

CHROM. 17 780

Note

Separation and identification of phenol-formaldehyde condensates by gas chromatography-mass spectrometry

I. Acid-catalysed condensation products

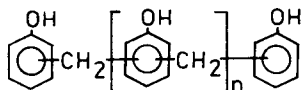
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Novolacs are prepared by acid-catalysed condensation of phenol and formaldehyde and used as prepolymers of cross-linked thermosetting resins. Since the properties of these resins strongly depend on the composition of the prepolymers, a number of analytical methods have been applied to the determination of the chemical composition and the structure of their molecular compounds¹.

Novolacs are reported to be oligomeric mixtures of diphenylmethane-type copolycondensates, which can be schematically depicted as follows²:



Separation and identification of isomeric oligomers have been restricted mainly to dimers because the number of possible isomers increases rapidly with the degree of polymerization (three for dimer, seven for trimer, *etc.*) owing to *ortho* and *para* substitution.

The isomers 2,2'-, 2,4'- and 4,4'-dihydroxydiphenylmethane have been separated by gas-liquid chromatography (GLC) without any derivatization³, but trimethylsilylation is useful because it increases the volatility of the oligomers and improves the separation of the isomers⁴. By means of gas chromatography-mass spectrometry (GC-MS) isomeric dimers were identified in the form of their trimethylsilyl derivatives, and an order of retention was suggested. However, no confirmation has been presented, either spectroscopic via the use of authentic reference compounds. Isomeric trimers have remained unidentified in this way.

In the present paper the GC-MS analysis of trimethylsilylated phenol-formaldehyde novolac is described in detail, with especial emphasis on the above-mentioned, unresolved problems.

EXPERIMENTAL

Novolac was prepared using 2 moles of phenol to 1.67 moles of formaldehyde [in 37% (w/w) aqueous solution] and 0.003 moles of sulphuric acid as catalyst. The stirred reaction mixture was refluxed in an oil-bath at $125 \pm 3^\circ\text{C}$ for 2 h. The liquid was neutralized by adding a calculated amount of calcium hydroxide in aqueous solution, then it was allowed to cool. The resinous (bottom) layer was separated and dehydrated in vacuum at $120\text{--}130^\circ\text{C}$ ⁵.

Novolac was trimethylsilylated for GC-MS investigation as follows: 20 mg of resin were dissolved in dry pyridine (*ca.* 100 μl) and 1 ml of N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) was added to the solution; the reaction vessel was kept at 60°C for 1 h prior to analysis.

Mass spectra were recorded on a JEOL JMS-01SG-2 (Japan) double-focusing instrument at 75 V ionizing voltage, 200 μA trap current, 250°C ion source temperature and 10 kV accelerating voltage. The gas chromatograph (JEOL JGC-20K) was interfaced to the spectrometer via a two-staged jet separator. A glass column (3 m \times 2 mm I.D.) packed with 10% SP-2100 on 100–120 mesh Supelcoport (Supelco, Bellefonte, U.S.A.) was used for packed column separation. Capillary GC was performed on a 50 m \times 0.33 mm I.D. BP-1 bonded phase fused-silica column with 1.0 μm film thickness (Scientific Glass Engineering, Australia). A split injection mode was used with a split ratio of 1:20. The injection port and the interface temperatures were 280 and 300°C , respectively. The flow-rate of the carrier gas (helium) was determined according to the optimal working condition of the jet separator (30–40 ml/min). With the capillary, a flow-rate of 1.0 ml/min and make-up gas at the column outlet were applied. The GC oven temperature were as follows: packed column, 200 to 300°C , $5^\circ\text{C}/\text{min}$ programme rate; capillary, initial hold at 150°C for 5 min, then programmed to 300°C at $4^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Fig. 1 shows the total ion chromatogram of trimethylsilylated novolac. The degree of polymerization can be readily obtained from the corresponding mass-to-

