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Antioxidants and Stabilizers

93. A Model Interaction of Polyolefine Melt Stabilizer 2,2 -Thiobis(4,6-di-*tert.*Butylphenol with *tert.* Butylhydroperoxide

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Summary

The efficiency of polyolefine melt stabilizer 2,2′-thiobis-(4,6-di-tert.butylphenol) (I) as a hydroperoxide decomposing antioxidant was studied under model conditions.tert.Butylhydroperoxide was used to simulate the reaction with polypropylene hydroperoxide. The reaction was performed at 85°C in chlorobenzene solution. Decomposition of tert.butylhydroperoxide by I and formation of the sulphoxide II and the sulphone III from sulphide I were followed quantitatively. Formation of small amounts of effective peroxidolytic species from II or III, responsible for acceleration of hydroperoxide decomposition was considered.

Introduction

Phenolic sulphides are very efficient melt stabilizers for polyolefins. They proved to be able to react both as chain-breaking antioxidants scavenging radicals $RO_2^{\bullet}$ (TKÁČ et al 1981) and as hydroperoxide decomposers (SON et al 1983). In the former case, phenoxy radicals are formed. Reaction of aliphatic sulphur-containing antioxidants with hydroperoxides involves generally a series of oxidative and thermal transformations on sulphur atom (SHELTON 1981). More mechanistic details on the transformation of phenolic sulphides are necessary for better understanding of their hydroperoxide decomposing activity and, at the same time, for the general knowledge of antioxidative mechanism of autosynergistic systems in polyolefins. We applied model conditions to obtain quantitative data for the first stage of the hydroperoxide decomposing process. 2,2′-Thiobis(4,6-di-tert.-butylphenol) (I) which belongs among most efficient melt stabilizers for polyolefins was used as the decomposer of tert.-butylhydroperoxide (t-BuOOH).

Experimental

A chlorobenzene solution of antioxidant 2,2′-thiobis(4,6-di-tert.butylphenol) (I,m.p. 104-105°C, 0.02 mol/l) and tert.-butylhydroperoxide (t-BuOOH, 0.2 mol/l) was heated in a closed reactor thermostated to 85°C. The reaction mixture was stirred using a magnetic stirrer. During the reaction, samples were withdrawn in regular time intervals for the iodometric titrations of unreacted t-BuOOH (method of WAGNER et al 1947) and for the liquid-chromatographic determination of the sulphide I and its two transformation products, i.e. the corresponding sulphoxide

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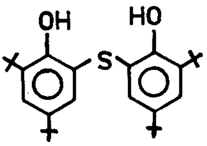
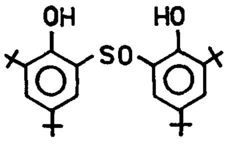
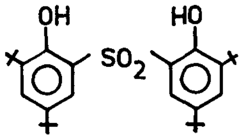
II (m.p. 146-147°C) and the sulphone III (m.p. 172-173°C) by the procedure described earlier (ROTSCHOVÁ et al 1982).



I



II



III

Results and Discussion

Thiobisphenol I is an efficient antioxidant for processing of polyolefins. The presence of two different reaction centers in its molecule enables assertion of both main antioxidant mechanisms involved in the melt stabilization. The ability to react under suitable conditions as a chain breaker and/or a hydroperoxide decomposer creates possibility of an intramolecular cooperation involving autosynergistic features. Model conditions were chosen to check the mechanism of the reaction with t-BuOOH and to follow quantitatively the transformation products of I. The sulphoxide II and the sulphone III were proved to be the simplest primary oxidation products of I (SON et al 1983). They were prepared by an independent synthesis and used as standards for the quantitative analysis of reaction mixture by liquid chromatography (ROTSCHOVÁ et al 1982). Temperature 85°C was chosen for this study: the reaction of I with t-BuOOH has similar features at this temperature as that carried out at the level of 100°C; its rate is still relatively low and allows to follow stepwise formation of II and III in the first stages of the hydroperoxide decomposition. Fig.1 shows changes in the contents of t-BuOOH and of I to III during the reaction.

