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ANTIOXIDANTS AND STABILIZERS—XXX*

INFLUENCE OF THE ALKYLIDENE- AND THIOBRIDGES ON THE ANTIOXIDATIVE ACTIVITY OF BISPHENOLS IN POLYPROPYLENE

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Abstract—An investigation was carried out of the stabilization activity of forty-three 2,2′- and 4,4′-biphenyldiols, alkylidenebisphenols, and thiobisphenols in isotactic polypropylene oxidized at 180°. With the various types of compounds, the optimal activity was achieved when the ring was substituted with *t*-butyl and methyl groups. By the comparison of activities of the optimal substituted bisphenols, a specific role was shown to be played by the bridges bonded at positions 2,2′ or 4,4′. In the series of alkylidenebisphenols, 2,2′-isomers having low steric requirements of the bridge were always more active. An increase in the volume of the bridge causes preference for isomers 4,4′. The highest activity was attained with 4,4′-thiobisphenols, for which a favourable effect of increase in the number of the sulphur atoms in the bridge can be observed.

INTRODUCTION

For the stabilization of isotactic polypropylene at about 200°, polynuclear phenols are quite suitable, and losses due to volatility are reduced. A knowledge of the influence of the structure on activity allows the choice of optimal stabilization systems. The antioxidative activity is affected by the character of substitution of the phenolic ring; the position and nature of the bridge must also be considered. The literature data(1–3) so far available do not give the necessary information. Therefore, we synthesized various biphenyldiols, alkylidenebisphenols, and thiobisphenols having bridges at positions 2,2′ and 4,4′; the chromatographically pure samples were used for the stabilization of isotactic polypropylene, oxidized at 180°.

EXPERIMENTAL

Substrate. Isotactic polypropylene (Research Institute of Macromolecular Chemistry, Brno; mol. wt. 510,000, atactic fraction 0·68%, stereoblocks 6·75%, ash 0·29%, titanium 0·017%, aluminium 0·11%) was stored before stabilization in argon at −5°.

Antioxidants. Phenolic compounds I–VIII were prepared and their purities were checked by means of paper chromatographic and TLC methods.

Method of determination of antioxidative activity and evaluation of the results. Activity of antioxidants was investigated during the oxidation of isotactic polypropylene at 180 ± 0·2° using oxygen absorption apparatus and procedure described previously.(4)

Concentration of antioxidants. 0·025 (c_1) and 0·05 (c_2) mol/kg of polypropylene. Standard: 2,2′-methylenebis (4-methyl-6-*t*-butylphenol) (IIIb), used at the same concentration as the antioxidant under investigation. The values of relative activity $A_r = (\tau_x - \tau_0)/(\tau_s - \tau_0)$ are calculated from $\tau_{0\cdot5}$, the time for 20 mg of the polymer to absorb 0·5 ml of oxygen (τ_x, τ_s are for polypropylene stabilized with compound under study and with standard, respectively; τ_0 is for nonstabilized polypropylene).

The values P_A representing the ratio of differences between the values of $\tau_{0\cdot5}$ determined at two concentrations (c_1 and c_2) of the phenol under investigation and the same value for unstabilized polymer,(5) and the values $S = 1/(\tau_{1\cdot5} - \tau_{0\cdot5})$ representing the slope of absorption curve after the induction period are given in Tables 1–4.

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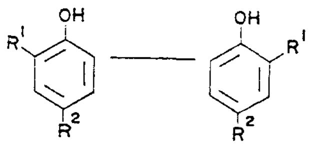

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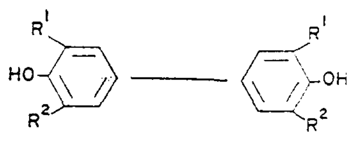

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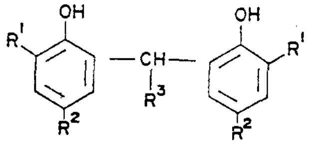

