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GEL CHROMATOGRAPHIC BEHAVIOUR OF BISPHENOLS*

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SUMMARY

The gel permeation chromatographic behaviour of fifty-one bisphenols was investigated with tetrahydrofuran as the eluent. In both isomeric series of compounds under investigation, the nature of the substitution of the aromatic ring has a greater influence than the volume and shape of the alkylidene bridge on the elution volume. The final effect also depends on the steric influence of substituents on the carbon atom that connects the phenolic rings and on the possibility of solvation of the phenolic groups which, in the series of 2,2'-bisphenols, is limited by the formation of intramolecular hydrogen bonds.

INTRODUCTION

Gel chromatography of low-molecular-weight compounds is becoming an important analytical method for the study of systems in which very mild conditions must be used, and in which other separation and analytical procedures are of limited applicability or have considerably lower accuracies. This method can be used advantageously in the quantitative analyses of stabilizing systems in polymers.

It follows from systematic investigations carried out so far on many structurally related compounds that the elution volume of a compound is in all cases inversely proportional to the size of the molecule. The more accurately defined the size of the molecule, the more correct is the predicted elution volume. However, the presence of an aromatic ring in the molecule and its substitution with solvatable groups render correlations much more difficult.

For polyolefin stabilization, complex mixtures of low-molecular-weight antioxidants, light stabilizers and synergists are frequently used. Most of the components of the stabilizing mixture are aromatic, and phenolic compounds are of great importance. For the separation and quantitative determination of the most important types, a gel chromatographic procedure has been suggested¹ which permitted the analysis of the extracts of isotactic polypropylene.

The present knowledge of the structural dependences that exist in the gel chromatography of low-molecular-weight phenolic compounds does not enable the conclusions of a general character to be drawn that are needed for the universal application and specific use of gel permeation chromatography (GPC) in the deter-

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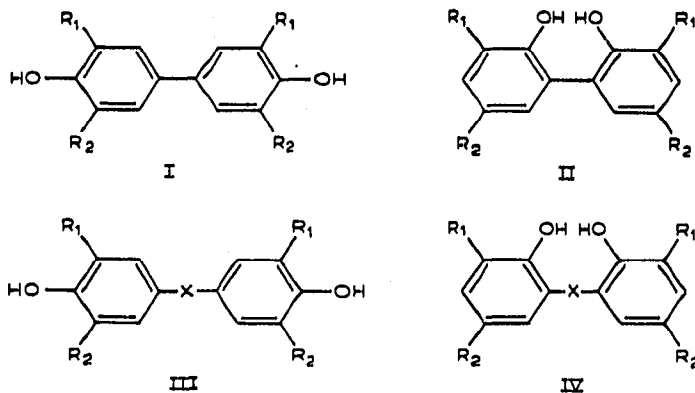
mination of the structures of some of the components of mixtures of structurally related compounds. Some data have been obtained on the effect of the solvation of the phenolic groups in tetrahydrofuran on the elution volumes of phenols in GPC^{2,3}. Some conclusions about the effect of the alkyl group were drawn in our previous work on substituted mononuclear phenols and 4,4'-isopropylidenebisphenols⁴.

In the systematic investigation of the properties of binuclear phenolic antioxidants, we prepared a number of compounds that differed in the character and position of the connecting bond between dialkylated phenolic rings. Exceptionally, non-alkylated derivatives or derivatives that contained only one alkyl group on each ring were also used. The molecules were in all cases symmetrical. The compounds investigated were phenolic compounds with the structure of 2,2'- and 4,4'-biphenyldiols (types I and II), and alkylidenebisphenols and thiobisphenols (types III and IV). The relationships between their structures and antioxidative activities were discussed in detail on the basis of results obtained in the oxidation of tetralin^{5,6} (60°) and isotactic polypropylene⁷ (180°). IR spectra of bisphenols with bridges bonded at the position 2,2'- to the hydroxyl groups were investigated⁸. This paper reports the results of the gel chromatographic study.

EXPERIMENTAL

Binuclear phenols

2,2'- and 4,4'-Biphenyldiols (I, II), alkylidenebisphenols (III, IV; X = methylene, ethylidene, butylidene, benzylidene, isopropylidene, cyclohexylidene) and thiobisphenols (III, IV; X = monothio, dithio, trithio) were prepared by procedures described in the literature or by analogous methods. All the samples prepared were free from phenolic impurities, according to the TLC data. Only exceptionally were some trace amounts of other impurities revealed by the GPC analysis.



Chromatography

Chromatographic measurements were performed on a gel chromatograph constructed in the Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague⁴, with tetrahydrofuran as the eluent. The stainless-steel

columns, 8×1200 mm in size, were packed with the styrene-divinylbenzene copolymer S-GEL-832 (Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague). The separation efficiency of the five-column system was 7000 theoretical plates per meter. The inlet pressure was 10 atm gauge and the flow-rate was 40 ml/h. Table I gives the elution volumes, V_e , of the compounds under investigation in volume counts (1 volume count = 2.72 ml; $V_e = 47.2$ volume counts).

