Short communication

Thermal degradation of novolac resins by pyrolysis-gas chromatography with a movable reaction zone

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Abstract

A previously described, a pyrolysis device with a movable reaction zone was used in the present work for thermal degradation of novolac resins. The products of thermal reactions were analysed by pyrolysis–GC. Owing to the heating of reaction zone to the maximal temperature of the chromatographic column, the high boiling pyrolysis products could be analysed. Bisphenols and trisphenols with aromatic rings coupled by methylene bridges and its methyl derivatives have been found among the compounds. The structure of the heavy pyrolysis products has been confirmed using GC–MS. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Pyrolysis; Instrumentation; Phenol–formaldehyde resins; Novolac resins

1. Introduction

Novolac resins are commonly obtained in the reaction of phenol with formaldehyde in an aqueous acidic environment. The product of the reaction is a mixture of linear oligomers with the structure shown in Fig. 1 [1,2]. The components consist of many position isomers because each OH group can be
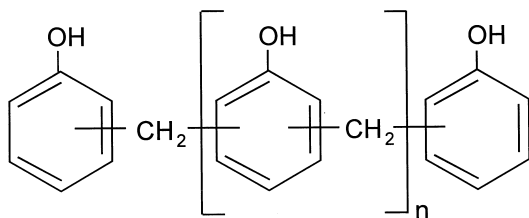

Fig. 1. Structure of novolac.

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placed in *ortho* or *para* position to a neighbouring methylene bridge.

The major components of the resin are bisphenols and trisphenols, but the number of aromatic rings in a molecule can exceed a dozen [3]. The linear oligomers, heated with urotropine, can be transformed into high molecular setting polymers.

Novolac resins are dissolvable in water, low-molecular mass alcohols and any others polar solvents but they lose these properties after thermosetting. Therefore, indirect chromatographic analysis of setting novolac resins is not possible. Instead, any spectroscopic methods (IR, ^{13}C NMR) or thermal destruction methods (thermal analysis (TA), pyrolysis (Py)–GC) can be used.

It has been known for a long time that thermal degradation of phenol formaldehyde resins leads mainly to phenol and its methyl derivatives, as well as small amounts of simple aromatic hydrocarbons [4]. Information from the analysis of phenols in

pyrolysate was employed identify the resin [5]. Recently, among the pyrolysis products of novolac resin, apart from the above mentioned, low volatile compounds, such as naphthalene, methylnaphthalenes, biphenyl, dibenzofuran, fluorene, phenanthrene and anthracene, were identified by Py–GC–MS [6].

In the present work, a Curie point pyrolyser with a movable reaction zone was used for the thermal decomposition of novolac resins. The construction and analytical possibilities of the new device were described in our earlier publication [7]. The main

advantage of this device is preventing irreversible condensation of the high boiling pyrolysate components in the reaction zone.