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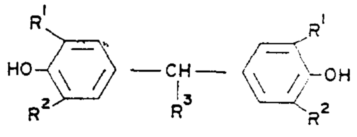

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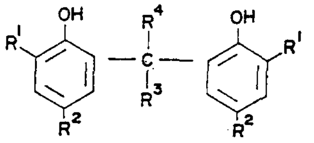

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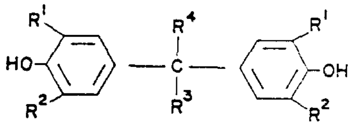

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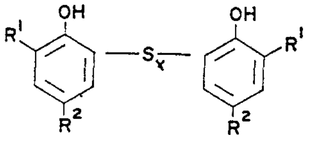

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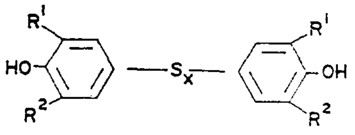

VIII

RESULTS

To obtain more information of the effect of the nature and position of the bridge in bisphenols, we investigated, for stabilization of isotactic polypropylene, series of tetra-alkylated derivatives of biphenyldiols (I, II), alkylidenebisphenols having a secondary, tertiary (III, IV), or quaternary (V, VI) carbon atom connecting the rings, and also thiobisphenols (VII, VIII). The standard compound used for comparing the activities was 2,2′-methylenebis (4-methyl-6-*t*-butylphenol) (IIIb).

By comparison of activities of both isomeric series of biphenyldiols, methylenebisphenols,(6,7) ethylidenebisphenols and isopropylidenebisphenols,(8) we confirmed that the optimal substitution of the phenolic rings is obtained by combination of the alkyl groups R^1 = *t*-Bu and R^2 = Me. Therefore, we used the derivatives thus substituted as a base for comparison of all the series under investigation.

Biphenyldiols (I, II): under the conditions chosen in this study, all the biphenyldiols under investigation were less active than the standard (Table 1) with the exception only of compound Ib measured at the concentration c_2. The isomers 2,2′ are more active. In the series of 4,4′-biphenyldiols (II), the optimal substitution of the ring is considerably affected by the concentration of the antioxidant.

Methylenebisphenols (III, IV, R^3 = H) were discussed in detail elsewhere.(6,7)

Ethylidenebisphenols (III, IV, R^3 = Me) are on the whole less active than methylenebisphenols (Table 2). The substitution of one hydrogen atom in the bridge with the methyl group plays its part, raising at the same time the steric requirements of the bridge. A comparison between the most active ethylidenebisphenols IIIf and IVd indicates preference for the 2,2′-isomer, even though the differences between the activities are not large and decrease with increasing concentration of the antioxidants.

TABLE 1. RELATIVE ACTIVITIES A_r, CONCENTRATION RATIOS P_A, AND SLOPES OF STRAIGHT LINES ON THE ABSORPTION CURVES S (ml min^{-1}) OF BIPHENYLDIOLS I AND II DURING THE INHIBITED OXIDATION OF ISOTACTIC POLYPROPYLENE AT 180° DETERMINED AT CONCENTRATIONS OF ANTIOXIDANT $c_1 = 0{\cdot}025$, AND $c_2 = 0{\cdot}05$ mol/kg OF POLYPROPYLENE; STANDARD: 2,2'-METHYLENEBIS (4-METHYL-6-*t*-BUTYLPHENOL) (IIIb) MEASURED AT THE SAME CONCENTRATION. FOR THE SIGNIFICANCE OF A_r, P_A AND S SEE EXPERIMENTAL SECTION.

