IDENTIFICATION OF SOME POLYMERS BY THE COMBINED GAS AND THIN-LAYER CHROMATOGRAPHIC ANALYSIS OF PHENOLS FORMED BY THEIR PYROLYSIS

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SUMMARY

A method for the identification of polymers is proposed, which consists in the analysis of their phenolic pyrolysis products by a combination of pyrolysis gas and thin-layer chromatography. Phenolic and epoxide resins, polycarbonates, polyphenyl ethers, polysulphones and some polyimides, that form volatile phenols when pyrolyzed, are included. A convenient method of vacuum ampoule pyrolysis is described and the interpretation of the results is discussed.

INTRODUCTION

Multicomponent chromatography, in which gas (GC) and thin-layer (TLC) chromatography are combined has been shown to be a useful method for the analysis of complicated chemical mixtures[1]. At first this technique was used as a discontinuous method[2] for the identification of fatty acids[3,4], the analysis of dicarboxylic and hydroxy acids[5], carbonyl compounds[6], alcohols[7] and anthracene oils[8], and later a continuous modification was developed in which the GC eluates were led on to the TLC plates without trapping[9–13]. The method was applied to the analysis of high-boiling coal tars[9,10], higher saturated and unsaturated fatty acids[11] and narrow xylenol fractions, and to the identification of the impurities in diamines[12]. For this purpose, a very simple arrangement was suggested by HUMPHREY[14]; the synchronized movement of the TLC plate with GC elution was ensured by fixing the plate on the paper of the GC recorder.

The pyrolysis products of polymers are complex chemical mixtures that could be analyzed by multicomponent chromatography. Some polymers, when heated in a vacuum or in an inert atmosphere, decompose to give low-molecular phenolic compounds, the compositions of which are characteristic of the original polymer. This decomposition occurs with phenol–formaldehyde polycondensates, epoxide resins, polycarbonates, polysulphones, polyphenyl ethers and some polyimides.

Phenol–formaldehyde resins are degraded into phenols with methyl groups in the *ortho* and *para*-positions (the residue of the methylene bridges) and the same alkyl groups as in the original phenolic monomers. Thus phenolic resins may form phenol, 2- and 4-methylphenols, 2,4- and 2,6-dimethylphenols and 2,4,6-trimethyl-

phenol[15-20]. Resins derived from *o*- and *p*-cresol form the same products, but the proportions of the individual phenols are different, with a predominance of 2-isomers[19]. The pyrolytic products of *m*-cresolic resins are richer in isomers with methyl groups in the 3-position[19,20].

Epoxide resins derived from bisphenol A undergo bond fission, dehydration and Claisen condensation to give very complex mixtures of phenols with C_1-C_3 alkyl groups in the 2- and 4-positions[21-25].

The thermal decomposition of polycarbonates, which have the same basic structure as epoxides, leads to products similar to those from the epoxides with the exception of 2-isomers[26-28]. Similar behaviour can be expected with polysulphones derived from bisphenol A[29-30]. Different structural units will naturally form different phenolic products.

The phenolic products of polyimides based on 4,4'-diaminodiphenyl ether are, on the contrary, very simple and contain only phenol[31]. The composition of the degradation products of polyphenyl ethers depends on the structure of the parent phenolic units. The presence of phenol, 2- and 3-methylphenol and 2,4- and 3,5-dimethylphenols was confirmed[32-35].

During the pyrolysis of these polymers, a large number of non-phenolic compounds are formed in addition to the phenols mentioned. Pyrolysis gas chromatography alone, although an excellent separation method for phenols, is not capable of achieving a complete analysis. A simple solution to this problem is to combine GC and TLC, so that the separation properties of GC and the specific detection possibilities of TLC are advantageously utilized.

EXPERIMENTAL

Materials

We used the following polymers: phenolic novolac, cresolic resols and 4-*tert.*-butylphenolic resol were prepared in this Institute. Epoxide resins (Epoxid 1200, SPCHH and Epoxy-novolac, DEN 438, Dow Chemical) were cured with a BF_3–amine complex. Other polymers were used as received (Macrolon S polycarbonate, Bayer; Polycron PSN polysulphone, Folex AG; W-190 polyphenylene oxide, Monti Martini; Kapton polyimide, Du Pont).

