

# Synthesis of phenol–formaldehyde resole resins in the presence of tetraalkylammonium hydroxides as catalysts

B. Kaładkowski<sup>a</sup>, J. Hetper<sup>b,\*</sup>

<sup>a</sup>Institute of Heavy Organic Synthesis, 47-225 Kędzierzyn-Koźle, Poland

<sup>b</sup>University of Opole, Institute of Chemistry, 45-052 Opole, Oleska Str. 48, Poland

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## Abstract

We synthesised phenol–formaldehyde resole resins in the presence of tetraalkylammonium hydroxides as catalysts. The activity of these catalysts was compared with the activity of sodium hydroxide. Gas chromatography, thin layer chromatography, <sup>13</sup>C NMR spectrometry, potentiometric titration and a few simple physicochemical methods were used to estimate the composition of the obtained resins and their properties. It was concluded from these studies that tetraalkylammonium hydroxides are active catalysts and the resins obtained in their presence show some interesting properties. © 1999 Elsevier Science Ltd. All rights reserved.

**Keywords:** Phenol–formaldehyde resins; Tetraalkylammonium hydroxides; Condensation reaction

## 1. Introduction

Resole resins are obtained in the reaction of phenol (P) and formaldehyde (F) in aqueous alkaline solutions. The resins synthesised within the temperature range of 40–70°C and at the mole ratio [F]/[P] of 2–4 consist of mono-, di- and trihydroxymethyl phenols and their condensation products [1,2]. The common catalysts of phenol–formaldehyde resole synthesis are: sodium, potassium and lithium hydroxides, and rarely hydroxides of divalent metals: magnesium, calcium or barium [1,2]. Also, carbonates (sodium carbonate) and oxides (calcium or magnesium oxides) can be used as the catalysts in this synthesis [3,4]. Tertiary amines, in particular triethylamine, were claimed recently as the catalysts for the resole synthesis [5,6].

The catalyst type is known to influence the rate of reaction of phenol and formaldehyde and the properties of the resins obtained. So, Peer found that the substitution of phenol with formaldehyde in the *ortho*-position versus *para*-position increased in the following sequence of hydroxide catalyst metals: K < Na < Li < Ba < Sr < Ca < Mg [7,8].

Grénier-Loustalot et al. [9] concluded that the rate at which phenol disappeared from the reaction mixture was dependent on the metal valence in the hydroxide catalyst

and on the size of the hydrated metal cation. Magnesium, calcium and barium hydroxides were found to be more effective catalysts than lithium, sodium or potassium hydroxides. The catalytic activity of the hydroxides decreases for both the groups of metals when the ionic radius of the hydrated cation diminishes. The authors also ascertained that LiOH and Ba(OH)<sub>2</sub> favoured the reaction of trihydroxymethylphenol to higher molecular weight species which was a desirable property from the view point of resin setting.

In the present work the properties of tetraalkylammonium hydroxides as the catalysts for the resole synthesis in relation to those for sodium hydroxide were studied. Up to now, the applicability of the compounds was not verified in the resoles synthesis.

## 2. Experimental

### 2.1. Chemicals

Phenol (P; purified by distillation; the fraction with b.p. = 182–182.5°C was used), formalin (F; containing 35.6% reactive formaldehyde), sodium hydroxide (POCh-Gliwice, Poland, puriss.), hydroxides of: tetramethylammonium (TMAH), tetrapropylammonium (TPAH) and tetrabutylammonium (TBAH), pure, supplied by Zalbommel CBV, and tetraethylammonium hydroxide (TEAH; pure, product of Aldrich).

\* Corresponding author.

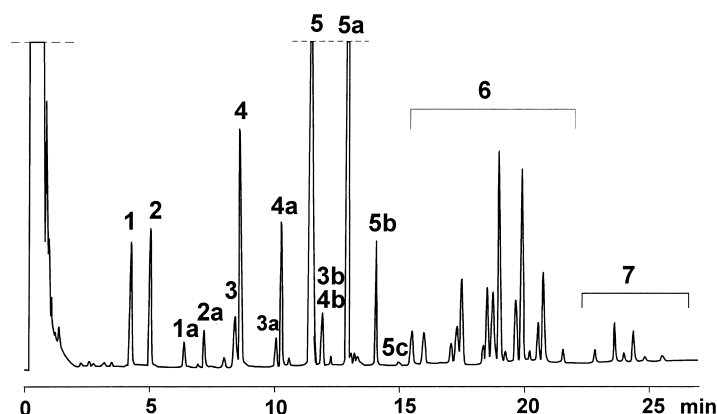


Fig. 1. A typical picture of gas chromatographic separation of components of the phenol–formaldehyde resole obtained in the presence of an alkaline catalyst (separation in 15 m RTX-1 capillary column with ID = 0.32 mm contained poly(dimethylsiloxane) resin as a stationary phase (layer of 0.2  $\mu\text{m}$ ). The column temperature programmed from 60 to 340°C at the rate of 10°C per minute. Sample trimethylsilylated with BSA before the analysis).

