Phenolic resins: 1. Mechanisms and kinetics of phenol and of the first polycondensates towards formaldehyde in solution

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Using chemically defined compounds (first reaction product intermediates of the phenol–formaldehyde system), we have studied the reaction mechanisms of formaldehyde condensation in perfectly controlled conditions (temperature, stoichiometry, catalyst and pH). The results obtained with a range of techniques, e.g. high-performance liquid chromatography, ^{13}C nuclear magnetic resonance and chemical assay, show that the reaction kinetics and the structures of the resole end-products depend on synthetic and operating conditions.

(Keywords: phenol–formaldehyde resins; reaction mechanisms; kinetics)

INTRODUCTION

Thermohardened polymers prepared from phenol–formaldehyde systems arise from condensation in basic medium. In light of their varied applications in industry, current demands are for specific and improved characteristics, requiring a thorough understanding of the base prepolymer[1–3]. Physicochemical characterization methods in solution and in the solid state (liquid and solid ^{13}C n.m.r. and h.p.l.c.) used for these systems have led to considerable progress in the understanding and composition of the species present in the reaction mixture or of transients[4–10].

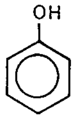
The combined use of these different methods of investigation should enable a reaction path for these systems to be proposed. Because of the complexity of the mechanisms involved, resulting from the experimental conditions (temperature, stoichiometry, catalyst, pH), however, we undertook a basic study of the phenol–formaldehyde system in the liquid state, starting with the first condensation products, and one of the phenol–formaldehyde (P–F) system itself in perfectly controlled conditions of pH, temperature and F/P concentration ratio.

EXPERIMENTAL

Synthesis of model compounds

Phenol (**1**) (99+%), 2-hydroxymethylphenol (**2**) (99%), 4-hydroxymethylphenol (**3**) (98%), 4,4′-dihydroxydiphenylmethane (**7**) (97%) and formaldehyde (37% solution w/w) were commercial products (Aldrich and Lancaster) and were used without further purification.

2,6-Dihydroxymethylphenol (**4**) and 2,4-dihydroxymethylphenol (**5**) were synthesized according to Freeman and Sprengling[11,12] and 2,4,6-trihydroxymethylphenol (**6**) according to Perrin *et al.*[13].



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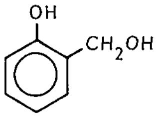

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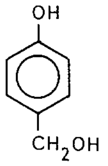

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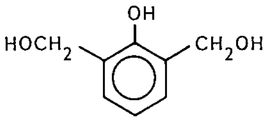

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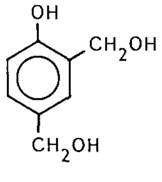

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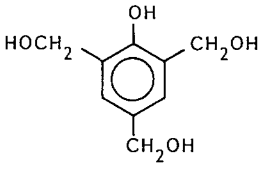

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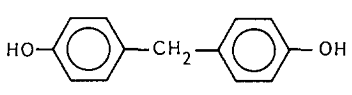

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Synthesis of resoles

Phenol (P) and formaldehyde (F) were mixed at 60°C in a variable ratio $R = F/P$. The pH was then adjusted to 8 with a titrated solution of sodium hydroxide.

Liquid chromatography (h.p.l.c.)

Analyses were conducted with a Varian 5000 chromatograph equipped with a u.v. detector set at 273 nm and Spherisorb ODS-2 (5 μm) columns, 25 cm long. The mobile phase of methanol/water was used with the elution gradient 10% to 100% methanol in 50 min. The precise analysis conditions for each system are provided in the figure legends. Samples were dissolved in methanol.

Nuclear magnetic resonance (n.m.r.)

High-resolution ^1H and ^{13}C n.m.r. spectra in liquids were recorded with a Bruker AM 400 spectrometer. The following conditions were used to record spectra: pulse angle 90° (7 μs ^1H, 4.2 μs ^{13}C); digital resolution 0.122 Hz/pt (^1H) and 0.375 Hz/pt (^{13}C) corresponding to a spectral length of 4000 Hz (^1H) and 20 000 Hz (^{13}C) for a memory space of 64K (^1H) and 128K (^{13}C).

Samples were dissolved in monodeuterated ethanol, deuterated dimethylsulfoxide or heavy water (D_2O). ^{13}C chemical shifts were measured with respect to tetramethylsilane (TMS) as internal standard: $\delta(CH_3CH_2OD) = 17.9$ and 57.3 ppm; $\delta(DMSO\text{-}d_6) = 39.5$ ppm.

Ultra-violet absorption spectroscopy

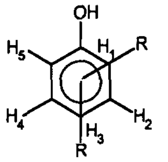
Spectra were recorded with a Shimadzu UV 2101/3101 PC spectrophotometer. The compounds studied were dissolved in acetonitrile. The spectral band analysed was from 190 to 400 nm.

Characterization of the compounds studied in this work

The simultaneous use of different physicochemical methods enabled each model compound to be characterized. *Tables 1* and *2* list the ^1H and ^{13}C n.m.r. chemical shifts. Since the different model compounds were reaction intermediates, these data enabled either the species created or transients to be identified in kinetic studies of the addition of formaldehyde to phenol in basic medium.

