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ANTIOXIDANTS AND STABILIZERS—XXIII

INFLUENCE OF THE STRUCTURE OF METHYLENEBISPHENOLS ON ANTIOXIDATIVE ACTIVITY IN ISOTACTIC POLYPROPYLENE

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Abstract—An investigation has been made of the antioxidative activity of methylenebisphenols, methylenebis(alkoxyphenols), methylenebis(pyrocatechols) and (3,4-dimethoxybenzyl)phenols in the stabilization of isotactic polypropylene. Methylenebisphenols appear to be the most active antioxidants if they are appropriately substituted. Methylenebis(pyrocatechols) are the least active, but their activity is improved by partial etherification.

INTRODUCTION

ALKYLATED mononuclear mono- and polyhydric phenols act as antioxidants in various organic substrates. However, owing to their volatility, they are less suitable for stabilizing macromolecular systems at elevated temperatures. The volatility can be lowered by condensing them with appropriate oxocompounds; methylenebisphenols are the compounds having the simplest carbon bridge. In spite of the importance, there is little knowledge about relations between structure and antioxidative activity. Approximate conclusions on the effect of substitution upon the activity of 2,2′- and 4,4′-methylenebisphenols can be derived by comparing values for a few compounds investigated in the stabilization of polyethylene(1,2,3) at temperatures between 110 and 170°, in the stabilization of paraffin wax(4) at 163°, or in the stabilization of an oil solution of carotene(5) at 75°. To include the effect of substituents completely and to compare them with other types of antioxidants under the same conditions, we have examined the antioxidative activities of a series of methylenebisphenols in isotactic polypropylene.

EXPERIMENTAL

Materials

Antioxidants. The phenols I–XVII were chromatographically pure; they were prepared by procedures based on those described in the literature.(6–10)

Substrate. Isotactic polypropylene (Research Institute of Macromolecular Chemistry, Brno): mol. wt. 510,000, atactic fractions 0·68%, stereoblocks 6·75%, ash 0·29%, titanium 0·017%, aluminium 0·11%.

Method of determination of the activity and evaluation of the results. The activities of methylenebisphenols and methylenebispyrocatechols were examined in the oxidation of isotactic polypropylene at 180 ± 0·2° in oxygen at atmospheric pressure; the concentration of the antioxidant was 0·025 mole/kg and 0·05 mole/kg, respectively (in the case of trinuclear phenols it was 0·0167 mole/kg). The time dependence of the oxygen absorption was measured with a volumetric apparatus, and the relative activity was calculated as described previously.(11) 2,2′-Methylenebis(4-methyl-6-tert-butylphenol) was used as standard in the calculations of the relative activity A_{r1}, at a concentration identical to that of the antioxidant under study. The relative activity A_{r2} was calculated using pyrocatechol (0·05 mole/kg of polypropylene) as standard. The values of A_{r1} and A_{r2} are given in Tables 1 to 3.

DISCUSSION

On substituting phenol with alkyls in positions 2 or 2,6, the antioxidative activity changes owing to the polar and steric effects of substituents. The substitution of 4,4′-methylenebisphenol (II, R^1, R^2 = H) also has a considerable effect; this compound itself is five to seven times more active than phenol. Apparently, the difference in the mechanism of participation of the compounds in the autoxidation process has a favourable effect. An increase in the activity of 4,4′-methylenebisphenol in the stabilization of polyethylene by substituting positions 2 and 6 of both nuclei with cyclohexyls, and more particularly with tert-butyls was observed by Clark and Havens.(3) A tert-butylated derivative (II, R^1, R^2 = *t*-Bu) is more active than those in which R^1 and R^2 are cyclohexyl, methyl, or isopropyl.(2) Better properties of 4,4′-methylenebis(2-methyl-6-tert-butylphenol) (II, R^1 = Me, R^2 = *t*-Bu) compared with the tetramethyl derivative (II, R^1, R^2 = Me) have been described.(1) In the series of antioxidants of Type II examined by us, an increase in the volume of the substituent R^2 manifests itself, in the case of a constant substitution at position R^1 with methyl, by a change of the activity in the following order: R^2 = Me < *t*-Bu > *t*-Oc (Table 1). A similar(2) influence of the substituents was also observed in the stabilization of tetralin(12) at 60°.

