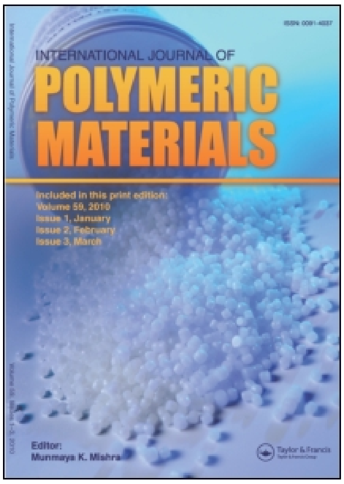

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Activity and Mechanism of Action of Thio and Dithiobisphenols in the Stabilization of Polyolefins

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Activity and Mechanism of Action of Thio and Dithiobisphenols in the Stabilization of Polyolefins

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Diphenol substituted sulfides have been studied as stabilizers poypropylene against thermal oxidation. Both phenol groups of antioxidants are reacting with oxidation reaction centres, the sulfide group reacting with hydroperoxides.

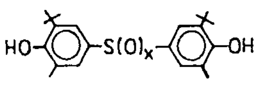
The reaction of phenol-substituted disulfides with *tert*-butylhydroperoxide was also studied.

The role of unstable sulfur-containing intermediates is discussed.

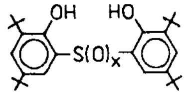
KEYWORDS: Thiobisphenols, dithiobisphenols, polyolefins, degradation, stabilization, mechanism

Resistivity of polyolefins against thermooxidation is achieved by the addition of compounds which are able to enter actively the initiation or propagation stage of this radical reaction. The most effective way is the utilization of a stabilizing system which slows down the autoxidation of the polyolefin in several stages simultaneously. In the industrial practice this is usually achieved by using a mixture of sterically hindered phenol and aliphatic sulfide having the structure of dialkyl 3,3-thiodipropionate or dialkyldisulfide. The phenolic component is an effective radical scavenger, and thus retards the propagation stage of the oxidation of the polyolefin, while sulfide is effective in the nonradical decomposition of hydroperoxides, thus retarding the initiation stage. It can be assumed that suitable combinations of the phenolic and sulfidic structure in one molecule will also possess an important antioxidant activity. Polyfunctional compounds of this type are represented by phenolic sulfides and disulfides; of these, compounds having the structure of 2,2′- and 4,4′-thiobisphenol are commercially used as processing stabilizers of polyolefins.[1]

Using 4,4′-thiobis(2-tert-butyl-6-methylphenol)(Ia), 2,2′-thiobis(4,6-ditert-butylphenol)(IIA), 4,4′-dithiobis(2-tert-butyl-6-methylphenol)(IIIa) and 2,2′-dithiobis(4,6-ditert-butylphenol)(IVa), we investigated the contribution of the individual active sites in phenolic sulfides and disulfides to the antioxidant activity in various oxidation processes: (a) in the reaction with tert-butylhydroperoxide (TBH) in chlorobenzene at 65°–100°C, (b) in the oxidation of tetraline with oxygen with azobis(isobutyronitrile) (AIBN) at 60°C, (c) in the oxidation of isotactic polypropylene with oxygen at 180°C. The importance of the chemical transformation of the antioxidant in the process of stabilization was investigated also by using compounds, the formation of which was observed in the oxidation reaction ad (a). The antioxidant activity of these products of oxidation transformation was studied independently under the same conditions as that of parent thiobisphenols Ia through IVa.



I



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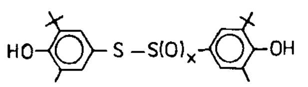

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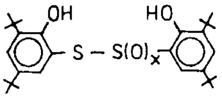