Finally, a system for analysing resoles was developed, involving high-performance liquid chromatography with u.v. detection. In order to quantify the species present in

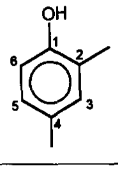
Table 1 ^1H n.m.r. chemical shifts. Solvents: DMSO-d_6 (*), D_2O (†)



Compound (solvent)	–OH	H1	H2	H3	H4	H5	–CH_2– (*ortho*)	–OH *ortho*	–CH_2– (*para*)	–OH (*para*)
2 2-HMP (*)	9.27		7.27	6.76[a]	7.02[a]	6.75[a]	4.47	4.93		
3 4-HMP (*)	9.22	6.69[b]	7.09[b]		7.09[b]	6.69[b]			4.34	4.93
4 2,6-DHMP (†)			7.26[c]	6.98[c]	7.26[c]		4.80			
5 2,4-DHMP (†)			7.29[d]		7.23[d]	6.91[d]	4.54		4.65	
6 2,4,6-THMP (*)			6.89		6.89		4.33	3.14	4.17	4.75

[a] $J_{2\text{-}3} = 7.29$ Hz; $J_{3\text{-}4} = 7.60$ Hz; $J_{4\text{-}5} = 7.60$ Hz
[b] $J_{1\text{-}2} = 8.12$ Hz
[c] $J_{2\text{-}3} = J_{3\text{-}4} = 7.49$ Hz
[d] $J_{2\text{-}4} = 2.12$ Hz; $J_{4\text{-}5} = 8.20$ Hz

Table 2 ^{13}C n.m.r. chemical shifts. Solvents: DMSO-d_6 (*), D_2O (†)



Compound (solvent)	C1	C2	C3	C4	C5	C6	CH_2OH (*ortho*)	CH_2OH (*ortho'*)	CH_2OH (*para*)
1 Phenol (†)	158.4	118.2	132.6	123.1	132.6	118.2			
2 2-HMP (†)	157.0	129.3	132.3	123.0	132.2	118.4	62.4		
3 4-HMP (†)	158.3	118.3	132.3	134.6	132.3	118.3			66.3
4 2,6-DHMP (†)	155.0	129.9	131.7	123.5	131.7	129.9	62.9	62.9	
5 2,4-DHMP (†)	156.1	129.2	131.8	134.7	131.6	118.2	62.1		66.2
6 2,4,6-THMP (†)	154.7	130.1	131.1	135.1	131.1	130.1	62.8	62.8	66.2
7 4,4′-DHDPM (*)	155.9	115.6	129.9	132.6	129.9	115.6			40.59[a]

[a] Ar–CH_2–Ar

Table 3 U.v. spectroscopy: molar absorption coefficients at 273 nm

Compounds		ε ($l\,mol^{-1}$)
1	Phenol	1700
2	2-HMP	1700
3	4-HMP	1500
4	2,6-DHMP	1900
5	2,4-DHMP	1500
6	2,4,6-THMP	1900
7	4,4'-DHDPM	3000

the reaction mixture, however, it was necessary to determine the molar absorption coefficient ε of each compound. The results enabled the validation of data obtained with external standards for unknown high-molecular-weight species not synthesized. The data indicate that the ε values of monomeric substituted compounds were similar regardless of the position and number of substituent(s), while absorption of the dinuclear compound **7** was twice as high at 273 nm (*Table 3*).

KINETIC AND MECHANISTIC MONITORING

Reaction mechanisms described in the literature[15-18]

Figure 1 shows the different reaction mechanisms presented in the literature. They can be described in two steps. The first (*Figure 1a*) is attributable to formaldehyde substitution on the free *ortho* and *para* positions of the phenol ring. The products formed are the first mono-, di- and trifunctionalized monomeric reaction products studied above. Published results[15,16] have shown that monofunctionalized derivatives (**2** and **3**) are the major species in comparison to difunctional species (**5** and **4**). Concerning the trifunctional compound **6**, it was present in the reaction medium in the conditions described only in very small quantities.

The second step involves co-condensations between two molecules (substituted or not) (*Figures 1b–d*), and several mechanisms have been described at this level. The first (*Figure 1b*) can be envisioned only in neutral or acidic conditions and up to a temperature of 130°C. Beyond this, the ether bond formed becomes a methylene bridge after the departure of one molecule of formaldehyde[2], and the product described in *Figure 1c* is obtained. The second reaction describes the two simultaneous mechanisms and occurs most often in basic medium. Finally, the third mechanism (*Figure 1d*) is attack on an aromatic ring proton by a hydroxymethyl group.

In order for mechanism (b) to occur, the medium must contain formaldehyde to enable the reaction to continue. This is not the case for mechanisms (c) and (d), where any condensation releases a molecule of formaldehyde, which enables new substitutions and may cause new condensations. In contrast to the first mechanisms ((b) and (c)) that require a reaction between two hydroxymethyl groups, mechanism (d) is by far the most interesting since the *ortho* and *para* hydroxyl protons of phenol are considered to be reactive and so condensation consumes only one hydroxymethyl group. The condensation reaction thus no longer forms formaldehyde, which at the end of the reaction has no more functional sites available and may hinder the quality of the final product.