All the examined antioxidants of type II were more active than trialkylphenols of type I, some of which, e.g. 2,6-ditert-butyl-4-methylphenol (I, R^1, R^3 = *t*-Bu, R^2 = Me) or 2,4-dimethyl-6-tert-butylphenol (I, R^1, R^2 = Me, R^3 = *t*-Bu) are commonly suggested for the stabilization of polyolefins. The generally higher activity of the corresponding binuclear phenols with a methylene bridge can be explained by differences in their roles in the mechanism of the inhibition process. For example, the possibility of participation of the hydrogen atoms of the methylene group in the interruption of the autoxidation reaction cannot be neglected. It can be demonstrated for the antioxidant groups I and II that the effect of substitution at both ortho positions to the hydroxyl group is markedly influenced by the substitution in the para position. In the antioxidants I, where R^2 = Me, position 4 can be easily attacked by the alkylhydroperoxide radical, derived from the oxidized substrate. As a consequence, rather bulky substituents can be present in positions 2 and 6. In the case of appropriate hindrance of the hydroxyl in the compounds of type I, the antioxidative activity is reduced by increase in the volume of the substituent at the para position. This can be explained by the reduced possibility of reaction with the alkylhydroperoxide radical at that position. Compared with trialkylphenols I, methylenebisphenols II exhibit their greatest activity for lower steric hindrance of the hydroxyl with the substituents R^1 and R^2. It can be explained by the fact that in this case the reaction of the antioxidant with the radical $ROO^{\cdot}$ (or $RO^{\cdot}$) occurs more easily at the position ortho to the hydroxyl than at the para position, since the latter (in which the methylene bridge is bonded) is less accessible. This is in agreement with the finding that still less favourable influence upon the antioxidative activity by the presence of two bulky alkyls in positions 2,6 was observed in the series of 4,4′-*iso*propylidenebisphenols;(13) the isopropylidene bridge in the para position is a substituent which plays an even more important part sterically than the methylene bridge in compounds of type II.

The nature of the substituents manifests itself markedly also in the activity of 2,2′-methylenebisphenols (III), isomeric with the preceding series of antioxidants of Type II.

The literature data do not allow unambiguous comparison of the activities of both groups. The antioxidative activities of bisphenols II and III are approximately the same in the stabilization of polyethylene and tetralin.(1,12) A higher activity of 4,4'-methylenebisphenols compared with the 2,2'-isomers follows from the data on the stabilization of polypropylene,(3) white medicinal oil,(14) and paraffin wax;(4) a reverse order of isomers was found in the stabilization of carotene.(5) Some conclusions on the effect of substitution of methylenebisphenols III in the oxidation of polypropylene can be drawn from the results of our investigation (Table 1).

TABLE 1. RELATIVE ACTIVITIES, A_{r1}, OF THE ANTIOXIDANTS II TO V AND XII IN THE INHIBITED OXIDATION OF ISOTACTIC POLYPROPYLENE AT 180°; STANDARD: 2,2'-METHYLENEBIS(4-METHYL-6-TERT-BUTYLPHENOL) MEASURED AT THE SAME CONCENTRATION

Substance	Substituent		Antioxidant concentration	Mole/kg of polymer
	R^1	R^2	0·025	0·05
II	H	H	0·18	0·24
	Me	Me	0·56	0·61
	Me	*t*-Bu	1·02	0·92
	Me	*t*-Oc	0·47	0·45
	t-Bu	*t*-Bu	0·73	0·66
	EtO	Me	0·53	0·59
	MeO	H	0·36	0·55
III	Me	Me	0·62	0·68
	Me	*t*-Bu	0·24	0·32
	Me	*t*-Oc	0·23	0·25
	t-Bu	Me	1·00	1·00
	t-Oc	Me	0·77	0·98
	t-Bu	*t*-Bu	0·37	0·37
	MeO	Me	0·91	0·98
IV	MeO	Me	0·66	0·62
	EtO	Me	0·88	0·69
V	EtO	Me	0·80	0·77
XII	H	H	0·10	0·09
	Me	H	0·06	0·09
	H	Me	0·09	0·08