The dipole moments were calculated after GUGGENHEIM⁹ from the dielectric constants measured at 25° in benzene solutions with a DMor dipolemeter (Wissenschaftlich-technische Werkstätten GmbH, Weilheim, G.F.R.) and from refractive indexes measured with an immersed refractometer produced by C. Zeiss, Jena. The dipole moments are given in Table II.

TABLE I

ELUTION VOLUMES, V_e , OF BIPHENYLDIOLS (I, II) AND ALKYLIDENEBISPHENOLS AND THIOBISPHENOLS (III, IV).

Bridge	Phenolic ring ^a								
—	68.2	75.2	67.7	63.6	72.4	72.1	71.2	64.6	62.4
—CH ₂ —	66.7	73.7	66.3	61.8	72.7	—	69.6	64.2	62.0
—CH—	66.8	—	65.6	62.0	—	—	—	65.9	62.0
—CH— CH ₃	65.5	—	—	—	69.8	—	—	62.5	—
—CH— C ₆ H ₅	65.9	—	—	—	—	—	—	62.8	—
—C— CH ₃	70.0	74.7	67.1	62.5	69.0	—	68.0	66.0	61.3
—C— CH ₃ CH ₃	69.4	—	—	—	69.4	68.2	—	63.2	—
—C— C ₂ H ₅	—	—	—	—	—	68.7	—	63.3	—
—S—	67.9	74.0	66.2	62.4	—	—	69.8	64.3	61.8
—S—S—	67.7	—	—	—	—	—	—	64.2	—
—S—S—S—	—	—	—	—	—	—	—	63.4	—

^a ~ = Position of bridge connection; / = methyl; + = *tert.*-butyl.

TABLE II

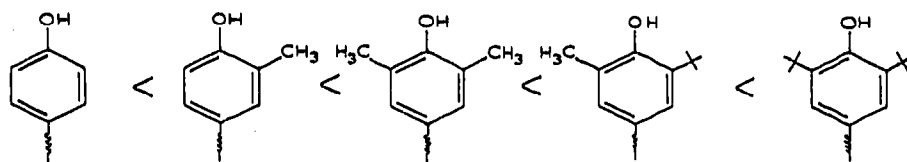
DIPOLE MOMENTS OF BISPHENOLS

Compound	μ (D)
2,2'-Methylenebis(4-methyl-6- <i>tert.</i> -butylphenol)	1.98
2,2'-Isopropylidenebis(4-methyl-6- <i>tert.</i> -butylphenol)	1.21
2,2'-Thiobis(4-methyl-6- <i>tert.</i> -butylphenol)	1.51
3,3'-Di- <i>tert.</i> -butyl-5,5'-dimethyl-2,2'-biphenyldiol	1.23
4,4'-Methylenebis(2-methyl-6- <i>tert.</i> -butylphenol)	1.73
4,4'-Butylidenebis(2-methyl-6- <i>tert.</i> -butylphenol)	1.84
4,4'-Isopropylidenebis(2-methyl-6- <i>tert.</i> -butylphenol)	1.56
4,4'-Thiobis(2-methyl-6- <i>tert.</i> -butylphenol)	2.48

RESULTS AND DISCUSSION

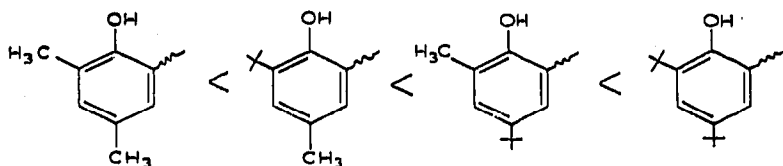
The precisely symmetrical shape of the chromatographic peaks of all the bisphenols investigated and their identical widths permit the assumption that adsorption effects during gel chromatography can be neglected. The elution volumes of the individual compounds are then determined by the size of the molecules and by their shape in solution. The polarity of the molecules is also important, especially during the formation of solvated complexes³ and of intramolecular hydrogen bonds⁸, which can markedly affect the elution volume. Owing to this fact, and also to the complications involved in the determination of the effective dimensions of binuclear phenolic molecules, the increments in elution volume for a given substituent on the ring and the position of the latter can as yet only be estimated.

In the series of bisphenols that always have the same bonds at the 4,4'-position, the volume of the molecule increases from the unsubstituted to the disubstituted nucleus, in accordance with the assumed influence of alkylation of the phenolic ring on the elution volume in GPC. This dependence on the increase in the volume of the alkyl groups is also observed, irrespective of the fact that YOSHIKAWA *et al.*³ concluded that a major distortion of the results could be expected owing to solvation, especially if the 2,6-di-*tert.*-butyl derivative is compared with the other members of the series under investigation. The effective volume of the molecule increases in the series:



For bisphenols with bridges at the 2,2'-positions, the characteristic effect of substitution at the positions *ortho* and *para* to the hydroxyl group that had been observed earlier with mononuclear phenols⁴ has been confirmed. The position of the alkyl group on the ring plays the decisive role in influencing the elution volume. A more important role is played by the substituent in the *para* position, as has been demonstrated by comparing compounds substituted on each ring by a combination of the methyl and *tert.*-butyl groups. According to the V_e values, all bisphenols derived

from 2-*tert.*-butyl-4-methylphenol have a smaller effective molecular volume than the condensation products of 2-methyl-4-*tert.*-butylphenol.