## 2.2. Synthesis of resoles

Weighed amounts of phenol, formalin and water were introduced to a 1 dm<sup>3</sup> heated reactor, which was equipped with a stirrer, cooler and thermometer. The mixture was stirred and heated to 60°C. When the temperature became stable, a catalyst was added. The mole ratio [F]/[P] was 3.0 in all experiments. The mole fraction of water in the reaction mixture was 71.9% and that of the catalyst was 0.93%. The synthesis was carried out for 8 h. The reaction mixture was sampled for analysis after 1/6, 1/3, 1/2, 1, 2, 4, 6 and 8 h from adding the catalyst to the reactor. A part of the end product was cured at 230°C. This procedure was repeated for each catalyst. The symbols of synthesised resoles are: Resole M (synthesised in the presence of TMAH), Resole E (catalyst: TEAH), Resole P (catalyst: TPAH), Resole B (catalyst: TBAH) and Resole N (catalyst: NaOH).

## 2.3. Experimental techniques

### 2.3.1. Potentiometric titration

The analysis of reactive formaldehyde present in the reaction mixtures was performed with the standard method [10]. Formaldehyde was condensed with hydroxylamine hydrochloride. Hydrochloric acid evolved from this reaction was determined by potentiometric titration with sodium hydroxide, using a glass electrode.

### 2.3.2. Elementary analysis

A Fisons EA 1108 CHNS-O instrument was used to analyse the nitrogen content in the cured resins.

### 2.3.3. Thin layer chromatography

The Camag thin layer chromatography (TLC) set equipped with the computer controlled densitometer was employed to estimate the free phenol concentration in the reaction mixture. The mixtures were separated on the plates coated with 60 F<sub>254</sub> silicagel. Calibration mixtures were used for the quantitative analysis.

### 2.3.4. Capillary gas chromatography

A Perkin–Elmer 8700 gas chromatograph equipped with a flame ionisation detector was applied to determine the reaction product composition. The samples were separated in the 15 m RTX-1 capillary column (Restek) with ID = 0.32 mm. Poly(dimethylsiloxane) resin was the stationary phase (layer of 0.2  $\mu\text{m}$ ). The column temperature was programmed from 60°C to 340°C at the rate of 10°C per minute. All the samples were trimethylsilylated with BSA [bis(trimethylsilyl)acetamide] before the analysis. Prókai's works [11,12] were helpful in selecting the analysis parameters and in qualitative interpretation of the analysis.

### 2.3.5. Solid state NMR

Solid state <sup>13</sup>C NMR spectra of the cured resins were obtained with a Varian VXR-300 spectrometer (nominal frequency of 75 MHz). The high power dipolar decoupling and magic angle sample spinning methods were used during the analysis. Hexamethylbenzene was the standard for the chemical shift calculations.

## 2.4. Methods for study of the physicochemical properties of resins

- *Density of the reaction mixtures* was estimated by an areometer.
- *Ash content* of the resins was estimated after incineration (4 h) at a temperature of 900°C.
- *Gelation time* of the resins was studied by a simple test in which the sample placed on a metal plate was heated up to temperature of 150°C and the resin was mixed all the time with a thin glass rod. The time was measured when the resin material could not flow down the glass rod.
- *Resin miscibility with water* was studied by the ISO method [13].
- *Binding ability of resin* was measured according to Ref. [14]. The resin was mixed with glass beads (OD = 0.3 mm) and cured at 230°C. This material

Table 1

List of major components of analysed mixtures (Hemiformals of hydroxymethyl derivatives of phenol are marked by letters a,b,c for mono-, di- and trihemiformals, respectively)

