



Pyrolysis–gas chromatography–mass spectrometry of cured phenolic resins

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Abstract

A previously described pyrolysis device with a movable reaction zone was used in the present work for thermal degradation of cured novolac and resol resins. After the pyrolysis the usual major components were identified, as well as relatively low-volatile aromatic compounds which were revealed after their separation in a capillary chromatographic column. Among the latter components, for both types of cured resins, xanthene and its methyl derivatives were found. The isomers of bis(hydroxyphenyl)methane were found in considerable quantities only in the case of partially cured novolac resins which contained any linear sequences in their structure.

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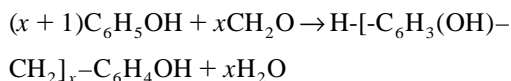
1. Introduction

Phenol–formaldehyde resins can be obtained by phenol (P) and formaldehyde (F) polycondensation. Polycondensation is carried out in the alkali and also acid environment with different aldehyde to phenol ratios [3,4]. Different condensation products are obtained depending on the pH environment, the temperature of the reaction and the mole ratio of reagents.

In an alkaline environment with mole ratio $F/P > 1$ resol resins are obtained, which in the previous stage of the reaction are a mixture of mono-, di- and trihydroxymethylphenols [5]. After extending the

heating time or after raising the temperature, these compounds enter into a reaction of mutual condensation and create a more or less cured system with methylene (rarely oxydimethyl) bridges joining the benzene rings [6].

Novolacs, which are linear polymers, can be synthesized in the presence of acid catalysts at a mole ratio $F/P < 1$ according to the general scheme:



where x takes the value of 1 to anywhere from 10 to 20.

Heating novolac resins with urotropin or paraformaldehyde, a polymer with a three-dimensional structure can be obtained [4].

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Primary resol resins are soluble in water, however, novolac resins dissolve in organic solvents. Cured phenol resins lose their properties and become brittle solids, neither fusible nor soluble in any solvent [4]. Therefore direct chromatographic analysis of phenol–formaldehyde cured resins is not possible, although spectroscopic methods (IR, ^{13}C NMR) or methods involving thermal degradation of a sample can be used successfully (TGA, pyrolysis–GC).

It has been known for a long time that thermal degradation of phenol–formaldehyde resins leads mainly to the creation of phenol and its methyl derivatives as well as small amounts of simple aromatic hydrocarbons [7]. These types of products were used in an attempt at correlation with the resin structure [8,9]. In recent research utilizing pyrolysis (Py)–GC–MS, among the pyrolysis products of novolac resin, low-volatile compounds, such as naphthalene, methyl naphthalenes, biphenyl, dibenzofuran, fluorene, phenanthrene and anthracene were identified at trace levels [10]. In our previous work on pyrolysis of uncured novolacs we have proved that the use of the movable reaction zone allows us to identify (apart from previously mentioned products) a group of ring compounds which were not confirmed as pyrolysis products until now: bis(hydroxyphenyl)methane, bis(hydroxybenzyl)phenol and their methyl and dimethyl derivatives. Trace amounts of xanthene were also found [2].

The main objective of the present work was the comparison of the pyrolysis products of cured novolac and resol resins particularly in relation to low-volatile degradation products. We have also focused on the influence of the time of the curing process and the temperature of the pyrolysis on the quality and quantity composition of the pyrolysate.

2. Experimental

2.1. Reagents

Acetone, phenol, methanol, oxalic acid were all analytical grade from POCh (Gliwice, Poland); formalin was a 35% aqueous solution of formaldehyde, also from POCh.

2.2. Preparation and setting of phenolic resins

Two kinds of resins were used in this study—resol and novolac. Resol resin was synthesized with the mole ratio of the ingredients, phenol–formaldehyde–water–catalyst=1:3:11.58:0.15. The synthesis time was 8 h at a temperature of 60 °C. Novolac resin was synthesized in an acid medium with the mole ratio of the substrates, formaldehyde–phenol–oxalic acid=1:1.25:0.2 at a temperature of 60 °C.

The resin was prepared for the curing process as a 10% acetone solution, to which 20% of urotropin was added. Samples of 1 μl were deposited on the surface of the ferromagnetic wire and after the evaporation of the solvent they were heated at a temperature of 150 °C for 10, 30 or 60 min.

However, resol resin was deposited before curing directly onto the ferromagnetic wire and the rest of the procedure was as for novolac.

2.3. Instrumentation

A Hewlett-Packard HP 5890/2 gas chromatograph with a flame ionization detector was used for the main experiments. A laboratory-made pyrolysis device was employed instead of a sample injector in the gas chromatograph according to the description of the device in our previous publications [1,2]. The sample deposited on the surface of the ferromagnetic wire had been introduced before analysis to the inside of the short precolumn placed inside movable head. At the end of the wire the sample reached the level of the inside of the induction coil where pyrolysis takes place. After pyrolysis, the whole head was lifted or lowered by means of a telescopic joint together with the upper part of the precolumn, which could be introduced to the thermostat of the chromatographic column.