$S_{\text{uninhibited polypropylene}} = 25{\cdot}6 \times 10^{-3}$ ml min^{-1}

Compound	Substituent		A_r		P_A	$S \times 10^3$ ml min^{-1}	
	R^1	R^2	c_1	c_2		c_1	c_2
Ia	Me	Me	0·64	0·72	1·21	16·1	18·2
b	*t*-Bu	Me	0·65	1·39	2·31	25·4	24·4
c	Me	*t*-Bu	0·67	0·80	1·31	30·5	23·3
d	*t*-Bu	*t*-Bu	0·12	0·19	1·68	26·2	27·2
IIa	Me	Me	0·34	0·35	1·1	21·3	29·1
b	*t*-Bu	Me	0·54	0·59	1·2	26·6	27·9
c	*t*-Bu	*t*-Bu	0·49	0·71	1·58	19·0	16·8

Butylidenebisphenols IIIh and IVf are less active than both methylenebisphenols and ethylidenebisphenols, which is consistent with a change in the steric hindrance caused by the bridge as a consequence of the increase in the volume of the substituent R^3. It was established, at the same time, that the 2,2'-isomer is more active also in this series. The difference between the activities of both isomers is larger than in the preceding series.

Benzylidenebisphenols (III, IV, R^3 = Ph). 4,4'-Benzylidenebis(4-methyl-6-*t*-butylphenol) (IVg) is an active antioxidant. On the contrary, a very low A_r was found for 2,2'-benzylidenebis(4-methyl-6-*t*-butylphenol) (IIIi). This is in good agreement with the findings, according to which the activity of 2,2'-methylenebisphenol steeply dropped

TABLE 2. ANTIOXIDATIVE PROPERTIES OF ALKYLIDENEBISPHENOLS III AND IV; SYMBOLS AND CONDITIONS AS IN TABLE 1.

Compound	Substituent			A_r		P_A	$S \times 10^3$ ml min^{-1}	
	R^1	R^2	R^3	c_1	c_2		c_1	c_2
IIIa	Me	Me	H	0·61	0·67	1·18	16·8	22·6
b	*t*-Bu	Me	H	1·00	1·00	1·09	21·1	16·7
c	Me	Me	H	0·23	0·31	1·46	26·0	26·6
d	*t*-Bu	*t*-Bu	H	0·36	0·37	1·11	23·3	20·0
e	Me	*t*-Bu	Me	0·56	0·61	1·18	26·9	26·6
f	*t*-Bu	Me	Me	0·82	1·00	1·32	24·6	20·8
g	*t*-Bu	*t*-Bu	Me	0·43	0·52	1·32	23·9	19·3
h	*t*-Bu	Me	Pr	0·57	0·71	1·37	26·6	25·3
i	*t*-Bu	Me	Ph	0·04	0·08	2·26	28·2	23·8
IVa	Me	Me	H	0·55	0·60	1·18	23·8	26·3
b	*t*-Bu	Me	H	1·02	0·92	0·96	31·0	22·5
c	*t*-Bu	*t*-Bu	H	0·72	0·66	0·98	29·0	23·4
d	*t*-Bu	Me	Me	0·77	0·97	1·36	30·0	23·2
e	*t*-Bu	*t*-Bu	Me	0·49	0·63	1·41	23·0	22·3
f	*t*-Bu	Me	Pr	0·43	0·49	1·26	32·7	24·5
g	*t*-Bu	Me	Ph	0·76	0·96	1·37	25·7	23·8

after one hydrogen atom of the bridge had been substituted with a phenyl group during stabilization of β-carotene(2) or vulcanized rubber.(9)

Isopropylidenebisphenols (V, VI; $R^3 = R^4 = Me$). The structural dependences in the series of 4,4′-isopropylidenebisphenols were discussed previously.(8) The stabilizing activity of four different 2,2′-isopropylidenebisphenols (V, $R^3 = R^4 = Me$) can be seen in Table 3. In contrast with the preceding couples of isomeric alkylidenebisphenols under study, 4,4′-isopropylidenebisphenols are stronger inhibitors than the 2,2′-isomers, at both concentrations under investigation. 4,4′-Isopropylidenebisphenol VIb is approached as to its activity by 4,4′-cyclohexylidenebis(2-methyl-6-*t*-butyl phenol) (VIe).