No	Name of compound	Mol. weight
1	2-Hydroxymethylphenol	124.1
2	4- Hydroxymethylphenol	124.1
1a	2-(3-Hydroxy-2-oxapropyl)phenol (hemiformal of compound 1)	154.1
2a	4-(3-Hydroxy-2-oxapropyl)phenol (hemiformal of compound 2)	154.1
3	2,6-Dihydroxymethylphenol	154.1
4	2,4-Dihydroxymethylphenol	154.1
3a, 4a	Hydroxymethyl (3-hydroxy-2-oxapropyl)phenol (isomers of hemiformal of compounds 5 and 6)	184.2
5	2,4,6-Trihydroxymethylphenol	182.2
3b, 4b	bis(3-Hydroxy-2-oxapropyl)phenol (isomers of dihemiformals of compounds 5 and 6)	210.2
5a	Dihydroxymethyl (3-hydroxy-2-oxapropyl)phenol (hemiformal of compound 9)	240.2
5b	bis(3-Hydroxy-2-oxapropyl)hydroxymethylphenol (dihemiformal of compound 9)	270.3
5c	tris(3-Hydroxy-2-oxapropyl)phenol (trihemiformal of compound 9)	300.3
6	Hydroxymethyl derivatives of bis(hydroxyphenyl)methane	
7	Hydroxymethyl derivatives of hydroxybenzyl[bis(hydroxyphenyl)methane]	

obtained in form of the rod was subjected to the bending strength tests with the use of an Instron 1112 instrument. For each resin five measurements were taken and the mean value was calculated. Another set of specimens was tested after the materials were maintained during 72 h in the atmosphere of saturated steam at 20°C. The same investigation was performed for specimens which were kept for 4 h in boiling water.

### 3. Results and discussion

The typical gas chromatogram of resole, which has been synthesised in the presence of alkaline catalyst, is shown in Fig. 1. The components of the mixture marked by numbers 1–7 are listed in Table 1.

The major components are formed in the reactions [15] as shown in Fig. 2. The hydroxymethyl derivatives of phenol are in equilibrium with respective hemiformals, which are formed by adding one more molecule of formaldehyde [15]. The changes of the concentrations of hydroxymethyl derivatives of phenol (together with its hemiformals) and the condensation products during the synthesis process have been compared for Resole E and Resole N in Fig. 3. As can be seen, the directions for these changes are similar. The pictures obtained are typical for sequential reactions if the reaction rate constants are close to one another. In order to compare the activity of catalysts, the rate constants for the reaction of phenol and formaldehyde have been calculated from the simple equation for the second order reaction:

$$d[P]/dt = -k[F][P].$$

The obtained results are provided in Table 2, which indicates that the activity of tetraalkylammonium hydroxides with 2–3 C atoms in alkyl groups is only a little lower than that of NaOH. The activity of the former decreases in the sequence: TMAH > TEAH > TPAH > TBAH.

It is known that the size of hydrated tetraalkylammonium ions increases with the growing number of C atoms in alkyl substituents [16]. The above results can lead to the conclusion that the activity of studied ammonium hydroxides against that of metal hydroxides decreases when the ionic radius of the hydrated cation increases. Probably, in this case the activity does not depend on the ion diameter but rather on the screening effect of alkyl groups.

The ratio of the concentrations of the *ortho*- and *para*-hydroxymethylphenols, which are the primary reaction

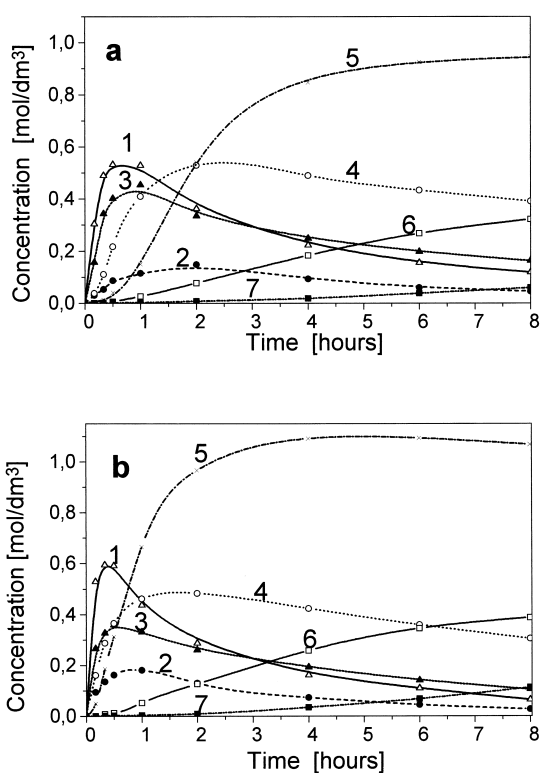


Fig. 2. Concentration profiles for the main products of the resole synthesis: (a) resole E; (b) resole N.