2. Experimental

2.1. Materials

The novolac resins were obtained by the conventional method in a laboratory reactor by using 35%
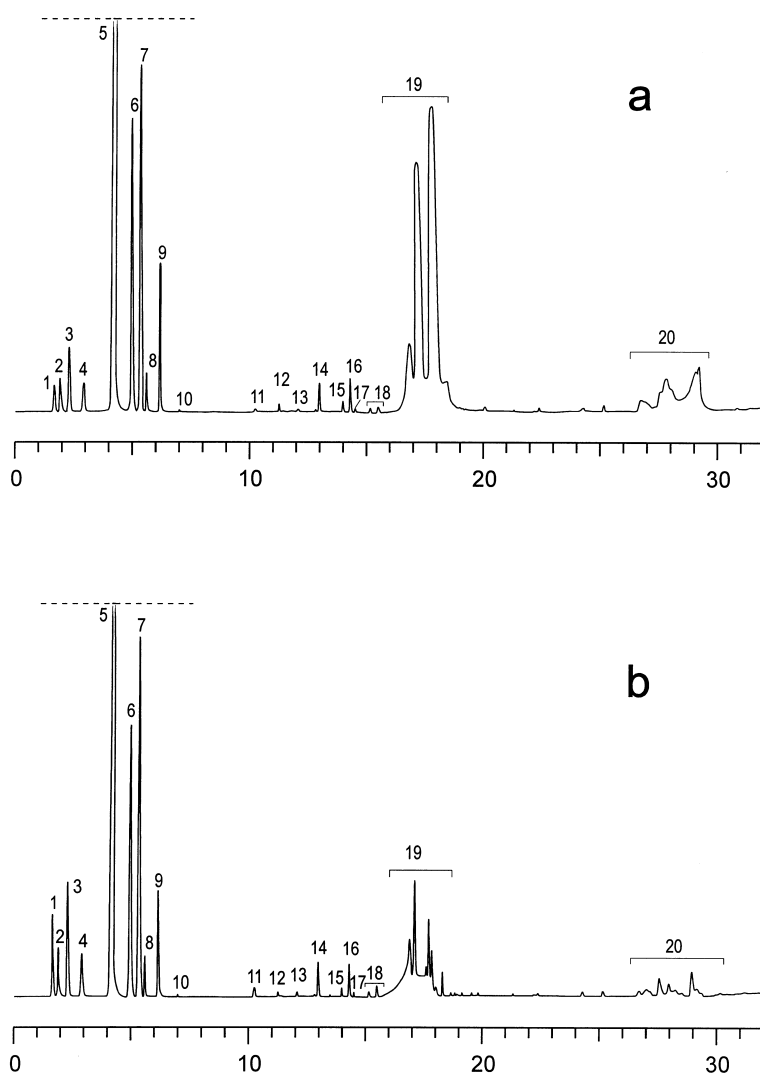

Fig. 2. Pyrograms of novolac resin. (a) Products of pyrolysis of whole resin; (b) products of pyrolysis of residue after evaporation of light components.

formalin and phenol (*pure*, POCh, Gliwice, Poland). The mol ratio of formaldehyde to phenol was 1.5:1. Oxalic acid was a catalyst of the reaction. The resin was dissolved in methanol (*analytical grade*, ZA Oświęcim, Poland). The solution was deposited on the surface of a ferromagnetic wire of pyrolyser. After the evaporation of the dissolvent, the wire was introduced into the pyrolysis device.

2.2. Instrumentation

A Hewlett-Packard HP 5890/2 gas chromatograph with a flame ionisation detector was used to separate the volatile compounds from the thermal decomposition of resin. The laboratory-made pyrolysis device was employed instead of a sample injector in the gas chromatograph. According to the description of the device in our earlier paper [7], the sample deposited on the surface of the ferromagnetic wire had been introduced before analysis to the inside of the short movable precolumn. In the upper position of the precolumn (a), pyrolysis of the sample could be executed, and in the lower position (b), the reaction zone was situated inside the column thermostat, where it could be heated according to the program for the capillary column. The compounds were

separated in a 30-m capillary column (Restek) with 0.28 mm diameter. The stationary phase was poly(5% phenylmethyl)siloxane (layer of 0.2 μm). The column temperature was programmed at a rate of 10°C/min from 60 to 280°C. The carrier gas was helium.

The high boiling pyrolysis products were identified by a 5971 Hewlett-Packard GC–MS system with an electron impact ion source. For that purpose, a few milligram samples placed inside the spiral wire were pyrolysed by using the Curie point pyrolyser in a closed glass tube (in a helium atmosphere) beyond the chromatograph. After pyrolysis, the heavy products, which had condensed on the internal wall of the glass tube were washed by methanol and introduced to the GC–MS system by 'on-column' injection. The separation parameters in GC–MS system were similar to those in the Py–GC experiments.