TABLE 3. ANTIOXIDATIVE PROPERTIES OF ALKYLIDENEBISPHENOLS V AND VI; SYMBOLS AND CONDITIONS AS IN TABLE 1.

Compound	Substituent				A_r		P_A	$S \times 10^3$ ml min^{-1}	
	R^1	R^2	R^3	R^4	c_1	c_2		c_1	c_2
Va	Me	Me	Me	Me	0·12	0·25	2·17	21·8	24·0
b	*t*-Bu	Me	Me	Me	0·19	0·33	1·84	22·9	22·6
c	Me	*t*-Bu	Me	Me	0·12	0·13	1·20	23·3	22·5
d	*t*-Bu	*t*-Bu	Me	Me	0·14	0·15	1·08	21·0	25·5
e	*t*-Bu	Me	Et	Me	0·05	0·16	3·21	22·7	23·7
VIa	Me	Me	Me	Me	0·20	0·27	1·67	24·2	20·7
b	*t*-Bu	Me	Me	Me	0·26	0·42	1·71	20·1	23·1
c	*t*-Bu	*t*-Bu	Me	Me	0·27	0·38	1·53	26·4	26·7
d	*t*-Bu	Me	Et	Me	0·18	0·32	1·69	26·3	25·4
e	*t*-Bu	Me	$—(CH_2)_5—$*		0·22	0·34	1·63	30·8	29·0

* Part of a cyclohexylidine ring.

sec-Butylidenebisphenols (V, VI, $R^3 = Me$, $R^4 = Et$). Both the isomeric compounds under investigation, Ve and VId, are only slightly active. A comparison between the A_r values of the two respective pairs of isopropylidenebisphenols and *sec*-butylidenebisphenols, Vb–Ve and VIb–VId, clearly shows that an increase in the steric effect of the bridge is less pronounced at position 4,4′. This isomer is more active, too.

Thiobisphenols (VII, VIII). It can be seen from results presented in Table 4 that the effect of the substitution at the ring on the activity of 2,2′-monothiobisphenols (VII, $x = 1$) at 180° depends on concentration: at a lower concentration (c_1), and with the exception of a very active thiosbiphenol VIIb, A_r of the other compounds of this series is not affected by the nature of substitution in the ring. At a higher concentration of the inhibitor, however, the structural effects become clearly perceptible. For 4,4′-thiobisphenols (VII, $x = 1$), the same rules concerning the effect of substitution in the ring can be applied as in the series of 4,4′-alkylidenebisphenols.

A very favourable effect was observed when a further sulphur atom was introduced into the bridge of the optimally substituted 2,2′- and 4,4′-thiobisphenols: A_r increases by approximately a multiple of 1·4 for each additional sulphur atom. This result can be regarded as proof of the active participation of the sulphur forming the bridge in the mechanism of the inhibition process.

TABLE 4. ANTIOXIDATIVE PROPERTIES OF THIOBISPHENOLS VII AND VIII; SYMBOLS AND CONDITIONS AS IN TABLE 1.

Compound	Substituent			A_r		P_A	$S \times 10^3$ ml min^{-1}	
	R^1	R^2	x	c_1	c_2		c_1	c_2
VIIa	Me	Me	1	0·46	1·11	2·6	10·6	4·8
b	*t*-Bu	Me	1	1·10	2·50	2·48	8·15	5·9
c	Me	*t*-Bu	1	0·42	0·95	2·49	7·05	6·9
d	*t*-Bu	*t*-Bu	1	0·48	1·71	3·86	11·2	5·7
e	*t*-Bu	Me	2	1·41	4·76	3·66	5·9	1·9
VIIIa	Me	Me	1	0·76	1·29	1·83	9·2	2·4
b	*t*-Bu	Me	1	0·98	2·95	3·26	7·0	3·9
c	*t*-Bu	*t*-Bu	1	0·47	0·81	1·87	7·6	3·4
d	*t*-Bu	Me	2	1·47	6·40	4·8	5·6	3·1
e	*t*-Bu	Me	3	1·80	6·08	3·67	2·8	1·4