Pyrolysis

For pyrolysis, 2–3 mg samples were weighed into glass ampoules, 3 mm I.D. and 15 mm long, and sealed at 0.5 torr. One end of the ampoule was previously drawn out so as to form a micro-trap, separated from the sample by a quartz-wool plug. The ampoules containing the sample were heated in a horizontal electric oven pre-heated to 550° in such a way that the micro-trap protruded, forming a cold zone. After 10 min, the ampoules were cooled, their tops were cut off and 10 μl of acetone were introduced by means of a micro-syringe. During a short centrifugation, the solvent passed through the ampoule into the trap and dissolved the soluble pyrolysis products. After cutting off the trap, 1–3 μl of the solution was injected into the gas chromatograph.

Chromatography

A Fractovap Model P-AID/f chromatograph (Carlo Erba) was used, with a glass column 3 mm I.D. and 140 cm long, filled with 0.15–0.20 mm glass micro-beads

(balotina kryštál, Jablonecké sklárny), treated with hydrofluoric acid[36] and impregnated with 0.01 % of phosphoric acid and 0.13 % of 2,4-trixylenylphosphate (Merck). The temperature of the column was programmed from 90 to 130° at 1.8°/min with a nitrogen inlet pressure of 0.4 kp/cm².

Between the column outlet and the detector, a stripper with a 1:1 ratio was situated. One part of the eluate was led on to the TLC plate with the aid of a stainless-steel tube, 1 mm I.D. and 1 m long, heated to 150° by an electrical resistance wire wound around it.

The silica gel TLC plates (Silufol®, Kavalier) were fixed on the registration paper of GC according to the method of HUMPHREY[14]. After a GC run, the plates were developed with chloroform and detected with diazonium salt of sulphanilic acid (0.1 g in 20 ml of 10 % sodium carbonate solution).

RESULTS AND DISCUSSION

We analyzed 17 alkylphenol standards (methyl, propyl and *tert.*-butyl) and combined the two chromatographic spectra obtained to give one "bichromatogram" (Fig. 1). It can be seen from Fig. 1 and also from the elution characteristics (Table I) that the main separation is achieved by GC, whereas the importance of TLC lies in both the specific detection of phenols and the distinction of compounds that are poorly separated. The latter compounds are phenol and 2,6-xylenol; 2,4-, 2,5-xylenol and 2-ethylphenol; 3,5-xylenol, 2-isopropylphenol and 4-ethylphenol; and 2,3,5-xylenol and 3- and 4-isopropylphenol. With the aid of the "bichromatograms" all these phenols can also be detected in complicated mixtures.
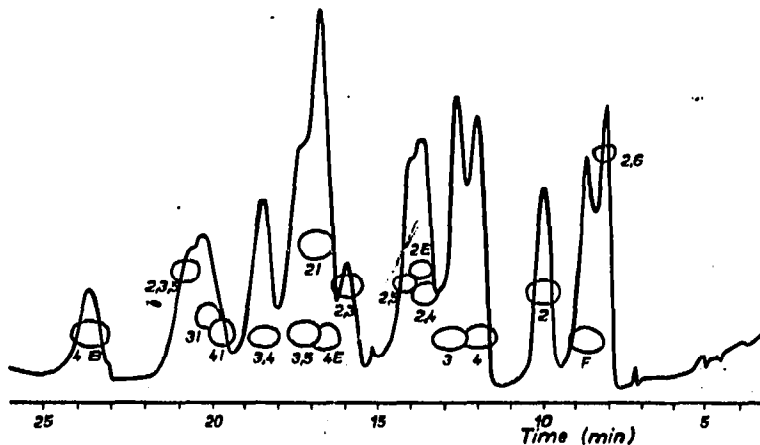

Fig. 1. "Bichromatogram" of standard phenols. For symbols, see Table I.

We used the described method for the identification of phenolic pyrolysis products of all the polymers mentioned. We also measured the peak heights of individual phenols and expressed them as relative percentages. The results were plotted as "fingerprints" (Fig. 2), from which the following conclusions can be drawn.