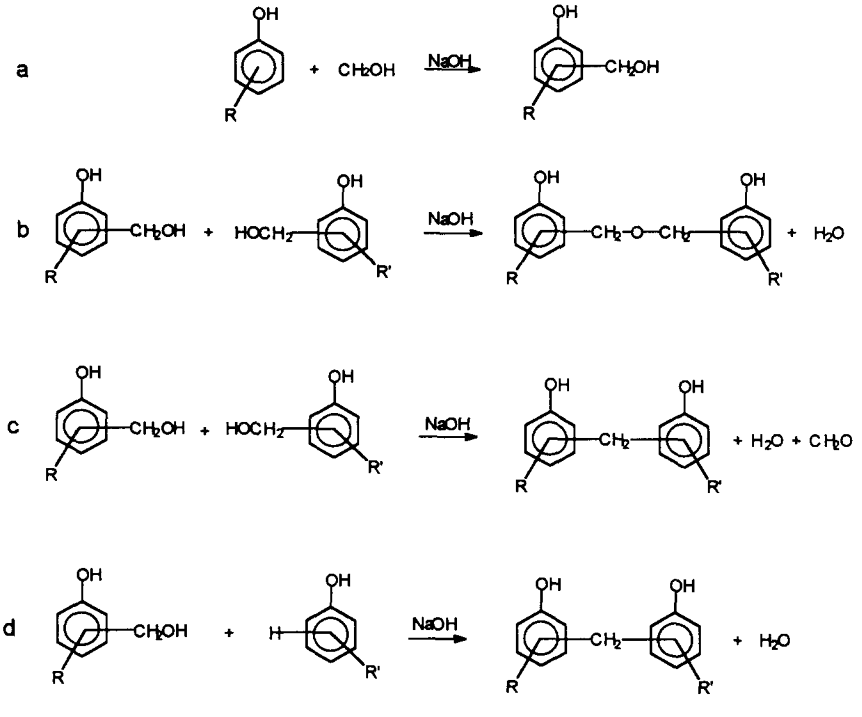


Figure 1 Reaction mechanisms: (a) condensation; (b) dehydration by loss of one molecule of water; (c) dehydration and condensation by loss of one molecule of water and of formaldehyde; (d) attack on aromatic proton by a hydroxymethyl group

Methodology

Several physicochemical techniques were used to follow changes in the reaction mixture with time. The methods employed enabled the reaction rates to be determined and the products formed to be identified.

Method (*a*). Chemical assays[14] (determination of the formaldehyde concentration in the reaction mixture at all times).

Method (*b*). High-performance liquid chromatography, assay of residual products and identification of products formed.

Method (*c*). ^{13}C nuclear magnetic resonance, used to identify the chemical species formed and to assay them; substitution on phenol (160–150 ppm region) and co-condensations (45–30 ppm region).

Results

Reactivity of the different monomers 1 to 5 with formaldehyde at constant F/monomer ratio and temperature. The study of condensation of five monomers (phenol (**1**), 2-HMP (**2**), 4-HMP (**3**), 2,6-DHMP (**4**) and 2,4-DHMP (**5**)) with formaldehyde in the same conditions of temperature (60°C) and stoichiometry (formaldehyde/monomer ratio of 1) shows that their reactivities differed as a function of their substitution (site and number) on the aromatic ring. Thus, the reactivity of each carbon not substituted *ortho* or *para* to the hydroxyl group was modified by the site and number of substitutions of the benzene ring.

The expected reactions for each compound are described in *Figure 1*. The kinetics was followed simultaneously by h.p.l.c. and ^{13}C n.m.r. for 50 h in the same samples. Initially, mononuclear polysubstituted species were created (compounds **2** to **5**), followed by the rapid appearance of dimeric compounds and finally trimers beyond 24 h, confirming the different reactions described previously. These results are graphically represented in *Figure 2*.

In spite of differing reactivities during the first 10 h, it is noted that the residuals of each compound were similar, between 30 and 40%, except for compound **4**, *ortho–ortho'* disubstituted, where the residual level was less than 10%. The *para* aromatic carbon was more reactive towards formaldehyde or hydroxymethyl groups (condensations) than the *ortho* aromatic carbon. This led to the practically total disappearance of compound **4** during kinetic measurements. Other compounds with one or two substituents (compounds **2**, **3** and **5**) were less reactive and there were more residuals after 50 h (40%).

The limiting step in the disappearance of phenolic monomers is thus the reaction between formaldehyde and the aromatic carbons in *ortho* position and/or the condensation of hydroxymethyl groups on the same carbons.