3. Results and discussion

The pyrogram for novolac resin is presented in Fig. 2a. Before pyrolysis, the reaction zone was kept at room temperature (precolumn position (a)). The temperature of pyrolysis was 770°C and the time of

Table 1
Major volatile compounds found among the products of pyrolysis of novolac resin

No.	Names of identified compounds	Mol. weight
1	Benzene	78
2	Toluene	92
3	*o*-Xylene	106
4	*p*-Xylene	106
5	Phenol	94
6	*o*-Cresol	108
7	*p*-Cresol	108
8	2,6-Dimethylphenol	122
9	2,4-Dimethylphenol	122
10	2,4,6-Trimethylphenol	136
11	Diphenylmethane	168
12	Dibenzofuran	168
13	Fluorene	166
14	10H-Xanthene	182
15	1-Methylfluorene	180
16	Unknown	196
17	Anthracene and phenanthrene	178
18	Methyl-2-benzylphenols	198
19	Hydroxybenzylphenols and mono- and dimethyl derivatives	200, 214, 228
20	Bis(hydroxybenzyl)phenols and their mono- and dimethyl derivatives	306, 320, 334

reaction 1 s[1]. After pyrolysis, the reaction zone was introduced to the column thermostat (precolumn position (b)), where separation of the pyrolysate components was carried out within the temperature range from 60 to 280°C. This pyrogram differs from the obvious picture obtained in the conventional pyrolysis of phenolic resins. It contains additional peaks of heavy products, which in commercial pyrolysis devices cannot reach the chromatographic column due to irreversible condensation of the products in pyrolyser chamber.

To identify the heavy product, the same resin was pyrolysed at 770°C in a glass tube, as described in Section 2. The pyrolysate in the methanol solution was analysed in the GC-MS system. The results of the identification of major heavy components are specified and enumerated in Table 1. The retention times of benzene and its homologues have been estimated from a chromatogram of respective standards.

Similar to the results of previous work [6], the presence of inconsiderable amounts of the aromatic compound with condensed rings has been confirmed as a result of thermal decomposition of the resin. However, in our experiment, additionally significant peaks of bisphenols and trisphenols appear.

Respective images of single ion currents for molecular ions of bis- and trisphenol and their mono- and dimethyl derivatives (m/z 200, 214, 228 and 306, 320, 334) can be seen in Figs. 3 and 4. Isomers of both groups of compounds overlap one on another.

There is no doubt but that methyl derivatives of bisphenols and trisphenols are the products of pyrolysis, similarly to the cresols and di-methylphenols, while the origin of non-substituted bis- and trisphenols was not clear. They could be light components of resin, which evaporated during the heating of the sample, as well as pyrolysis products.

To explain this problem, two-step analysis (GC–Py–GC) was carried out. First, precolumn was

Fig. 3. Single ion detection of ions with m/z 200, 214 and 228.

placed in position (b) and the volatile compounds of the sample were evaporated from the wire surface and eluted at the temperature range 60–280°C.

Fig. 4. Single ion detection of ions with m/z 306, 320 and 334.