In the substitution of the position para to hydroxyl with methyl (III, R^2 = Me), the relative antioxidative activity increases with increase in the volume of the substituent R^1, as long as a certain limiting volume is not exceeded. For the conditions under study, the best substitution was achieved for 2,2'-methylenebis(4-methyl-6-tert-butylphenol) (III, R^1 = *t*-Bu, R^2 = Me). The antioxidative activity of this compound is practically identical with that of 4,4'-methylenebis(2-methyl-6-tert-butyphenol) (II, R^1 = Me, R^2 = *t*-Bu). However, an antioxidant of type III having substituent R^1 of larger volume (R^1 = *t*-Oc, R^2 = Me) is less active. A very favourable effect is observed when the methoxyl group is present in positions 6,6' (III, R^1 = OMe, R^2 = Me).

A condition for attaining a high antioxidative activity for compounds of type III in the stabilization of polypropylene is therefore to be seen in the substitution of the position para to hydroxyl with methyl, and of the ortho position with a tertiary alkyl (preferably tert-butyl) or alkoxyl. Deviations from this rule lead to a considerable reduction in the antioxidative activity. The importance of substitution is obvious from the fact that the activity of an antioxidant containing tertiary alkyls in positions 4 and 6 (III, R^1, R^2 = *t*-Bu) lies between those of the groups of compounds for which substitution is the cause of a high (III, R^1 = tert-alkyl, R^2 = Me) or a weak (III, R^1 = Me, R^2 = tert-alkyl) antioxidative activity.

Some interesting conclusions follow from the investigation of the activity of methylenebispyrocatechols; they allowed us to complete our knowledge obtained by the investigation of alkylpyrocatechols and 2-alkoxyphenols.(11) It followed from previous work that pyrocatechol was, in the stabilization of isotactic polypropylene and other substrates, a considerably stronger antioxidant than phenol. The activity of its monomethyl derivatives was, however, even greater. In agreement with the behaviour of mononuclear phenols, 4,4′-methylenebispyrocatechol (XII, R^1, R^2 = H) was a better antioxidant in the oxidation of tetralin(12) than 4,4′-methylenebisphenol (II, R^1, R^2 = H). It is therefore surprising that, contrary to what was said above, the relative activity of 4,4′-methylenebispyrocatechol in the stabilization of polypropylene is less than that of 4,4′-methylenebisphenol (Table 1). A weak activity was also observed with the methyl derivatives of compound XII. All the studied methylenebispyrocatechols XII and XIII are less active than pyrocatechol alone. The activity of methylenebispyrocatechols, however, is specifically enhanced by partial etherification, contrary to that of alkylpyrocatechols (Tables 1 and 2). Compare now the compounds II (R^1 = EtO, R^2 = H), VI, VII (R = H), VIII (R = H), and IX with 2-alkoxyphenols, from which they have been derived. Guaiacol or/and guaethol have a weak antioxidative activity. Rather a small increase in activity follows the substitution of guaethol with methyl in positions 4, 5, or 6; the activity decreases in the above order of isomers. Thus, partial etherification of mononuclear pyrocatechols causes a significant reduction of antioxidative activity.(11) The above mentioned 2-alkoxyphenols can be compared with binuclear model antioxidants: 4-(3,4-dimethoxybenzyl)pyrocatechol (IX), 2-methoxy-4-(3,4-dimethoxybenzyl)phenol (VI), 2-methoxy-5-(3,4-dimethoxybenzyl)phenol (VII, R = H), and 2-methoxy-6-(3,4-dimethoxybenzyl)phenol (VIII, R = H). All these compounds are derivatives of pyrocatechol or guaiacol, substituted with the 3,4-dimethoxybenzyl group. Veratrol is completely inactive as an oxidation inhibitor.(11) However, the presence of the veratryl groups bound to methyls in position 4 or 5 of the molecule of guaiacol had a very favourable effect; the relative activities of compounds VI and VII (R = H) (Table 2) are very high in comparison with pyrocatechol, and particularly with 4,4′-methylenebispyrocatechol (XII, R^1, R^2 = H). The activity is also enhanced by the presence of methyl in the phenolic nucleus (compounds VIII, R = Me and VII, R = H). 4-(3,4-Dimethoxybenzyl)-pyrocatechol (XI) also is a significantly stronger antioxidant than 4,4′-methylenebispyrocatechol and can be compared with 4-methylpyrocatechol.(11)