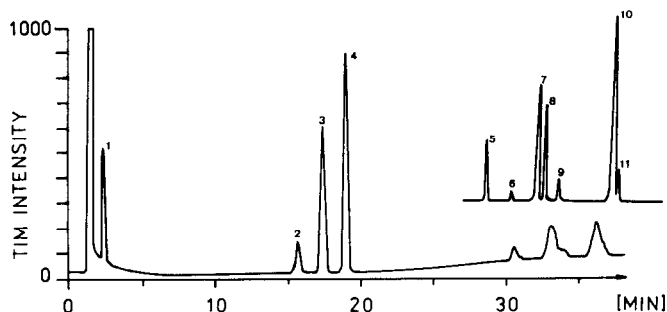
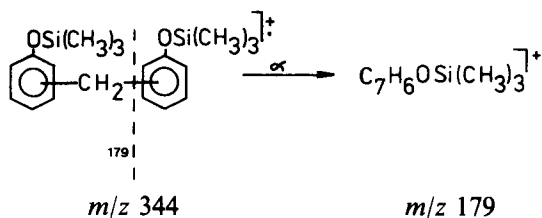


Fig. 1. Total ion chromatogram of trimethylsilylated novolac. Glass column (3 m \times 2 mm I.D.) packed with 10% SP-2100 on 100–120 mesh Supelcoport; carrier gas, helium; flow-rate, 30 ml/min; injection port temperature, 280°C ; GC oven programmed from 200 to 300°C at $5^\circ\text{C}/\text{min}$. Inset: separation of isomeric trimers by capillary column. BP-1 bonded phase fused-silica (50 m \times 0.33 mm I.D.) with 1 μm film thickness; flow-rate, 1.0 ml/min; initial hold for 5 min, then to 300°C at $4^\circ\text{C}/\text{min}$. Peaks: 1 = phenol; 2–4 = dihydroxydiphenylmethanes; 5–11 = (hydroxybenzyl)dihydroxydiphenylmethanes.

charge (m/z) values of the molecular ions, *i.e.* peak 1 in the chromatographm is the phenol (m/z 166), peaks 2–4 are dimers (m/z 344) and peaks 5–11 are trimers (m/z 522). In the latter case the separation of the positional isomers was incomplete and a capillary column was required to resolve all the seven possible trimers.

Mass spectra of 2, 3 and 4 are shown in Fig. 2. There are characteristic differences in the molecular (parent) ion and certain fragment ion intensities. It has already been shown⁶ that sterically crowded functional groups increase the competitiveness of fragmentation reactions (rearrangements, first of all) and weaken the abundance of the parent ion. Therefore, an increase in the molecular ion intensity could be expected in the order of 2,2'- < 2,4'- < 4,4'-substitution. Moreover, the following α -cleavage reaction is most favourable in case of the greatest separation of the trimethylsilyloxy groups, *i.e.* for the 4,4'-isomer:



The abundant $[\text{M} - \cdot\text{CH}_2\text{OSi(CH}_3)_3]^+$ (m/z 241) and $(\text{CH}_3)_3\text{Si}-\overset{+}{\text{O}}=\text{Si(CH}_3)_2$ (m/z 147)⁷ ions which involve extensive rearrangements with the participation of the sterically crowded silicon-containing substituents in case of 2, give further support to the proposed identification. The above facts confirm the assignment of peak 2 to bis(trimethylsilyl)-2,2'-dihydroxydiphenylmethane, peak 3 to bis(trimethylsilyl)-2,4'-

TABLE I

PRINCIPAL IONS IN THE MASS SPECTRA OF TRIS-TRIMETHYLSILYLATED TRIMER COMPOUNDS

Relative intensities are given in parentheses and proportional to 100 for the most abundant ion.

Peak No.	Compound	m/z
5	3-(2-Hydroxybenzyl)-2,2'-dihydroxydiphenylmethane	343 (100), 73 (58), 344 (35), 522 (21), 345 (11), 523 (10), 521 (9), 507 (7)
6	5-(2-Hydroxybenzyl)-2,2'-dihydroxydiphenylmethane	343 (100), 73 (62), 344 (32), 522 (25), 523 (13), 345 (12), 521 (10), 179 (8)
7	3-(4-Hydroxybenzyl)-2,2'-dihydroxydiphenylmethane	343 (100), 73 (61), 522 (48), 344 (31), 523 (23), 521 (15), 179 (12), 345 (11)
8	5-(4-Hydroxybenzyl)-2,2'-dihydroxydiphenylmethane	343 (100), 73 (66), 522 (54), 344 (29), 523 (25), 521 (17), 179 (15), 345 (11)
9	5-(2-Hydroxybenzyl)-2,4'-dihydroxydiphenylmethane	343 (100), 73 (69), 522 (56), 344 (30), 523 (26), 521 (17), 179 (16), 345 (10)
10	3-(4-Hydroxybenzyl)-2,4'-dihydroxydiphenylmethane	343 (100), 522 (98), 73 (95), 523 (46), 344 (32), 521 (20), 179 (18), 345 (13)
11	5-(4-Hydroxybenzyl)-2,4'-dihydroxydiphenylmethane	522 (100), 73 (97), 343 (94), 523 (48), 344 (30), 521 (22), 179 (21), 345 (12)