Reactivity of phenol towards formaldehyde: influence of the ratio R = *F/P on the kinetics of the phenol–formaldehyde reaction at constant temperature* (*60°C*) *and pH* (*8*). The kinetics of the addition of formaldehyde on phenol at variable stoichiometric F/P ratios (1, 1.3 and 1.5) at constant temperature and pH were followed for 50 h by chemically assaying residual formaldehyde (*Figure 3*) and by following the disappearance of phenol by ^{13}C n.m.r. (peak at 157 ppm) (*Figure 4*). The results obtained with both monomers were consistent: as formaldehyde is further from stoichiometry, the substitution is favoured more and formaldehyde residuals are more abundant.

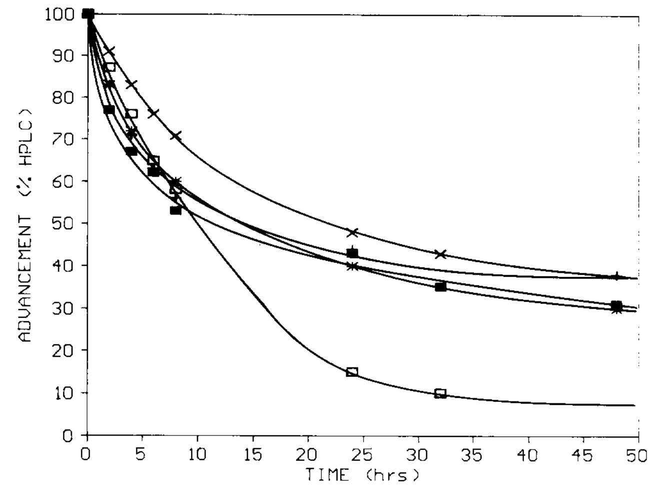


Figure 2 H.p.l.c. kinetics of monomers at $R=1$, 60°C, pH=8: (■) phenol; (+) 2-HMP; (∗) 4-HMP; (□) 2,6-DHMP; (×) 2,4-DHMP

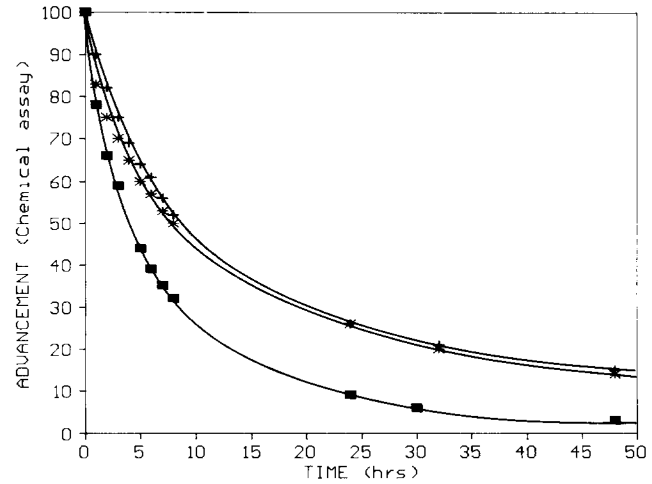


Figure 3 Disappearance of formaldehyde by chemical assay, showing influence of stoichiometry: (■) $R=1$; (+) $R=1.3$; (∗) $R=1.5$

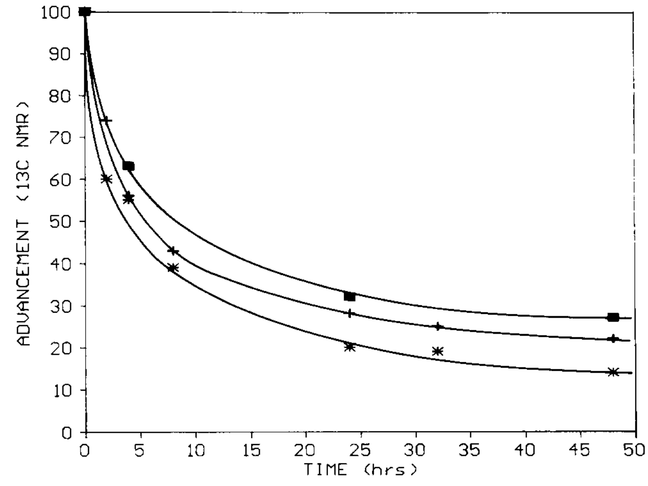


Figure 4 Disappearance of phenol by ^{13}C n.m.r., showing influence of stoichiometry: (■) $R=1$; (+) $R=1.3$; (∗) $R=1.5$

The rate constants obtained after simulating the curves in *Figure 4* with the equations:

$$P + F \rightarrow X \qquad \frac{d[X]}{dt} = k[P][F]$$

with P = phenol, F = formaldehyde and X = formed products, lead to the conclusion of overall second-order kinetics for the disappearance of phenol. The constants changed from 12.4×10^{-2} mol h^{-1} for $R = 1$, to 16.7×10^{-2} mol h^{-1} for $R = 1.3$, up to 19.4×10^{-2} mol h^{-1} for $R = 1.5$, indicating an acceleration of the process as a function of the formaldehyde content. Kinetics followed by h.p.l.c. (*Figure 5*) enabled the species created and residuals to be quantified. Thus, the disappearance of phenol (the disappearance of formaldehyde cannot be followed by u.v. detection) was accompanied by the formation of mononuclear substituted compounds during the first 10 h, which were identified on the basis of our standard compounds. They reacted with time to form higher-order substituted compounds, indicating competition between addition reactions of formaldehyde on the phenol ring and also between co-condensation reactions starting after 8 h and which subsequently became predominant, depending on experimental conditions.