During pyrolysis, the polycondensates of phenol and alkylphenols with formaldehyde form low-molecular phenols, the type of which depends on the composition of the initial phenolic monomers. Thus, resins derived from phenol form only phenol, 2- and 4-methylphenol and 2,6-dimethylphenol. Cresolic monomers lead to phenol, 2-

TABLE I

RETENTION CHARACTERISTICS OF INDIVIDUAL PHENOLS IN A STANDARD MIXTURE

| Phenol	Symbol (Fig. 1)	GC		TLC R_F
		t_R (min)	t_T (°C)	
2,6-Dimethylphenol	2,6	7.5	103	0.68
Phenol	F	7.9	104	0.20
2-Methylphenol	2	9.4	106	0.34
4-Methylphenol	4	11.3	110	0.20
3-Methylphenol	3	12.0	112	0.21
2,4-Dimethylphenol	2,4	13.1	113	0.34
2-Ethylphenol	2E	13.1	113	0.40
2,5-Dimethylphenol	2,5	13.5	114	0.37
2,3-Dimethylphenol	2,3	15.5	118	0.35
4-Ethylphenol	4E	16.2	119	0.21
2-Isopropylphenol	2I	16.2	119	0.44
3,5-Dimethylphenol	3,5	16.9	120	0.23
3,4-Dimethylphenol	3,4	18.1	122	0.23
3-Isopropylphenol	3I	19.9	126	0.25
4-Isopropylphenol	4I	19.9	126	0.22
2,3,5-Trimethylphenol	2,3,5	20.4	127	0.38
4-tert.-Butylphenol	4tB	23.3	130	0.24
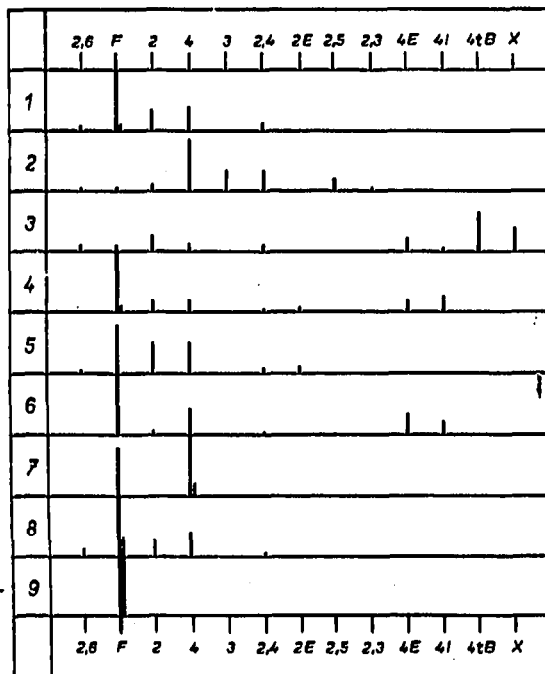
Fig. 2. "Fingerprint" of phenolic pyrolysis products of polymers. One line represents 50% relative. 1 = phenolic novolac; 2 = cresolic resol; 3 = p-tert.-butyl resol; 4 = bisphenol A epoxide; 5 = epoxide novolac; 6 = polycarbonate; 7 = polysulphone; 8 = polyphenyl ether; 9 = polyimide.

methylphenol, 2,3-, 2,4-, 2,5- and 2,6-dimethylphenol and a large proportion of 4-methylphenol. Phenol, methyl- and dimethylphenols with methyl groups in the 2-, 4- and 6-positions and alkylphenols (ethyl, isopropyl and *tert.*-butyl) with alkyl groups in the 4-position are formed during pyrolysis of the resin based on 4-*tert.*-butylphenol.

The polymers derived from bisphenol A (epoxides and polycarbonates) in addition to a large proportion of phenol and a small proportion of 2- and 4-methylphenols and 2,4-dimethylphenol, are characterized by the presence of 4-ethyl-, 4-isopropyl- or isopropenylphenols and especially 2-ethylphenol.

The chromatographic spectra of phenolic products from the other polymers are comparatively simple. Thus, the pyrolysis products of the polysulphone investigated consist only of phenol and 4-methylphenol, which indicates the absence of bisphenol A. The polyphenylene oxide tested forms phenol, 2- and 4-methylphenols and 2,6-dimethylphenol. The only phenolic product from the polyimide based on 4,4'-diaminodiphenyl ether is phenol.