IV

a : x = 0, b : x = 1, c : x = 2

ACTIVITY OF THIO AND DITHIOBISPHENOLS IN THE DECOMPOSITION OF TERT-BUTYLHYDROPEROXIDE

Owing to the presence of the sulfide group, thiobisphenols Ia and IIa are able to decompose hydroperoxides. This was checked on their reaction with TBH in chlorobenzene in the temperature range 65°–100°C and with hydroperoxide present in molar excess ranging from twofold to tenfold. The rate of decomposition of TBH increases with temperature and with the concentration of thiobisphenol (2–5). Independently of these two factors, two stages of decomposition of TBH can be distinguished. In the first, initial stage, in which the oxidation of phenolic sulfide to sulfoxide Ib or IIb predominates the concentration of TBH decreases distinctly more slowly than in the second stage. During this stage the concentration of TBH (though present in a considerable molar excess) decreases quickly to low values, and the amount of TBH decomposed exceeds the stoichiomatric amount which would correspond to the oxidation of thiobisphenols Ia and IIa to the highest degree of oxidation, i.e. to the formation of the corresponding sulfones Ic, IIc, and even—if the fragmentation of the bisphenolic skeleton takes place—to the formation of SO_3. An example of the characteristic decomposition of TBH and of the oxidation transformation of the starting thiobisphenol is illustrated in Figure 1. The fast decomposition of TBH is given by the fact that, along with the oxidation of phenolic sulfoxide to the corresponding sulfone Ic or IIc, sulfoxides Ib and IIb decompose with formation of compounds which catalyze the decomposition of TBH. Together with inactive

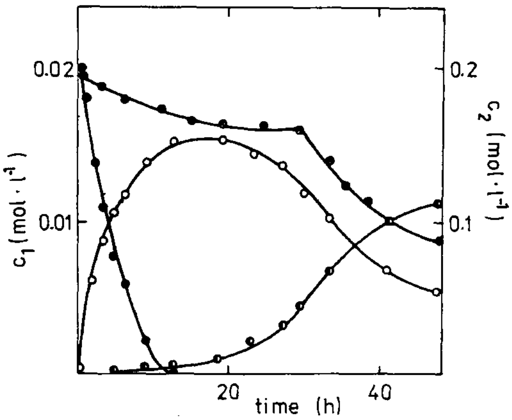
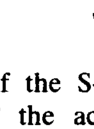
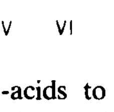
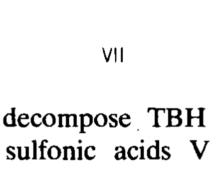
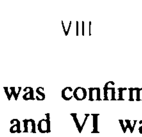


FIGURE 1 Changes in the concentrations of IIa, IIb, IIc (c_1) and TBH (c_2) during the reaction of TBH (0.2) mol/l) with sulfide IIa (0.02 mol/l) at 65°C in chlorobenzene (●) IIa, (○) IIb, (◐) IIc, (⊗) TBH.

sulfur-free quinoid compounds, of which 2-methyl-6-tert-butyl-1,4-benzoquinone was identified in greater detail in the case of sulfide Ia, sulfur dioxide, sulfuric acid and sulfonic acids V or VI are also formed in the mixture. On the contrary, no formation of bisphenyldiols VII and VIII and of the corresponding diphenoquinones could be detected, even though this is mechanistically possible, by way of coupling of sulfur-free phenolic fragments. Phenolic sulfones Ic, IIc react in a way qualitatively similar to phenolic sulfoxides Ib, IIb, though much more slowly; hence, they too have a peroxidolytic character in the decomposition of TBH (3, 5).

V VI VII VIII

The ability of the S-acids to decompose TBH was confirmed by separate experiments,[2,3,6] the activity of sulfonic acids V and VI was found to be comparable with that of sulfuric acid. The importance of formation of V and VI for an effective decomposition of TBH with thiobisphenols has also been confirmed by experiments in the presence of $CaCO_3$ or calcium (II) stearate ($CaSt_2$). The decomposition of TBH is markedly slowed down in the presence of these bases. At a sufficiently high concentration of the base, which is also affected by its compatibility with the reaction system, the decrease in the concentration of TBH in the system corresponds to oxidation transformations of thiobisphenol. Its oxidation transformation into phenolic sulfoxide and sulfone is slower in this case.