As an example, *Figure 6* shows the kinetics of species for an F/P ratio of 1.5. It is seen that the different mononuclear compounds disappeared slowly starting at 8 h, at the expense of dimers. The results gathered for $R = 1.5$ and $R = 1$ indicate that the level of dimers after 24 h was proportional to the F/P ratio (30% for $R = 1.5$ and 15 to 20% for $R = 1$).

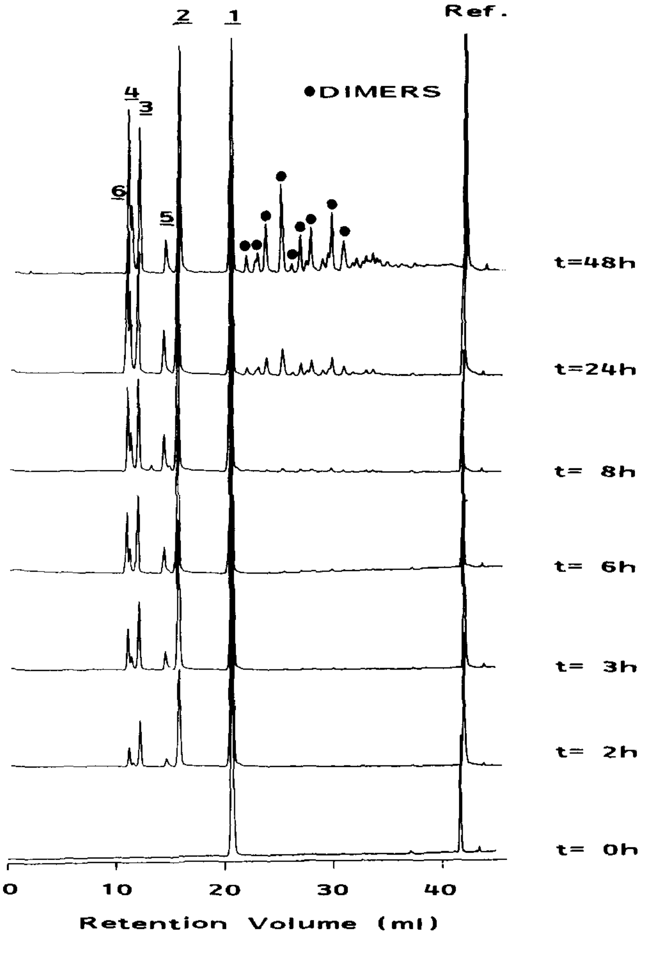


Figure 5 H.p.l.c. kinetics of the system F/P = 1.5. Column: Spherisorb ODS-2 (Bischoff ICS +), 25 cm long, 5 μm particle size. Mobile phase: methanol/water, 10/90 to 100/0 in 40 min. Detection: u.v. at 273 nm

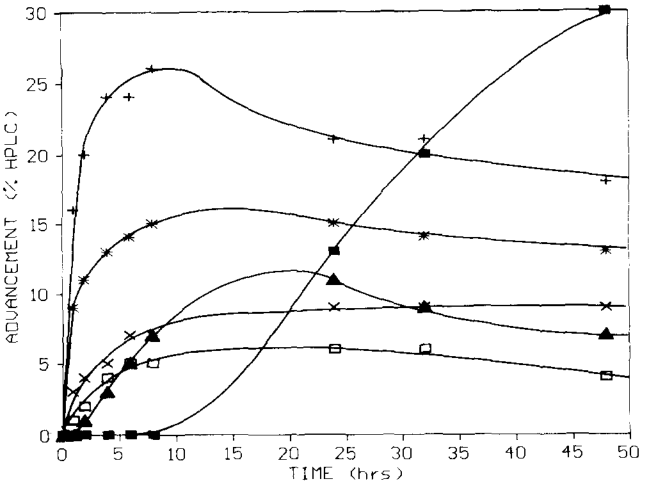


Figure 6 Quantification of chemical species by h.p.l.c. for F/P = 1.5, 60°C: (+) 2-HMP; (*) 4-HMP; (□) 2,6-DHMP; (×) 2,4-DHMP; (▲) 2,4,6-THMP; (■) dimers

Similarly, the kinetics was followed simultaneously with ^{13}C n.m.r., a technique that can detect only residual chemical groups or those formed. Particular attention was paid to the zone of quaternary carbons bearing hydroxyl groups (150–160 ppm), a carbon that is stereosensitive to chemical environments. In particular, the bands around 156, 153 and 151 ppm (*para* substituted carbons of phenol rings) and 155.7, 154 and 151 ppm (attributable to *ortho* substituted carbons of phenol rings) (*Figure 7* is an example) are probes that can be used to characterize the products formed.