This fact probably reflects the steric effects due to an interaction between the phenolic hydroxyl group, the bridge, the alkyl group in the *ortho* position and the aromatic rings. The effective volumes of bisphenol molecules with bridges at the 2,2'-positions are in almost all instances smaller in GPC analysis than those of 4,4'-bisphenols similarly substituted on the ring. The influence on the effective volume of solvation of the hydroxyl groups at the 4,4'-positions is more distinct. There is an exception for tetra-*tert.*-butylated compounds derived from both isomeric di-*tert.*-butylphenols for which the dependence is not so obvious.



The steric requirements of bisphenol molecules in a tetrahydrofuran solution also depend on the shape of the bridge. From a comparison of members of a large series of 4,4'-bisphenols comprising 3,3'-dimethyl-5,5'-di-*tert.*-butyl-4,4'-biphenyldiol, 4,4'-alkylidenebis- and 4,4'-thiobis (2-methyl-6-*tert.*-butylphenols), some conclusions can be drawn that have also been confirmed by investigating compounds belonging to other series of 4,4'-bisphenols with fewer members. Replacement of one or both hydrogen atoms of the methylene bridge with alkyl groups, which leads to an increase in the volume of the bridge, is reflected in the GPC measurements by the fact that the presence of one or two methyl groups on the bridge does not result in an increase in the total effective volume of the molecule. It is only the presence of one more bulky alkyl group (butylidene, cyclohexylidene or benzylidene bridge) or a combination of the alkyl group with a larger one (*sec.*-butylidene bridge) that makes the volume of the molecule larger. The effective volume of 4,4'-thiobisphenols is virtually identical with similarly substituted 4,4'-methylenebisphenols. An increasing number of sulphur atoms in the bridge has no important influence.

A series of effective volumes of molecules, depending on the changing effect of the bridge for 2,2'-bisphenols derived from 2-*tert.*-butyl-4-methylphenol, has been determined in a similar way. It appears that compared with 2,2'-methylenebisphenol (used as a basis for discussing the effect of an increase in the bridge volume of alkylidenebisphenols by substitution of the hydrogen atoms of the methylene group), the increase in the volume of the whole bisphenol molecule caused by replacement of the one hydrogen atom with a methyl group (ethylidene bridge) will be insignificant. An increase in the effective volume of the molecule due to the presence of propyl and phenyl groups (butylidene and benzylidene bridge) is pronounced.

However, not only 2,2'-dihydroxybiphenyl, but also alkylidenebisphenols in which the phenolic rings are connected by a quaternary carbon atom, have smaller effective volumes than that of 2,2'-methylenebisphenol. In this case, solvation of the hydroxyl group³ also plays an important role, along with the volume of the substituents on the bridge. This solvation is negligible for the compounds having a quaternary carbon atom connecting both rings (according to IR measurements, all OH groups present in their molecules are bonded by the $-\text{OH}\dots\text{O}$ or $-\text{OH}\dots\pi$ bridges), while the molecule of methylenebisphenol contains, besides bonded hydroxyl groups, also free and readily solvated hydroxyl groups in a considerable concentration. The molecule of 2,2'-thiobisphenol has a somewhat larger elution volume than that of 2,2'-methylenebisphenol substituted on the ring in a similar way; an increase in the number of sulphur atoms in the bridge does not have any effect in this case either.

It can be expected that the polarity of the molecule will also affect the final value of the elution volume. So far, it has not been possible to determine unambiguously the influence of the dipole character of the molecule on the conformation of the molecule in solution from the experimental values of the dielectric constant. It is clear, however, that with the exception of 4,4'-thiobisphenol with its high dipole moment, higher dipole moments are found in both isomeric bisphenol series for compounds that exhibit a smaller elution volume in tetrahydrofuran.

For both isomeric bisphenol series, a change in the character of the bridge between the phenolic rings generally has a less pronounced effect on the GPC behaviour than substitution of the rings themselves. While the differences observed for the V_e values of tetraalkylated bisphenols and caused by the character of the bridge varying within a broad range, are 3.5 volume counts for 4,4'-bisphenols and 4.5 volume counts for 2,2'-bisphenols, the differences between the values of variously tetrasubstituted 4,4'-bisphenols with the same bridge are 8.8 volume counts, and for tetrasubstituted 2,2'-bisphenols even about 12 volume counts. However, 4,4'-bisphenols had in most instances smaller elution volumes than those of similarly alkylated 2,2'-bisphenols.

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