The separation of the pyrolysis products of the resins was performed in a 30-m quartz capillary column type HP-5 (Hewlett-Packard) of 0.28 mm diameter. The temperature of the column was increased from 60 to 280 °C at a rate of 10 °C/min. Helium was used as the carrier gas.

Part of the experiment was carried out by Py–GC–MS to identify the pyrolysis products. For this purpose a Curie point pyrolyser type 1040 PSC (Fischer) joined with the injector of gas chromatography was used.

graph HP 6890 coupled with the MS 5973 system was used. The pyrolysis chamber before turning on the induction heating and during the separation of the pyrolysis products was maintained at a temperature of 200 °C. Conditions of the chromatographic separation were as described above.

3. Results and discussion

The pyrolysis of the phenol and formaldehyde cured resins was carried out in two systems: Py–GC and Py–GC–MS. The usage of the movable reaction zone in the first case, and the raising the temperature of the pyrolyser chamber to 200 °C in the second case made the analysis of the product with relatively high mole mass possible. The pyrolysis products of the two kinds of resin were identified on the basis of the obtained mass spectra. The resol resin pyrogram is shown in Fig. 1. The results of the identification are collected in Table 1.

The course of the experiments with the resin cured at 150 °C with different reaction times: 10, 30 and 60 min showed that the composition of the pyrolysates is not considerably different. So the influence of the time in the curing process on the pyrolysate composition for both types of resin is not noticeable. The curing process is relatively fast. It has been found that freshly synthesized resol resin subjected to pyrolysis gave similar composition of the pyrolysate as the resin previously heated for 10 min at 150 °C. Therefore the actual curing takes

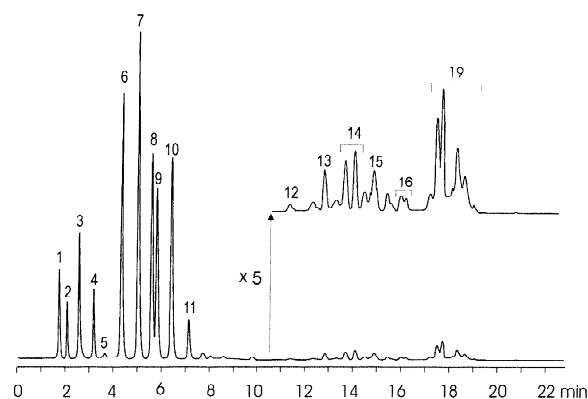


Fig. 1. Pyrogram of resol resin cured at 150 °C for 30 min and pyrolysed at 770 °C.

Table 1
List of components identified in pyrolysates

No.	Compound name	M_r
1	Benzene	78
2	Toluene	92
3	<i>o</i> -Xylene	106
4	<i>p</i> -Xylene	106
5	Mesitylene	120
6	Phenol	94
7	<i>o</i> -Cresol	108
8	<i>p</i> -Cresol	108
9	2,6-Dimethylphenol	122
10	2,4-Dimethylphenol	122
11	2,4,6-Trimethylphenol	136
12	Dibenzofuran	168
13	9H-Xanthene	182
14	Methyl-9H-xanthenes	196
15	Dimethyl-9H-xanthenes	210
16	Trimethyl-9H-xanthenes	224
17	Tetramethyl-9H-xanthene	238
18	Trimethylanthracene	220

place in the entry phase of the heating of the resin inside pyrolyser before the real pyrolysis process.

Further experiments aimed to show the influence of the temperature on the composition of the pyrolysis products. Resol resin, which was heated to 150 °C in 30 min and novolac resin with the addition of 20% urotropin heated at the same temperature were used in the experiments. Both resins were pyrolysed at 650, 770 and 900 °C. The results are shown in Table 2.

The temperature has some, but not much, influence on the pyrolysis products. Its increase promotes (among other things) the creation of relatively low-volatile products built differently. Unnoticed to date, the creation of considerable amounts of xanthene and its methyl derivatives is characteristic for cured products.

Figs. 2 and 3 show mass spectra of xanthene and of one of the methyloxanthene isomers obtained for peaks 13 and 14, respectively. The presence of the molecular ions of both compounds and also the fragmentary ions $[M-1]^+$, $[M-30]^+$ and $[M-29]^+$ characteristic for this type of compounds in the spectra confirm the structure of these compounds [11].

Undoubtedly, xanthenes are created as a result of the reaction of cyclisation (Fig. 4) with the participation of the hydroxyl groups in the *ortho* position in

Table 2
Pyrolysis products concentrations (mass%) in relation to pyrolysis temperature

Component	Resol			Novolac		
	Temperature (°C)	650	770	650	770	900
Aromatic hydrocarbons (sum)	1.8	21.4	22.6	1.9	25.4	26.6
Phenol	9.4	11.3	11.3	15.0	16.4	14.5
2-Methylphenol	22.0	16.7	16.8	27.1	20.6	20.4
4-Methylphenol	12.1	10.0	9.7	13.4	12.1	13.5
2,6-Dimethylphenol	15.8	11.4	11.2	16.1	9.2	7.3
2,4-Dimethylphenol	23.7	16.6	15.9	18.9	12.2	12.0
2,4,6-Trimethylphenol	13.7	10.2	9.8	7.0	3.0	2.5
Xanthene and its methyl derivatives	1.5	2.3	2.7	0.5	1.1	3.2

The components present in pyrolysate on the trace level have been omitted.