Another region that is also of interest for monitoring kinetics is 45–30 ppm, which contains the resonance bands of methylene carbons between two aromatic rings formed during the reactions described in *Figure 1*. Thus, three lines are expected, around 40, 35 and 30 ppm, corresponding to *para–para*, *ortho–para* and *ortho–ortho* linkages.

Based on the integration of the two regions, we were able to determine either substitutions on the ring or binuclear and higher co-condensations. The expected difficulties in quantitative assays accompanying the use of ^{13}C n.m.r. were minimized in this study, since quantification was done on the same carbon class (quaternary or methylene).

The use of deuterated ethanol and/or dimethylsulfoxide as solvent resulted in perfectly resolved spectra in the field used in this study (100 MHz).

The quantification of chemical groups, either stable or transitory with time, is shown in *Figures 8a* and *8b*. The results obtained in the study of the 160–150 ppm region are very similar to those found by h.p.l.c. for the first condensation products. Majority compounds were **2** and **3**, while derivative **4** remained in very low concentrations in the medium because of its high reactivity, disappearing as soon as it was created. The same is true for **6**, which could form from **4** and **5** (*Figure 8a*).

The study of the 45–30 ppm region (*Figure 8b*) shows the presence of two broad bands at 41 and 35 ppm; *ortho–ortho* linkage at 30 ppm was not observed. Even though there are two *ortho* positions in the

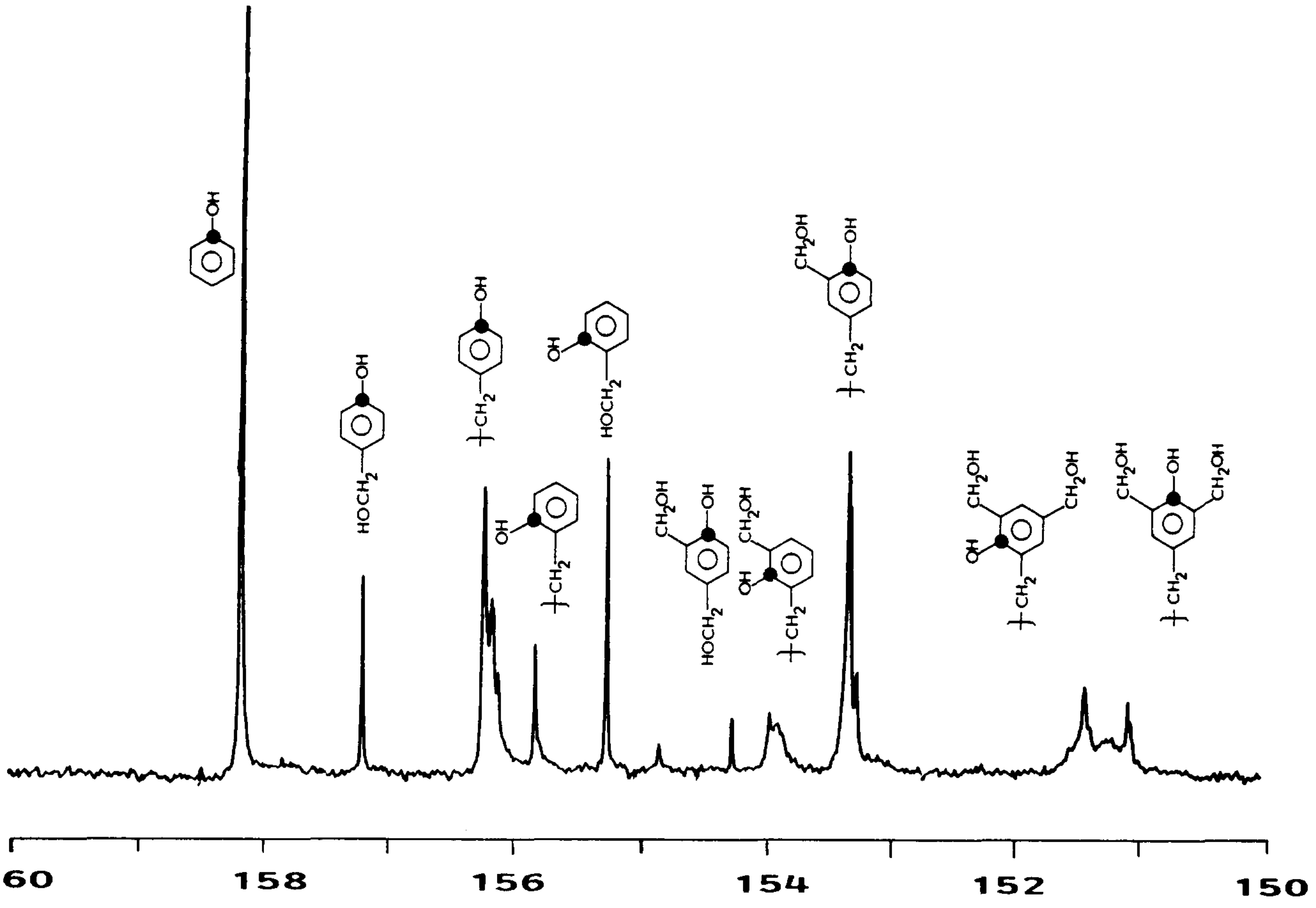


Figure 7 ^{13}C n.m.r. spectrum (solution) in the 160–150 ppm region, with identification of species