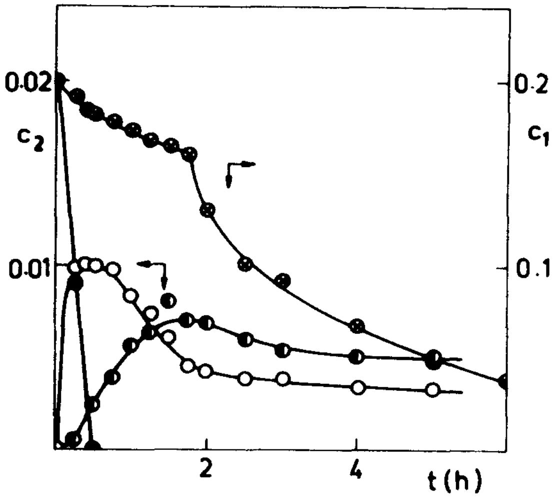


Fig.1. The changes in the content of ⊗ t-BuOOH (c_1,mol/l), ● antioxidant I and its transformation products ◐ II and ○ III (c_2,mol/l) during the reaction of I with t-BuOOH at 85°C in chlorobenzene

The curves indicate an interesting course of the reaction. The hydroperoxide concentration drops with the time and a break on the curve indicating an important change of the reaction mechanism is observed. This break can be seen also at temperature 65 and 75°C but it was not distinct at 100°C because of the high rate of t-BuOOH decomposition. The change of the reaction rate is connected with the oxidation transformations of sulphide I. Its concentration in the reaction mixture drops quickly and the content of the corresponding sulphoxide II increases. This first oxidation product of I accumulates in the mixture. Before reaching its maximum concentration, the consecutive oxidation product - sulphone III - starts to be formed. During a limited period of time, all three compounds I, II and III are present in the reaction mixture. Both transformation products II and III are further stepwise oxidized; as a consequence, their content decreases after reaching the maximum. The depletion of sulphoxide II is quicker than that of sulphone III. It is a consequence of the higher reactivity of the former with t-BuOOH. It is surprising that also the sulphone III contributes to the sum of depleted t-BuOOH.

The sulphoxide II decomposes t-BuOOH very efficiently in comparison with the starting sulphide I at 85°C (Fig.2). The characteristic break on the curve of t-BuOOH decomposition is lacking in this case. The curve, obtained as a result of the interaction of t-BuOOH with the sulphone III, has a long initial period characteristic by a very low mutual reactivity of both compounds. After this period, a steady-rate decomposition of t-BuOOH follows. The observation in Fig.2 is in agreement with the slow depletion of III formed during reaction of t-BuOOH with I (Fig.1). The break in the decomposition rate of t-BuOOH occurs after disappearance of I, a substantial drop in the concentration of primarily formed sulphoxide II, and after reaching the maximum concentration of sulphone III. It can be concluded from this fact, that efficient hydroperoxidolytic species are formed from the sulphide I in this reaction stage in appreciable concentration. These very reactive intermediates are responsible for the high hydroperoxide-decomposing efficiency of phenolic sulphides.

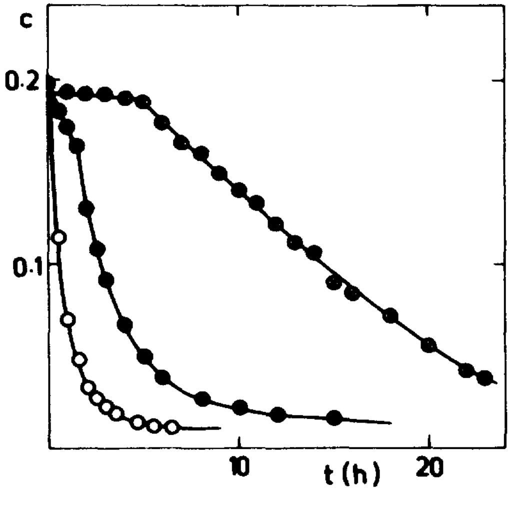


Fig.2. Time dependence of t-BuOOH decomposition (c,mol/l, chlorobenzene) at 85°C in the reaction with ● sulphide I, O sulphoxide II, and ⊗ sulphone III, respectively

It should be pointed out that the oxidation products II and III, considered as the source of peroxidolytic species, contain still phenolic hydroxy groups. This means that they are able to scavenge $RO_2^{\cdot}$ radicals. Active participation of I in the hydroperoxide-decomposing stabilization process is not connected with the lost of chain breaking activity of phenolic sulphides.

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