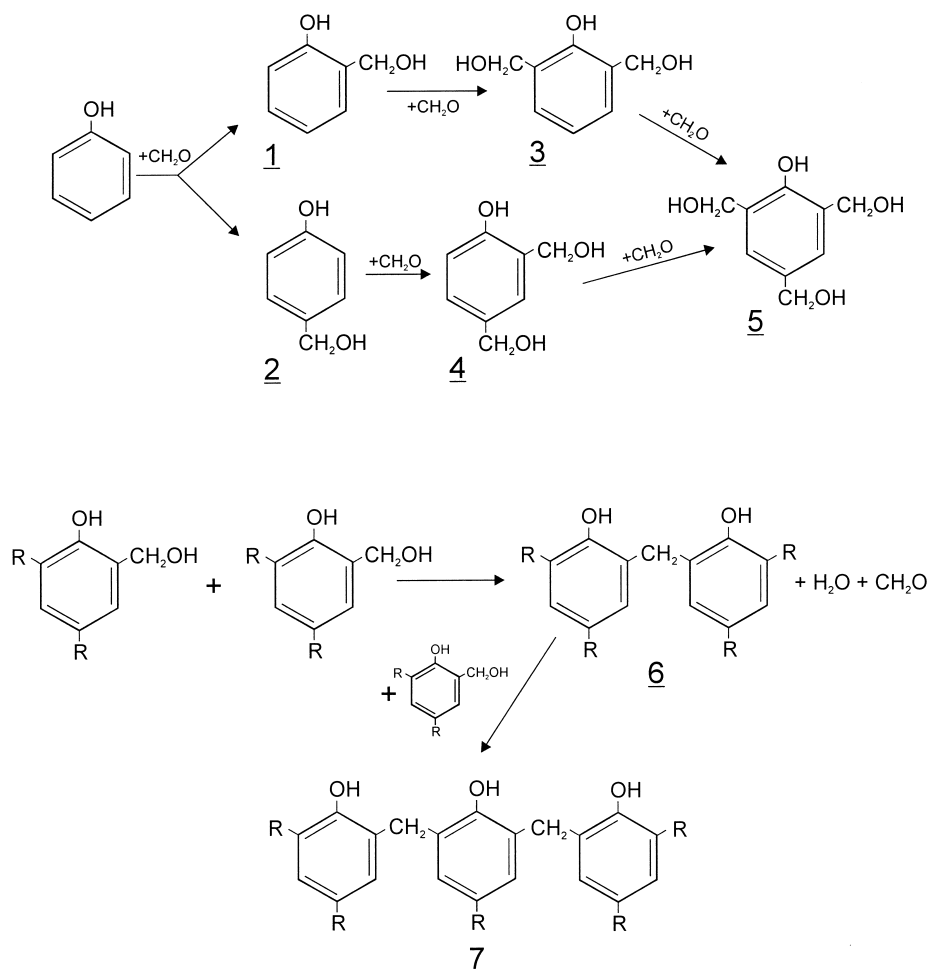


Fig. 3. Scheme of main reactions taking place during the synthesis of resoles. Note: R =  $\text{CH}_2\text{OH}$  or H.

Table 2

The rate constants of the reaction of phenol and formaldehyde (Note: The relative values of “k” (in relation to k of reaction catalysed by NaOH) are given in parentheses)

Reaction rate constants, k [ $\text{dm}^3/\text{mol}\cdot\text{h}$ ]		TPAH	TBAH	NaOH
TMAH	TEAH			
0.1551 (0.87)	0.1348 (0.76)	0.1280 (0.69)	0.1082 (0.61)	0.1774 (1.00)

products (see Fig. 2), reflects the ability of a catalyst to direct the substituents to the active position in phenol. The values of the ratio are shown in Table 3. The differences are not significant.

The physicochemical properties of the resins studied are given in Table 4. The Resoles P and B show the limited miscibility with water. This property restricts their application possibility and prefers the use of TEAH or TMAH as catalyst in the synthesis of this type of resins.

The gelation time of resoles obtained in the presence of tetraalkylammonium hydroxides is generally longer than the gelation time for the resins synthesised with the use of NaOH. The catalysts of resin synthesis are also known to influence the condensation reactions of resin components [17]. In this case it is possible that the catalytic properties

of ammonium hydroxides differ from those for sodium hydroxide. The long gelation time is an advantage during transportation and storage of the resoles at industrial conditions.