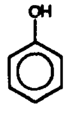
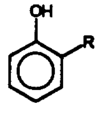
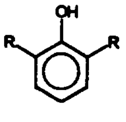
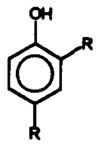
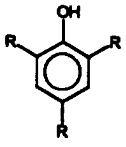
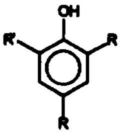
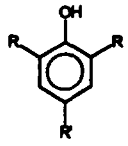
products formed, and in spite of the higher reactivity of hydroxymethyl groups in *para* positions, it is noted that during the 50 h of the kinetic study the peak at 35 ppm was greater than the peak at 40 ppm, regardless of the value of *R*.

Thus, following these different signals leads to the conclusion that condensation reactions involving *para* groups are favoured over those in *ortho* position, indicating a reactivity difference between the groups at these two sites.

Reactivity of phenol towards formaldehyde: influence of level of catalyst (pH) on reaction progress at constant temperature (60°C) and stoichiometry R = *1.5*. An important parameter in the kinetics of these systems is the level of catalyst, since it affects the initial pH of the reaction mixture. The disappearance of formaldehyde as a function of sodium hydroxide content (pH of the solution) was followed by chemical assay in order to determine its effect on reaction kinetics.

Kinetic curves were obtained at four pH values, in the sodium hydroxide concentration range of 8×10^{-4} M (pH = 5.5) to 9.8×10^{-2} M (pH = 9.25) (*Figure 9*). There was practically no reaction at pH 5.5, while it was almost complete (>90%) after 10 h at pH 9.25. It may thus be concluded that the quantity of sodium hydroxide in the medium, affecting the formation and the concentration of phenate ions, plays an important role in the progress of the reaction. It should nevertheless be noted that, at pH > 10, there were considerable Canizzaro

Table 4 Quantification of chemical species by ^{13}C n.m.r.: 160–150 ppm, $R = 1.5$, 60°C, 8 h, ethanol-d_1

	Identification[a,b]							
pH								
8	39	22	14	5	13	7		
9	21	19	15	5	16	11	5	8
9.25	21	15	13	5	17	12	6	11

[a] R = $-CH_2OH$, R′ = $-CH_2-Ar$

[b] Percentage of chemical structures

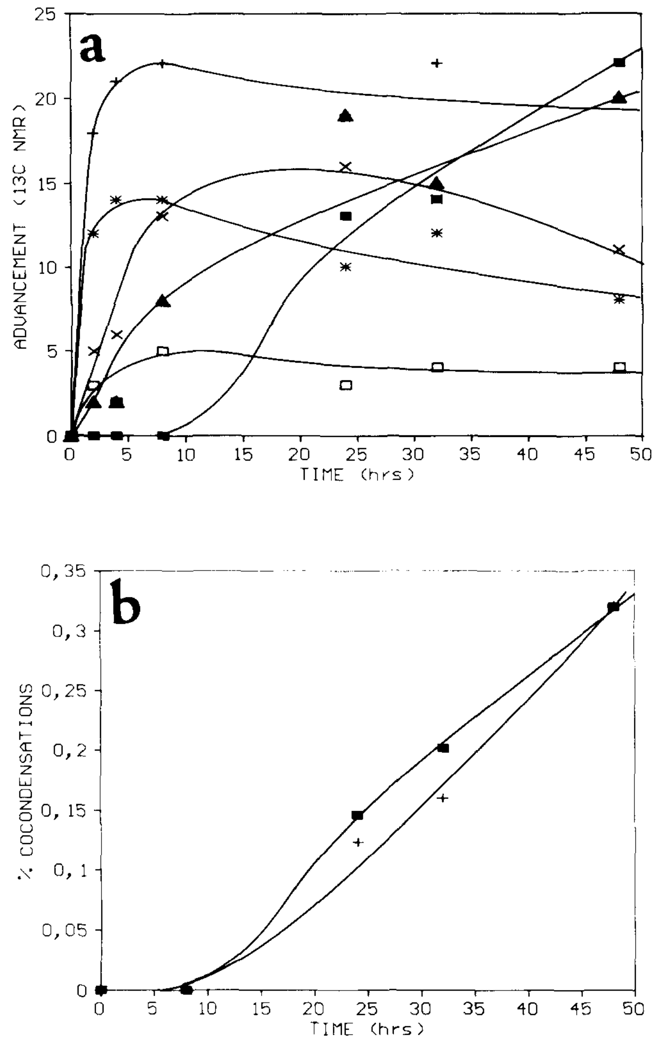


Figure 8 Quantification of chemical species by ^{13}C n.m.r. (a) Region of 160–150 ppm: (+) 2-HMP; (*) 4-HMP; (□) 2,6-DHMP; (×) 2,4-DHMP; (▲) 2,4,6-THMP; (■) dimers. (b) Region of 30–40 ppm: (*) band at 35 ppm; (□) band at 40 ppm