In agreement with the order of the effect of the methyl position upon the activity of three isomeric 2-ethoxymethylphenols, the activity of the 2,3-dimethoxybenzyl derivatives also decreases. An isomer substituted at position 6 (VIII, R = H) is the weakest antioxidant in the series under study; however, its relative activity in the stabilization of polypropylene is greatly affected by concentration.

Less active is an analogue of compound VIII (R = Me) derived from 3,5-dimethylpyrocatechol by replacing methyl at position 5 with veratryl, i.e. 3-(3,4-dimethoxybenzyl)-5-methylpyrocatechol (X) (Table 2). The reduction of activity is increased by

TABLE 2. RELATIVE ACTIVITIES OF THE ANTIOXIDANTS VI–XI, XIII IN THE INHIBITED OXIDATION OF POLYPROPYLENE AT 180°; A_{r1} (STANDARD: 2,2′-METHYLENEBIS(4-METHYL-6-TERT-BUTYLPHENOL) MEASURED AT THE SAME CONCENTRATION) AND A_{r2} (STANDARD: PYROCATECHOL AT 0·05 mole/kg OF POLYMER)

Substance	Substituent	A_{r1} antioxidant concentration		A_{r2} mole/kg of polymer	
	R	0·025	0·05	0·025	0·05
VI	—	0·52	0·59	2·15	2·67
VII	H	0·46	0·45	1·92	2·04
	Me	0·56	0·78	2·32	3·54
VIII	H	0·17	0·43	0·69	1·94
	Me	0·38	0·69	1·57	3·14
IX	—	0·29	0·35	1·22	1·60
X	—	0·22	0·31	0·91	1·40
XI	—	0·18	0·18	0·74	0·83
XIII	—	0·04	0·06	0·18	0·29

TABLE 3. RELATIVE ACTIVITIES OF THE ANTIOXIDANTS XIV TO XVII IN THE INHIBITED OXIDATION OF POLYPROPYLENE AT 180°; A_{r1} (STANDARD: 2,2′-METHYLENEBIS(4-METHYL-6-TERT-BUTYLPHENOL) MEASURED AT THE SAME CONCENTRATION) AND A_{r2} (STANDARD: PYROCATECHOL AT 0·05 mole/kg OF POLYMER)

Substance	A_{r1} antioxidant concentration			A_{r2} mole/kg of polymer	
	0·025	0·05	0·0167	0·025	0·05
XIV	0·96	1·14	3·29	3·98	5·16
XV	0·51	0·81	1·33	2·14	3·67
XVI	0·74	1·18	2·36	3·08	5·33
XVII	0·12	0·15	0·50	0·54	0·70

the substitution of both methyls of 3,5-dimethylpyrocatechol with the veratryl residue, as can be seen for 3,5-bis(3,4-dimethoxybenzyl)-pyrocatechol (XI). Further compounds under investigation contain hydroxyl and methoxyl groups in both nuclei of the molecule of diphenylmethane. The simplest of these compounds is 4,4′-methylenebis(2-methoxyphenol) (II, R^1 = MeO, R^2 = H); its activity exceeds that of 4,4′-methylenebispyrocatechol (XII, R^1, R^2 = H). Outstanding antioxidative properties have also been observed with isomeric methylenebisalkoxyphenols having structures II to V (where R^1 = alkoxyl, R^2 = Me), obtained by the condensation of isomeric 2-methoxy- (or 2-ethoxy-) cresols with formaldehyde. It can be seen from the values given in Table 1 that the ethoxy derivatives are slightly more active than the methoxy derivatives; this is the same phenomenon as was observed in the comparison of the methyl derivatives of guaiacol and guaethol.(11) The antioxidative activity is affected by the position of the methylene bridge in the case of a particular arrangement of methyls and alkoxyls. The antioxidative activity of all the investigated methylenebisalkoxyphenols, however, considerably exceeds that of pyrocatechol and approaches methylenebisphenols of types II and III (where R^1, R^2 = alkyl group).