DISCUSSION

Biphenyldiols and alkylidenebisphenols

A change in the optimal substitution of the rings of the series of phenols under comparison, characterized by the presence of the *t*-butyl (R^1) and methyl (R^2) groups, reduces the antioxidative activity. A very weak activity was found for the tetra-*t*-butyl-derivatives. The decrease in activity is particularly marked in the series of 2,2′-biphenyldiols; it can be explained as a consequence of the sum of the negative effects of the steric hindrance of hydroxy groups caused by both the ortho-*t*-butyl group and the substituted phenyl group. At the same time, the substitution of both positions 4 with a further *t*-butyl group limits the access of the radicals ROO· (or RO·) to these positions, and the reactivity of the mesomeric forms of aryloxyl.

If we compare the A_r values (for c_1) obtained by us for the optimal substituted 2,2′-bisphenols (I, III, V, $R^1 = t$-Bu, $R^2 =$ Me), we demonstrate the importance of the bridge: methylene > ethylidene > direct bond A_r–A_r (biphenyldiols) > butylidene ≫ isopropylidene > *sec*-butylidene > benzylidene. A slightly different trend follows from the data given by Bickoff and co-workers;(2) however, they were obtained under quite different conditions (stabilization of solutions of β-carotene at 75°). It is evident that 2,2′-alkylidenebisphenols form two distinct groups of antioxidants having very different activities. Biphenyldiols and (with exception of 2,2′-benzylidenebisphenols) all compounds having at least one hydrogen atom at the carbon atom connecting both phenolic rings are more active. It is therefore probable that these hydrogen atoms also participate in the interruption of the chains of radical oxidation, and the C—H bond of the bridge can be regarded as another active centre of the antioxidant. The order of the bridges also demonstrates the decrease in activity with increasing steric requirements of the substituent R^3, which influences the access of the alkylperoxy radicals to the hydroxyl group or to the carbon atoms of the phenolic ring to which the bridge is bonded. The high activity of 2,2′-bisphenyldiols I is probably due to an easy delocalization of the unpaired electron in the diphenosemiquinone radical formed from the inhibitor, leading to its higher stability. We wish here to note the extraordinary high relative activity of compound Ib at the concentration c_2. This fact changes the relations in the role of bridges given for the concentration c_1.

A very weak relative activity of 2,2'-benzylidenebis (4-methyl-6-*t*-butylphenol) (IIIi) can be explained as follows: with respect to the proximity and position of all the three benzene rings at the minimal strain of bonds in the molecule, it is possible to assume the formation of a strong hydrogen bond O—H . . . π between the hydroxyl groups and π-electrons of the phenyl group. The energy needed for splitting-off a hydrogen atom, thus bonded, by the radical ROO˙ (RO˙) is then higher than when a strong intramolecular bridge is absent, and the antioxidant is less active.

A weak activity is also observed with all 2,2'-alkylidenebisphenols V, in which both hydrogen atoms of the methylene bridge are substituted with alkyl groups. This substitution makes it impossible to increase the stoichiometric coefficient due to the participation of the C—H bonds of the bridge. The activity decreases with increasing volume of the alkyl groups R^3 and R^4.

The activity of 4,4'-alkylidenebisphenols II, IV and VI decreased according to the nature of the bridges in the following order: methylene > ethylidene, benzylidene > direct connection A_r—A_r (biphenyldiols) > butylidene $\gg$ isopropylidene, cyclohexylidene, *sec*-butylidene. Here, too, two groups of compounds can be distinguished, having different activities according to the nature of the alkylidene bridge. Biphenyldiols and compounds having a hydrogen atom at the carbon atom connecting the rings possess higher activity. A comparatively unimportant role is played by the steric effects of the substituents R^3. Very good antioxidative properties have been found with benzylidenebisphenol. It is as active as ethylidenebisphenol, although the benzene ring bonded at the bridge is bulkier than the methyl group, and its polar effect is negative. In this case, however, the negative inductive effect is probably less important than the resonance effect, which stabilizes the phenoxy radicals formed from bisphenol during autoxidation. The unpaired electron is delocalized to three aromatic nuclei. Moreover, the hydrogen atom bonded at the carbon atom connecting three aromatic rings has a reduced bond energy of the C—H bond; its participation in the interruption of the radical chain reaction during autoxidation may be considered.