The ability to decompose hydroperoxides has also been studied with phenolic disulfides IIIa and IVa.[7] Under conditions comparable with the preceding ones, both dithio compounds react with TBH much more quickly than thiobisphenols Ia and IIa. The reaction rate is proportional to temperature and to the concentration of dithiobisphenol. Also in the case of dithiobisphenols two stages of decomposition of TBH can be distinguished. The first, "stoichiometric" stage proceeds very quickly and can be seen only in experiments carried out at a sufficiently low temperature, i.e. 65°C. In the "stoichiometric" stage the starting dithiobisphenols are oxidized to thiosulfinates IIIb and IVb. As has been demonstrated by experiments aimed at isolation and independent synthesis, phenolic thiosulfinates IIIb, IVb are unstable at room temperature. Their formation in the reaction mixture was indirectly proved by the chromatographic method (TLC, LC), and also on the basis of a quantitative analysis of further S-oxidation products of the starting disulfide. In the second stage of decomposition of TBH its concentration decreases very quickly to zero, also after the addition of another amount of TBH to the reaction mixture after the initial amount of hydroperoxide has decomposed. It should be pointed out that in this stage not only thiosulfinates IIIb and IVb are oxidized to thiosulfonates IIIC and IVc, but in the first place thiosulfinates and thiosulfonates are decomposed, giving rise to compounds, some of which catalyzed the decomposition of TBH. In accordance with the experiments involving phenolic sulfides, the formation of sulfur dioxide, sulfuric acid and sulfonic acids V or VI has also been detected. Along with sulfur-free quinoid compounds, the reaction mixture contained sulfoxides Ib, IIb and sulfones Ic, IIc at concentrations below those of thiosulfonate IIIc or IVc. A typical example of the decomposition of TBH with phenolic disulfide is shown in Figure 2. Thiosulfonates IIIC, IVc alone still decompose TBH under similar conditions, although the decomposition is slower than that brought about by the respective phenolic disulfides. In this case the concentration of thiosulfonates IIIc, IVc in the reaction mixture quickly decreases, being accompanied by the formation of sulfur-free quinoid compounds and S-acids V or VI. No formation of phenolic sulfoxide Ib, IIb and sulfone Ic, IIc has been observed in this case.[7]

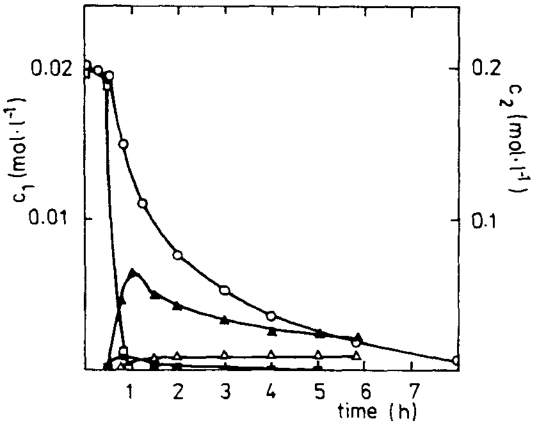


FIGURE 2 Changes in the concentrations of Ib, Ic, IIIa, IIIc (c_1) and TBH (c_2) during the reaction of TBH (0.2 mol/l) with disulfide IIIa (0.02 mol/l) at 65°C in chlorobenzene. (□) Ib, (△) Ic, (■) IIIa, (▲) IIIc, (O) TBH.

Similar investigations carried out in the presence of $CaSt_2$ again indicated a pronounced slowing-down of the decomposition of TBH, both by phenolic disulfides IIIA, IVa and by thiosulfonates IIIc, IVc. A stepwise quantitative LC analysis of the S-oxidation products of disulfide IIIa showed that the presence of $CaSt_2$ caused a considerable slowing-down of the formation of thiosulfonate IIIc, while sulfoxide Ib and sulfone Ic were not formed in this case at all.

THIO AND DITHIOBISPHENOLS AS ANTIOXIDANTS IN THE AUTOXIDATION OF TETRALIN

The effect of phenolic sulfide Ia, disulfide IIIa and of some of their oxidation products with the bisphenolic structure on the autoxidation of hydrocarbons at a temperature close to the atmospheric aging of polymers was investigated using tetralin as a model.[8] Its oxidation with oxygen under atmospheric pressure in chlorobenzene at 60°C was initiated with azobis(isobutyronitrile) which was used in a tenfold concentration, compared with the antioxidant under study. The consumption of oxygen indicated that the autoxidation of tetralin was considerably affected by the presence of all sulfur-containing bisphenols, except phenolic sulfone Ic. In addition to the induction period at the beginning of the experiment, the presence of the compounds under study in the subsequent process of autoxidation retarded the latter considerably. This retardation is due to the existence of a sulfur moiety in molecules of the compounds under study, as documented by a comparison with the activity of biphenyldiol VII which has a similar structure. The latter—by analogy with other biphenyldiols and alkylidenebisphenols—does not slow down the rate of oxidation of tetralin after a long induction period (Figure 3).

