated from temperature dependencies of the rates in initial (W_1), $E_1 = 92$ kJ/mol, differ from those at

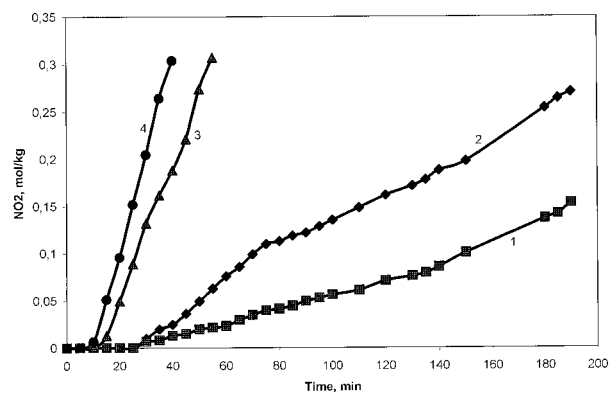


Figure 5 Oxygen consumption during oxidation of poly(ethylene ketone) at initial antioxidant concentration of 0.01 mol/kg, under an oxygen pressure of 300 mmHg, and temperatures of (1) 180, (2) 200, (3) 220, and (4) 230.

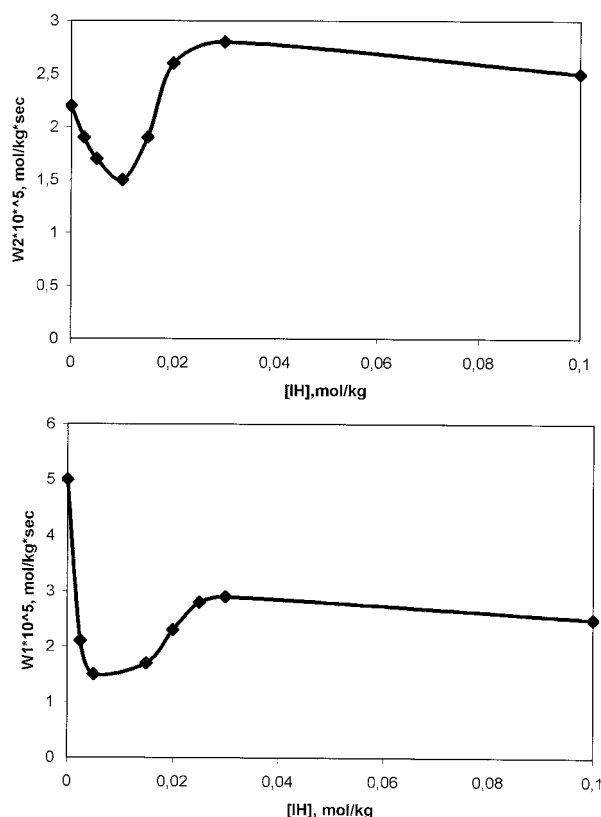


Figure 6 Dependencies of initial rate (W_1) and the rate at the later stage of oxidation (W_2) of poly(ethylene ketone) on the initial concentration of 2,2'-methylene-bis(4-methyl-6-*tert*-butylphenol) (200°C; oxygen, 300 mmHg).

later stages (W_2) $E_2 = 138$ kJ/mol (22 and 33 kcal/mol, respectively).

Both initial rate (W_1) and the rate at the later stage (W_2) also differ with the initial concentration of antioxidant, 2,2'-methylene-bis(4-methyl-6-*tert*-butylphe-

no). The rate of oxidation of polyolefins decreases 100-fold in the presence of antioxidants.⁷ In contrast, the same antioxidant, 2,2-methylene-bis(4-methyl-6-*tert*-butylphenol), in the range 0–0.01 mol/kg, causes only a 3.27-fold decrease in the initial rate of poly(ethylene ketone) oxidation (W_1) at 200°C. The decrease of the later rate of oxidation (W_2) in the presence of antioxidant does not exceed the experimental error. In addition, at $[IH]_0 > 0.02$ mol/kg, both W_1 and W_2 increase.

The of antioxidant-induced inhibition of oxidation of polyketones, the relatively new class of polymers, is complex. This inhibition is the result of both the superposition of at least two chemical reactions, those of polymer and antioxidant oxidations, and of structural effects, including the change of the polymer structure caused by the dissolved antioxidant.⁶

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