All bisphenols without a hydrogen atom at the carbon atom connecting the rings are weak inhibitors; only insignificant differences are observed between the individual types. It can be shown, comparing this series of compounds, that in the case of bridges bonded in the para position an increase in the steric requirements hardly affects the activity.

From a comparison of the activities of isomeric 2,2'- and 4,4'-alkylidenebisphenols according to the nature of the bridges, it follows that the isomers having bridges in the ortho position are always more active if at least one hydrogen atom is present in the bridge and if the steric requirement of the bridge is smaller. 2,2'-Alkylidenebisphenols are significantly more affected by bridge substitution than 4,4'-isomers.

Thiobisphenols

It can be seen from the comparison of activities of both isomeric groups of thiobisphenols that, at a lower concentration of inhibitors (c_1), the optimally substituted 2,2'-thiobisphenol (VIIb) is only insignificantly more active than the 4,4'-isomer (VIIIb). However, for identically substituted dithiobisphenols, the ratio of activities of both isomers is quite opposite; at a concentration c_2, all bisphenols having the bridge in the para position are always more active. This fact will be examined more closely later.

Comparison of alkylidenebisphenols and thiobisphenols

In some papers, the inhibition activity of thiobisphenols was compared with that of alkylidenebisphenols. It was stated that, in the oxidation of hydrocarbon substrates (in white medicinal oil or polyolefins) and particularly at elevated temperatures, thiobisphenols are very active antioxidants;(3,10–13) they are more active than identically substituted methylenebisphenols. Under other conditions, especially at a lower temperature of oxidation and in stabilization process of more complex substrates, i.e. vegetable oils,(14,15) solution of β-carotene(2) or vulcanized rubber,(9) thiobisphenols have a weaker stabilizing effect than methylenebisphenols. However, in these cases also, their antioxidative activity increases with temperature. However, it was also stated that thiobisphenols even exhibit a pro-oxidative effect(16) in polyacrylates.

From our comparison of activities of several series of isomeric 2,2′- and 4,4′-alkylidenebisphenols and -thiobisphenols in the oxidation of isotactic polypropylene at 180°, it follows that, at a concentration of the inhibitor 0·025 mol/kg, monothiobisphenols were in both isomeric series as strong inhibitors as methylenebisphenols (i.e. the most active group of alkylidenebisphenols under investigation). At a higher concentration of the inhibitor, the superiority of the sulphur derivatives is evident: 2,2′-thiobis(4-methyl-6-*t*-butylphenol) is almost twice as active as identically substituted methylenebisphenol. In bisphenols having the bridge in the para position, the sulphur derivative is even three times as active; the presence of two or three sulphur atoms in the bridge enhances the difference between alkylidene and thiobisphenols still further.

The cause of the high activity of thiobisphenols in polypropylene at high temperature can be seen in the simultaneous participation of two mechanisms of inhibition, especially at a higher concentration of the inhibitor. Behaving as phenols, they terminate the propagation step of the autoxidation by their reaction with the $ROO^\cdot$ radicals; as sulphides, they can decompose hydroperoxides into non-radical products.