dihydroxydiphenylmethane and peak 4 to bis(trimethylsilyl)-4,4'-dihydroxydiphenylmethane. Derivation of the structure of the precursor compounds is straightforward.

The general type of connection of phenolic rings in the trimers can be easily determined by considering the molecular ion abundance, but only slight differences in the fragment ion intensities are obtained. The most abundant ions in the mass spectra of compounds 5–11 are given in Table I. The retention order was estimated from the results obtained for trimethylsilylated dimers.

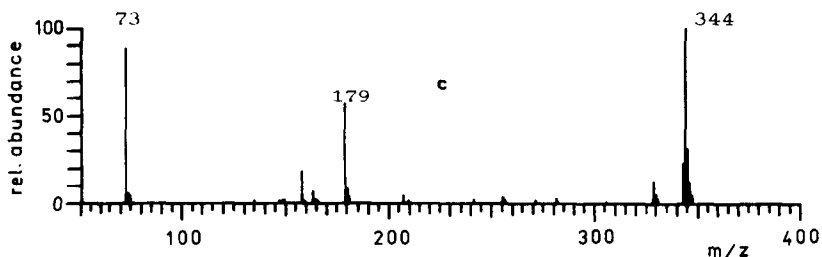
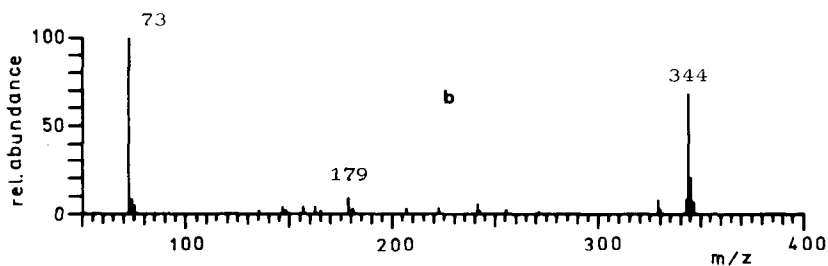
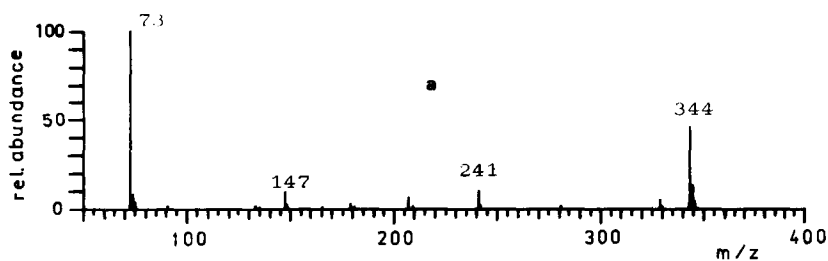


Fig. 2. Electron ionization mass spectra of bis(trimethylsilyl)-dihydroxydiphenylmethane isomers: (a) 2,2'-isomer; (b) 2,4'-isomer; (c) 4,4'-isomer.

CONCLUSION

Trimethylsilylation was successfully used to volatilize diphenylmethane-type phenol-formaldehyde condensation products in order to permit the GC analysis of the dimeric and trimeric compounds. The positional isomers were separated by means of capillary column. The method has the great advantage of making possible mass spectrometric investigation subsequent to chromatography by well-tried GC-MS systems. Electron ionization mass spectra of the isomers show characteristic differences that, after cautious interpretation, can be used to distinguish the positional isomers or to determine, at the least, the predominant type of connection of the phenolic nuclei. These results can be starting points of further investigations towards more complicated materials in the field of phenol-formaldehyde condensates.

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