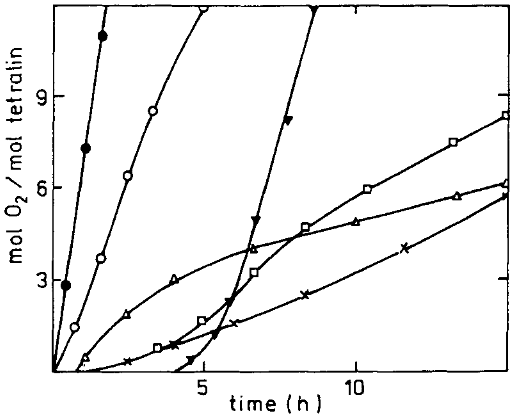


FIGURE 3 Oxygen consumption in the oxidation of tetralin (3.7 mol/l) at 60°C in chlorobenzene with AIBN as initiator (0.005 mol/l), antioxidant concentration 0.0005 mol/l. (●) without antioxidant; with addition of : (□) Ia, (△) Ib, (○) Ic, (×) IIIa, (▼) VII.

THIO AND DITHIOBISPHENOLS AS ANTIOXIDANTS IN THE AUTOXIDATION OF POLYPROPYLENE

The ability of thiobisphenols Ia, IIa, dithiobisphenols IIIa, IVa and of some of their oxidation products to slow down the autoxidation of polyolefins at processing temperatures was studied using isotactic polypropylene (PP) at 180°C. A PP melt with an admixture of antioxidant (at a concentration 0.025 mol/kg PP) was heated in an oxygen atmosphere at atmospheric pressure.[7,9,10] The consumption of oxygen showed that all the sulfur-containing bisphenols under study cause an induction period in the oxidation of PP at the beginning of the experiment and slow down its subsequent autoxidation (Figures 4, 5). According to the length of the induction period, in both isomeric series 2,2′ and 4,4′ phenolic disulfides possess the highest activity while phenolic sulfones, the weakest. The retardative

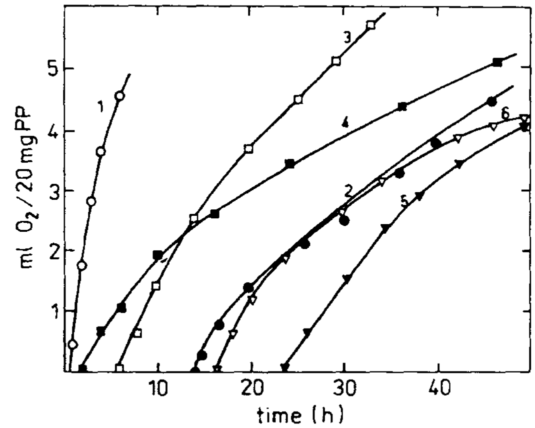


FIGURE 4 Oxygen consumption in the oxidation of PP at 180°C, antioxidant concentration 0.025 mol/kg PP. (1) unstabilized PP; PP stabilized with: (2) Ia, (3) Ib, (4) Ic, (5) IIIa, (6) IIIc.

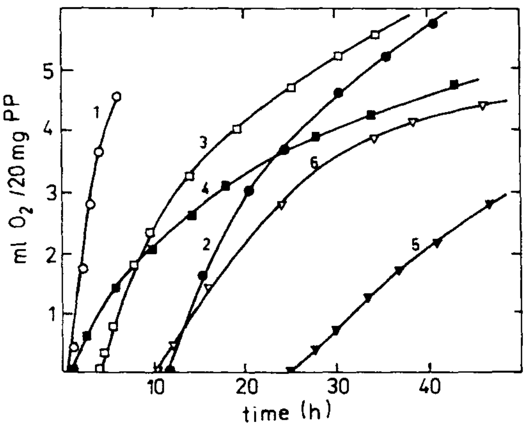


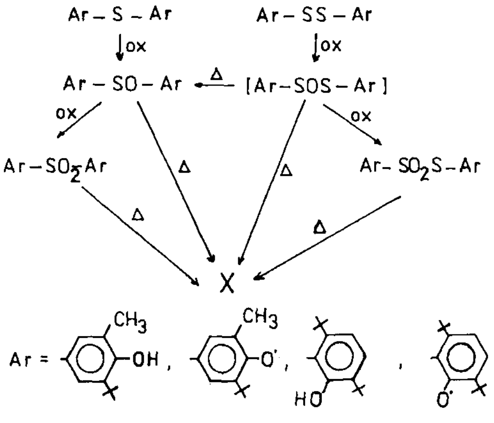
FIGURE 5 Oxygen consumption in the oxidation of PP at 180°C, antioxidant concentration 0.025 mol/kg PP. (1) unstabilized PP; PP stabilized with (2) IIa, (3) IIb, (4) IIc, (5) IVa, (6) IVc.