From the investigation of the course of inhibited oxidation of polypropylene, some preliminary conclusions have been drawn concerning the possible participation of the reaction products formed from the antioxidants used during autoxidation. Tables 1–4 show slopes of absorption curves after the induction period has ended. If the slopes of the curves of the inhibited and uninhibited oxidation reactions coincide, the products do not affect the reaction in the oxidation phase under investigation. If the slope has a value higher than in the uninhibited oxidation, pro-oxidative effect of some of the reaction products can be considered; on the contrary, a lower slope indicates retardation activity. For uninhibited polypropylene, the slope was found to be $25{\cdot}6 \times 10^{-3}$ ml min^{-1}; the slopes of all investigated alkylidenebisphenols and biphenyldiols lie within experimental error over the measured range of inhibitor concentrations and oxygen absorption in the same region. Judging by this, the reaction products do not affect the course of thermal oxidation. Generally the slopes of absorption curves found for polypropylene stabilized with thiobisphenols have a value much lower than that for polypropylene alone; at the same time, their values depend on the concentration of thiobisphenols and the number of the sulphur atoms in the bridge. This fact indicates an interference of the reaction products with the whole mechanism of autoxidation. To obtain a fuller explanation, more detailed experimental results on the action of thiobisphenols during inhibited oxidation of polyolefins are necessary.

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Résumé—On a étudié laction stabilisatrice de quarante trois biphényldiols 2-2′ et 4-4′ d'alkylidenbisphénols et de thiobisphénols dans l'oxydation à 180° du polypropylène isotactique. Avec les différents types de composés, l'activité optimale était atteinte quand le cycle était substitué par des groupes *t*-butyles et méthyles. En comparant les activités des bisphénols substitués optimaux, on a montré que les ponts liés en position 2-2′ et 4-4′ jouaient un rôle spécifique. Dans les séries des alkylidène bisphénols, les isomères 2-2′ ayant un encombrement stérique du pont plus faible, étaint toujours plus actifs. L'activité la plus élevée est obtenue avec les thiobisphébols 4-4′, pour lesquels on a observé un effet favorable de l'augmentation du nombre d'atomes de soufre dans le pont.

Sommario—Si è eseguita un'indagine dell'attività di stabilizzazione di 43 2,2′- e 4,4′-bifenildioli alchilidenebisfenoli e tiobisfenoli in propilene isotattico ossidato a 180°. Con i vari tipi di composti, l'attività ottimale viene raggiunta quando l'anello è sostituito da gruppi *t*-butil e metil. Comparando le attività dei bisfenoli sostituti in modo ottimale, si mostra che un ruolo particolare è giocato dai ponticelli in posizione 2,2′ e 4,4′. Nella serie degli alchilidenebisfenoli, gli isomeri 2,2′ con bassa stericità dei ponticelli sono sempre più attivi. Un aumento di volume dei ponticelli determina una preferenza per gli isomeri 4,4′. L'attività maggiore si ottiene con i 4,4′-tiobisfenoli, con i quali si osserva l'effetto favorevole dell'aumento del numero degli atomi di zolfo nei ponticelli.

Zusammenfassung—Die Stabilisierungsaktivität von 43 Proben von 2,2′- und 4,4′-Biphenyldiolen, Alkylidenbisphenolen und Thiobisphenolen wurde in isotaktischem Polypropylen durch Oxidation bei 180° untersucht. Unter den verschiedenartigen Produkten wurde optimale Aktivität erreicht, wenn der Ring durch *t*-Butyl- und Methylgruppen substituiert war. Bei einem Vergleich der Aktivitäten der optimal substituierten Bisphenole zeigte sich, daß die an den Positionen 2,2′ oder 4,4′ gebundenen Brücken eine spezifische Rolle spielen. In der Reihe der Alkylidenbisphenole waren die 2,2′-Isomeren, die geringe sterische Anforderungen für die Brücke haben, immer aktiver. Eine Zunahme des Volumens der Brücke bewirkt eine Bevorzugung für 4,4′-Isomere. Die höchste Aktivität wurde mit 4,4′-Thiobisphenolen erhalten, bei denen ein günstiger Einfluß mit zunehmender Zahl der Schwefelatome in der Brücke beobachtet werden kann.