Relationships obtained in the study of methylenebisphenols can be supplemented by the results found for the activity of several trinuclear phenols derived from 2-alkoxycresols (compounds XIV to XVI), or from 4-methylpyrocatechol (XVII, Table 3). So far, the structure of these compounds, which represent a component of the higher-molecular weight fraction in the synthesis of binuclear antioxidants, has not been determined with accuracy. Only scattered data can be found in the literature concerning the activity of similar trisphenols: alkylated 2,6-(2-hydroxybenzyl)phenols could be compared in their activity with 2,2′-methylenebisphenols in the stabilization of the oil solution of carotene.(5) Morawetz(4) has compared the activity of polynuclear phenols with that of methylenebisphenols in the stabilization of paraffin wax oxidized at 163°. It follows from his findings that the presence of more than three phenolic nuclei in the molecule has a negative effect upon the antioxidative activity. Bailey(9) gives a higher antioxidative activity of the trinuclear phenol formed from two molecules of 2-methoxy-4-methylphenol and one molecule of p-cresol in comparison with 2,2′-methylenebis(4-methyl-6-methoxyphenol) III, R^1=MeO, R^2=Me) in the stabilization of polyethylene.

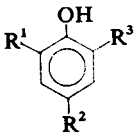
We have found that the trinuclear phenol XIV derived from 2-methoxy-4-methylphenol is more active in the stabilization of polypropylene than the binuclear analogues III and IV (R^1=MeO, R^2=Me). Compound XVI, formed from 2-ethoxy-6-methylphenol, also has an activity higher than that of the binuclear analogue (II, R^1=EtO, R^2=Me); it should be mentioned, however, that the last compound is the least active of the isomeric methylenebis(alkoxycresols). Compound XV prepared from 2-ethoxy-5-methylphenol is, at a concentration 0·025 mole/kg of polypropylene, less active than the binuclear analogue V (R^1=EtO, R^2=Me); at a concentration of 0·05 mole/kg of polymer, the activities of both antioxidants are balanced. Owing to incomplete knowledge about the structure of compounds XIV to XVI and to the small difference between their relative activities, no thorough analysis of the structural relationships can be carried out. It holds, however, that for compounds of the type of 2-alkoxyphenols the mononuclear phenols are the less active agents in the stabilization of polypropylene, and that the activity is considerably enhanced by transforming them into the binuclear phenols. A further increase in the size of the molecule has a favourable effect in most cases. A trinuclear compound derived from 4-methylpyrocatechol (XVII) is a very weak antioxidant; nevertheless, it is more active than the binuclear analogues, i.e. 3,3′-methylenebis(5-methylpyrocatechol) (XIII) and 4,4′-methylenebis(5-methylpyrocatechol) (XII, R^1=H, R^2=Me).

CONCLUSIONS

Polar and steric effects of the substituents on individual nuclei influence the antioxidative activity of methylenebisphenols in the stabilization of isotactic polypropylene. The differences between the activities of optimally substituted methylenebisphenols of types II and III are very small; therefore, the position of the methylene bridge is not important.

Antioxidative activity was found with guaiacol substituted by the 3,4-dimethoxybenzyl group; methylenebisphenols containing in each phenolic nucleus one alkoxyl and one methyl group, also exhibit sufficient antioxidative activity.

All the investigated methylenebispyrocatechols were less active antioxidants than



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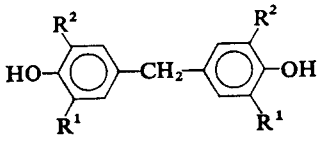

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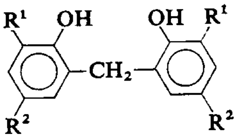

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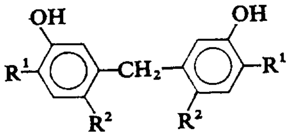

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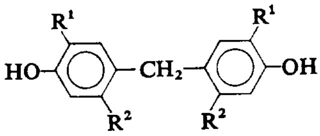

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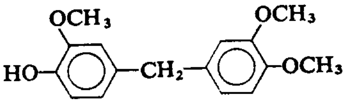