effect on the autoxidation of PP increase with the number of sulfur atoms in the molecule. This is also reflected in the fact that biphenyldiols VII and VIII, and methylene-bisphenols which have a similar structure, do not retard the autoxidation of PP which proceeds after a long induction period (9).

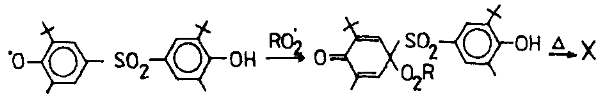
MECHANISM OF THE STABILIZATION PROCESS

Model experiments demonstrated the high antioxidant activity of thiobisphenols Ia, IIa and dithiobisphenols IIIa, IVa under various oxidation conditions. These bisphenolic compounds not only actively decompose hydroperoxides: experiments with the autoxidation of hydrocarbon substrates confirmed their ability to react with peroxy radicals[11] and to form the corresponding phenoxy radicals.[12,13] Both sites of these compounds possessing antioxidant activity, i.e. the phenolic and the sulfur moiety, preserve in molecules of thio and dithiobisphenols their properties of radical scavengers or hydroperoxide decomposers known from the monofunctional structures of phenols, sulfides and disulfides. Moreover, the presence of another active site in the molecule may raise the activity of the first one, as can best be seen in the ability of thiobisphenols Ia, IIa to decompose hydroperoxides. In contrast with the structurally similar bis(alkylphenyl) sulfides, the phenolic moiety facilitates the splitting of the Ar—S bond to such an extent that peroxidolytic compounds are formed from sulfoxides Ib, IIb and sulfones Ic, IIc in a significant concentration also at relatively low temperatures. This has not yet been observed in the case of sulfones having other structures. We have here an "activation" effect of the sulfide moiety similar to that found with molecules of 3,3-thiodipropionates.

The key part in the ability of thiobisphenols and dithiobisphenols to decompose hydroperoxides is played by their chemical transformations during the stabilization. The highly active peroxidolytic compounds (X), such as sulfur dioxide, sulfur trioxide, sulfuric acid and phenolic sulfonic acids V and VI are formed after the thermolysis of all compounds possessing the sulfidic or disulfidic site in a higher degree of oxidation. Hence, we have here either the thermolysis of



SCHEME 1.



SCHEME 2.

bisphenolic compounds Ib, Ic, IIb, IIc, IIIb, IIIc, IVb and IVc, or of phenoxy radicals derived from them (Scheme 1), or the decomposition of intermediates arising by the binding of $RO_2^{\cdot}$ to the bisphenolic skeleton. An example can be seen in Scheme 2.

DSC measurements of the compounds investigated in this study showed that along with the instability of phenolic thiosulfinates mentioned above, phenolic sulfoxides and thiosulfonates also decompose at temperatures below 180°C;[2] hence, at the processing temperature of polypropylene the mechanism of formation of compounds X according to Scheme 1 will be the predominant one.

Extrapolation of the data thus obtained to processing conditions leads to a conclusion that the chemical side of the antioxidant effects of thio and dithiobisphenols in the processing of polyolefins consists in the formation and transformations of phenoxy radicals and in the thermochemistry of thermally unstable S-oxidation products, predominantly, thiosulfinates, sulfoxides, and to some extent, thiosulfonates. Thus, both structures active in radical scavenging and strong peroxidolytic compounds are formed during the stabilization. The latter are of acid character, which may cause a change in the activity of thio and dithiobisphenols in their practical application in a mixture with additives possessing basic properties. An important feature for their use in multicomponent stabilization systems is that the particular active sites of these compounds keep their original character of antioxidant action. Thus, in order to raise the stabilization activity, thio and dithiobisphenols may be combined with monofunctional antioxidants of both the type of radical scavengers and that of hydroperoxide decomposers.

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