The results are in agreement with those of published work. They indicate that during pyrolysis fission of chemical linkages between aromatic rings and their side-chains in either the α-position (the origin of phenol) or β-position (the origin of methyl-isopropyl- and isopropenylphenols) occurs:

$$X = H, CH_3, Ph$$
$$Y = H, CH_3 \tag{1}$$

With aromatic ethers (where C in the side-chain is substituted with O and free phenolic OH groups are absent), the phenols are formed by β-fission and further radical reactions. In all these reactions, the positions of the side-chains are not changed. With epoxide resins, dehydration also occurs and the Claisen condensation of the propenyl ethers thus formed liberates 2-isomers, which were not originally present:

$$\tag{2}$$
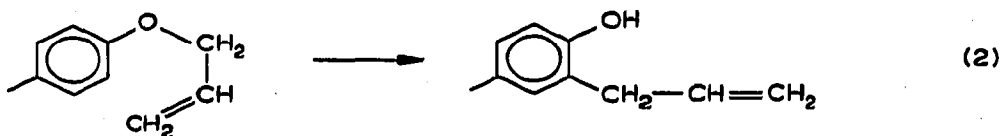
Therefore, the only possibility for distinguishing diane epoxide resins from other polymers based on bisphenol A is the presence of 2-alkylphenols in the pyrolysis products of the former.

In the pyrolysis of polyphenyl ethers, there are two possibilities for the formation of various isomers: fission either in the 1-position (to form 2-alkylphenols) or in the 2-position (to form 3-alkylphenols from *para*-linked polymers, or 4-alkylphenols from *meta*-linked polymers):

$$\tag{3}$$
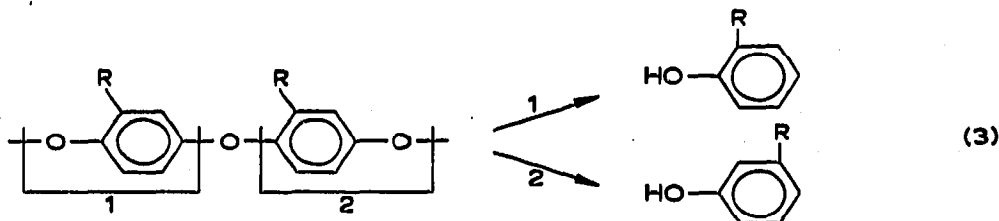
In fact, the pyrolysis of the polyether investigated confirmed the existence of both possibilities.

In using Fig. 2 for the identification of unknown polymers, one can proceed as follows. After obtaining the "bichromatogram", the peak heights of individual phenols on the GC record are evaluated as relative percentages. The results are drawn on tracing paper and compared with the standard diagram. In most instances a simple visual comparison leads to positive results, but sometimes a more detailed interpretation is necessary. Thus, phenolic resins and epoxide novolacs differ only by a small peak of 2-ethylphenol from the latter. Epoxides based on bisphenol A and epoxide novolacs are distinguished by the presence of 4-ethyl and 4-isopropyl derivatives from the former. The presence of 2-methyl and 2-ethylphenol is characteristic of bisphenol A epoxides in comparison with polycarbonates. The distinction between phenolic resins and the polyphenylene oxide tested is difficult and the proposed method must be complemented by other physico-chemical or chemical methods; in many instances the physical consistency is sufficiently characteristic.

The method described is very sensitive and specific. It can also be used for the analysis of the above polymers in combination with other materials, e.g., for identification of binders in laminates, and the analysis of systems of electrical insulating materials and complex mixtures with other polymers.

The discontinuous vacuum ampoule pyrolysis has many advantages, such as the prevention of contamination of the GC column with highly volatile impurities and the possibility of the repetition of unsatisfactory analyses on the stock solution of pyrolysates. The protrusion of the tip of the ampoule from the pyrolytic oven is important because it functions as a cold-trap in which the volatile products are condensed and thus removed from the hot zone; otherwise, the branched alkyl substituents will split off. Other pyrolysis methods can also be used, with preference for on-line pyrolysis-GC, but the discontinuous mode is more effective in this instance.

CONCLUSIONS

During the thermal degradation of polymers that have either free phenolic hydroxyl or aromatic ether linkages, low-molecular compounds with significant contents of free phenols are formed. Their composition depends on the chemical structure of the original polymer. By the analysis of phenolic pyrolysis products, it is possible not only to identify the type of polymer, but also the types of monomers used for its synthesis. For this purpose, a continuous combination of pyrolysis GC and TLC is a convenient method. Its applicability is, however, more general and we have also used this method for the identification of phenols in solvents for electrically insulating lacquer and for the elucidation of the composition of triaryl phosphates. The apparatus required is very simple and can be constructed in every chromatographic laboratory.

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