Table 3

Ratio of the concentration of *ortho*- to *para*-hydroxymethylphenols in the reaction mixtures

Symbol of resole	Ratio of concentrations
M	1.990
E	1.815
P	1.999
B	2.449
N	2.185

Table 4  
Physicochemical properties of obtained resins

Symbol of resole	Free phenol (%)	Reactive CH <sub>2</sub> O (%)	Density (g/cm <sup>3</sup> )	Gelation time (s)	Miscibility with water	Ash content (%)
M	0.48	5.12	1.121	102	1: ∞	0
E	0.53	5.37	1.115	118	1: ∞	0
P	0.70	5.15	1.114	100	1: 3	0
B	1.12	5.48	1.108	125	1: 0.2	0
N	0.36	4.76	1.138	62	1: ∞	1.13

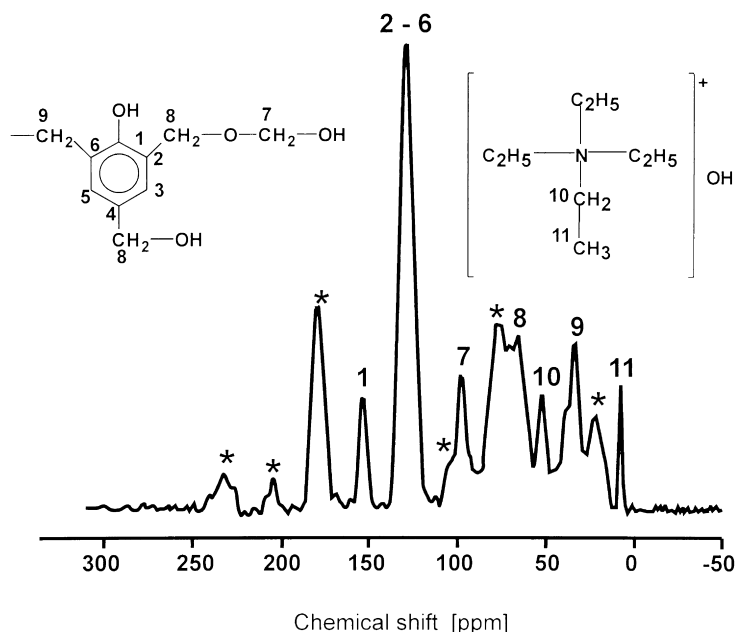


Fig. 4. A solid state <sup>13</sup>C NMR spectrum of resole E after curing. Note: the asterisked peaks (\*) represent the rotational bands of the main signals.

The important property, which differentiates the resins studied from the resins obtained in the presence of metal hydroxides, is no ash after incineration. It is an important advantage for any application.

The analysis of resoles M, E, P and B after curing shows that the catalysts do not evaporate during the curing process. Namely, the elementary analysis showed that almost the whole amount of nitrogen introduced to the system remained in the cured resin. It is still a question whether the ammonium catalysts are chemically bonded by the resoles during the curing process. To explain this problem, the <sup>13</sup>C NMR analysis of resoles obtained with the use of tetraalkylammonium hydroxides was carried out. The exemplary <sup>13</sup>C NMR spectrum of cured resole E is shown in Fig. 4. As can be seen, the NMR signals in the spectrum are derived either from the free resin or from the free catalyst. Hence, the catalyst remains in free state in resin.

In Table 5, the measurement results are provided for the bending strength of rods formed from glass beads and resoles E and N. The tests involved these materials immediately after their curing ( $\sigma_a$ ), after steaming ( $\sigma_b$ ), and after immersing in boiling water ( $\sigma_c$ ). The high value of  $\sigma$  indicates that resin adheres strongly to the glass bead surface.

Therefore, the results of these measurements express indirectly the “binding ability” of a resin. This is an important performance property of phenol–formaldehyde resins.

The first and the second tests indicate that the resin obtained in the presence of tetraalkylammonium hydroxide show a better binding ability than the conventional resin. The third test gives comparable results for both resins.

#### 4. Conclusions

The presented studies on the synthesis and properties of resoles obtained with the use of tetraalkylammonium hydroxides as catalysts indicate that the activity of these catalysts is only a little lower than the activity of sodium hydroxide.

Table 5  
Mechanical resistance of hardened resins with filler

Symbol of resin	Bending strength (MPa)		
	$\sigma_a$	$\sigma_b$	$\sigma_c$
E	6.08	0.19	0.11
N	4.10	0.13	0.11

However, the properties of the resoles differ from the properties of resins obtained with the use of conventional catalysts. Their characteristic features are: long gelation time, no ash after incineration and relatively better binding ability.

In practice, it is better to use tetramethyl- or tetraethyl-ammonium hydroxides as catalysts than tetrapropyl- or tetrabutyl-ammonium hydroxides because the latter give the limited miscibility of the resins obtained with water.

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