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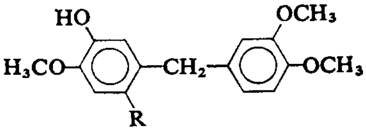

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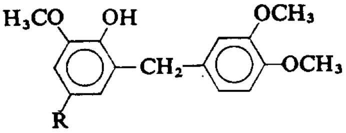

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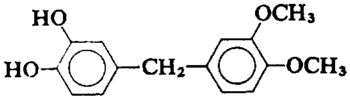

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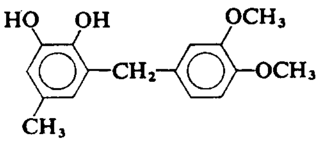

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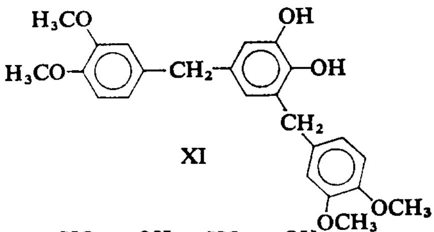

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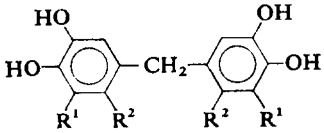

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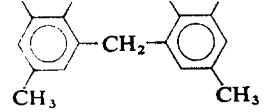

XIII

methylenebis(2-alkoxyphenols) and pyrocatechol itself. The activity is favourably influenced by partial etherification of at least one pyrocatechol nucleus.

The order of the types of binuclear antioxidants is as follows (the values of A_{r2} calculated for $\tau_{0\cdot5}$ are listed; $c_{\text{antiox.}} = 0\cdot05$ mole/kg of polypropylene, pyrocatechol used as standard):

2,2'-methylenebis(4-methyl-6-tert-butylphenol), III ($R^1 = t$-Bu, $R^2 = $Me), 4·52.
2,2'-methylenebis(4-methyl-6-methoxyphenol), III ($R^1 = $MeO, $R^2 = $Me), 4·18.
4,4'-methylenebis(2-methyl-6-tert-butylphenol), II ($R^1 = $Me, $R^2 = t$-Bu), 4·14.
3-(3,4-dimethoxybenzyl)-4-methyl-6-methoxyphenol, VII (R = Me), 3·54.
4-(3,4-dimethoxybenzyl)pyrocatechol, IX, 1·60.
4,4'-methylenebispyrocatechol, XII R^1, $R^2 = $H), 0·40.

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Résumé—On a étudié l'efficacité de l'action antioxydante de méthylène-bisphénols, de méthylène-bis(alcoxyphénols), de méthylène-bis(pyrocatéchols) et de diméthoxybenzyl 3,4 phénols sur la stabilisation du polypropylène isotactique.

Les méthylène-bisphénols se rélèvent être les antioxydants les plus actifs s'ils sont convenablement substitués. Les méthylène-bis(pyrocatéchols) sont les moins actifs, mais leur activité est renforcée par une éthérification partielle.

Sommario—Si sono effettuate delle indagini sull'attività antiossidante di metilenebisfenoli, metilenebis (alcossifenoli), metilenebis(pirocatecoli) e (3,4-dimetossibenzil)fenoli nella stabilizzazione di polipropilene isotattico. Sembra che i metilenebisfenoli siano gli antiossidanti più attivi, se essi sono sostituiti appropriatamente. I metilenebis(pirocatecoli) sono i meno attivi, però la loro attività viene migliorata con etirificazione parziale.

Zusammenfassung—Es wurde eine Untersuchung durchgeführt über die antioxydative Wirksamkeit von Methylenbisphenolen, Methylenbis (alkoxyphenolen), Methylenbis (pyrocatecholen) und (3,4-Dimethyloxygenzyl) phenolen bei der Stabilisierung von isotaktischem Polypropylen. Methylenbisphenole scheinen, wenn sie in geeigneter Weise substituiert sind, die aktivsten Antioxydantien zu sein. Methylenbis (pyrocatechole) sind die am wenigsten aktiven, aber ihre Wirksamkeit wird durch teilweise Veresterung verbessert.