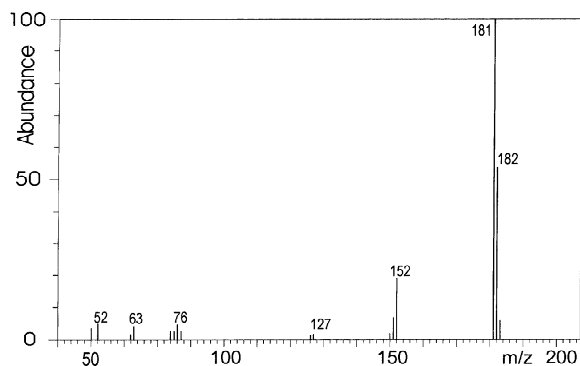


Fig. 2. Mass spectrum of the compound no. 13 (according to numbering in Table 1).

relation to methylene bridges [2]. The presence of xanthene and its derivatives in both types of the resin reveals the similarity of their cured structures.

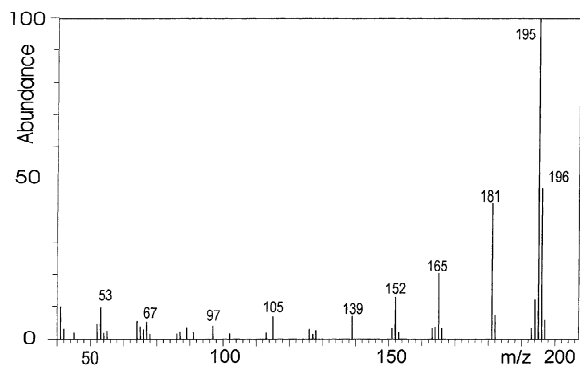


Fig. 3. Mass spectrum of the compound no. 14 (according to numbering in Table 1).

Novolac resin cured with a shortage of urotropine (addition of 10% instead of 20%) was also subjected to pyrolysis. Among the pyrolysis products (apart from xanthene and its methyl derivatives) the presence of the isomer bis(hydroxyphenyl)methane was observed (Fig. 5, peak 19) as in the case of uncured novolacs [2]. This may indicate the existence of linear sequences in cured novolac resin. However, the presence of xanthenes ought to be correlated with the cured structure.

4. Conclusions

The pyrolysis of cured novolac and resol resin leads mainly to phenol and its derivatives as well as a certain amount of low-volatile compounds with two condensed rings. The creation of considerable amounts of xanthene and its methyl derivatives is characteristic for both types of cured resins. In the

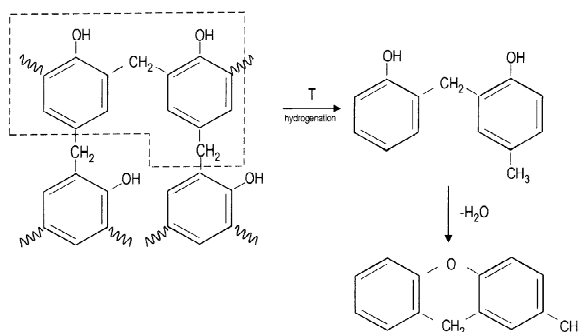


Fig. 4. Scheme of cyclization reaction of cured phenolic resin.

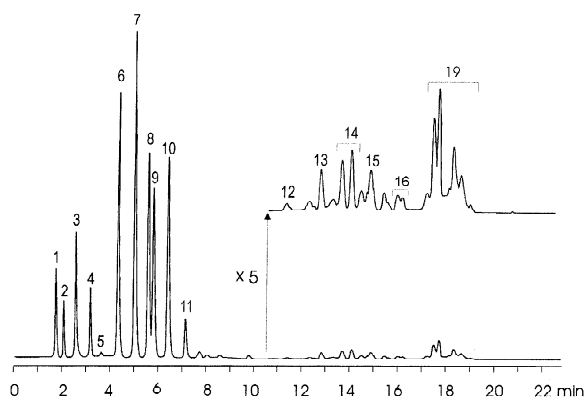


Fig. 5. Pyrogram of novolac resin cured with addition of 10% urotropin at 150 °C and pyrolysed at 770 °C.

case of partially cured novolac, as well as xanthere, bisphenols are created which indicates the presence of linear sequences in the macromolecule.

The curing process of resol resin at high temperature takes place in a very short period of time, therefore the dependence of the composition of pyrolysate on the time of curing process is negli-

gible. However, the increase of the temperature in the range of 650–900 °C influences the quantity of the low-volatile ingredients in pyrolysis products.

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