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[1]Results of our experiments at 500 and 600°C were close to those obtained at 770°C. Direction of degradation reactions of novolacs is not temperature sensitive in range 500–800°C. Temperature changes influence the amount of degradation products and their quantitative relations.
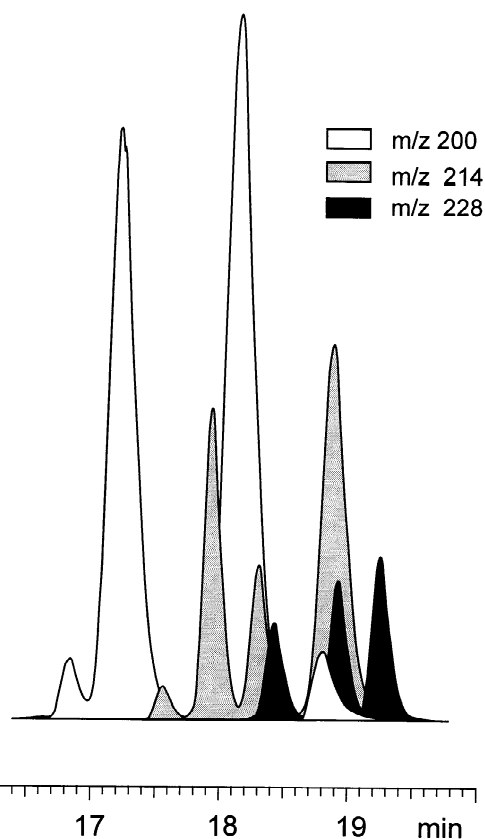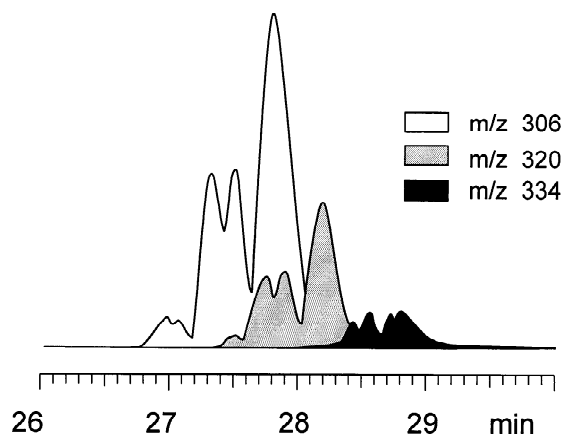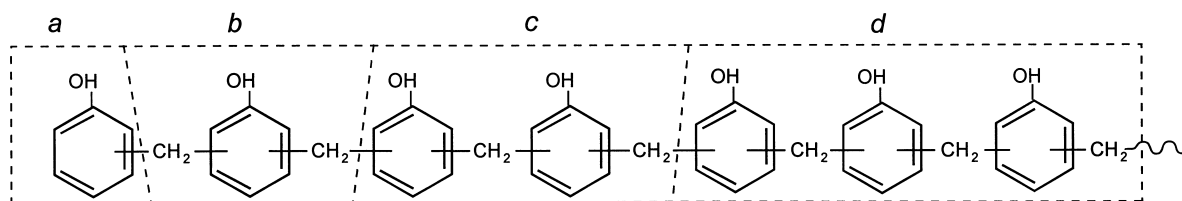
Fig. 5. Scheme of thermal degradation of novolac.

Secondly, the precolumn was elevated to upper position (a) and the column thermostat was cooled. After the cooling, the non-volatile residue of the sample was pyrolysed. The reaction zone was then inserted into the column thermostat. From that moment the components of pyrolysate could be evaporated gradually from the reaction zone and separated in the capillary column at linearly increasing temperature up to 280°C (pyrogram in Fig. 2b).

The comparison of Fig. 2a with Fig. 2b indicates that part of the non-substituted bis- and trisphenols, which can be seen on the pyrogram (Fig. 2a), originates rather from evaporation of the light component than pyrolysis of the resin.

4. Conclusion

The results of this work are in accordance with the common opinion that thermal decomposition of phenol–formaldehyde resins consists of breaking of the bonds between aromatic rings and methylene bridges. After joining hydrogen atoms to the formed radicals, phenol (a) and methylphenols (b) are created, as shown in Fig. 5.
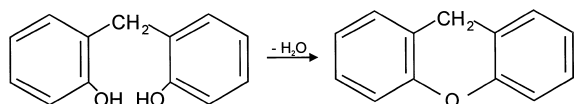
Similarly, the bis-, trisphenols, etc., and their methyl derivatives can be created (Fig. 5c and d). During the usual Py–GC experiments, the heavy compounds condense on the inner walls of the pyrolyser or a tube between the pyrolyser and the chromatographic column. The heating of the reaction zone after pyrolysis, up to the maximal temperature of the chromatographic column, permits to avoid this problem.

The imperceptible, yet characteristic products of pyrolysis of phenol–formaldehyde resins are components with three condensed rings: fluorene, dibenzofuran, xanthene, anthracene and phenanthrene. The components can be created in a cyclization reaction with the participation of hydroxyl or methyl groups in an *ortho* position to methylene bridges, as shown in Fig. 6. The presence of polynuclear aromatics (e.g., anthracene, xanthene, etc.) suggests that some dehydration and dehydrogenation occurs, which may not be free radical in nature.

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Fig. 6. Cyclization reaction with the participation of hydroxyl or methyl groups.