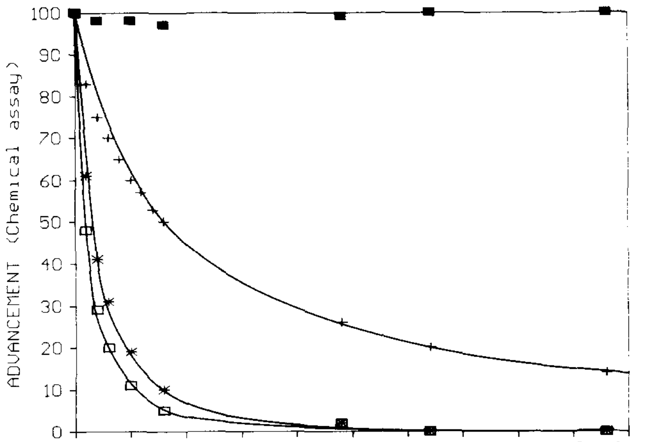


Figure 9 Kinetics of the disappearance of formaldehyde, 60°C, $R = 1.5$, showing influence of pH: (■) pH = 5.5; (+) pH = 8; (*) pH = 9; (□) pH = 9.25

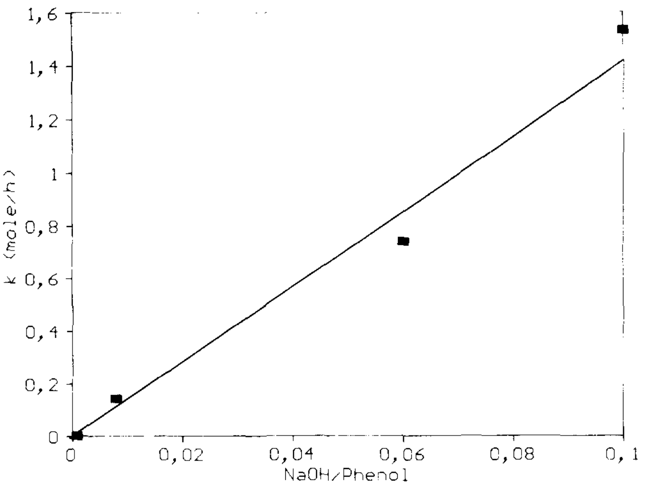


Figure 10 Influence of the concentration ratio $R = [NaOH]/P$ on rate constants

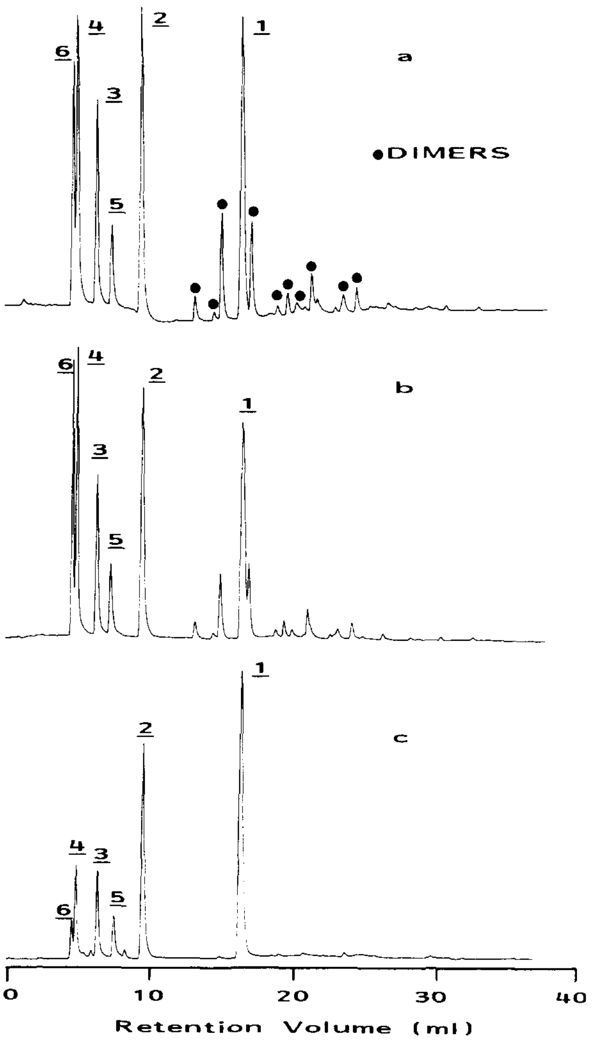


Figure 11 Monitoring kinetics and mechanism by h.p.l.c. at constant stoichiometry $F/P = 1.5$ and temperature: (a) pH = 9.25; (b) pH = 9; (c) pH = 8. Column: Spherisorb ODS-2 (Bischoff ICS +), 25 cm long, 5 μm particle size. Mobile phase: acetonitrile/water, 10/90 to 80/20 in 70 min. Detection: u.v. at 273 nm

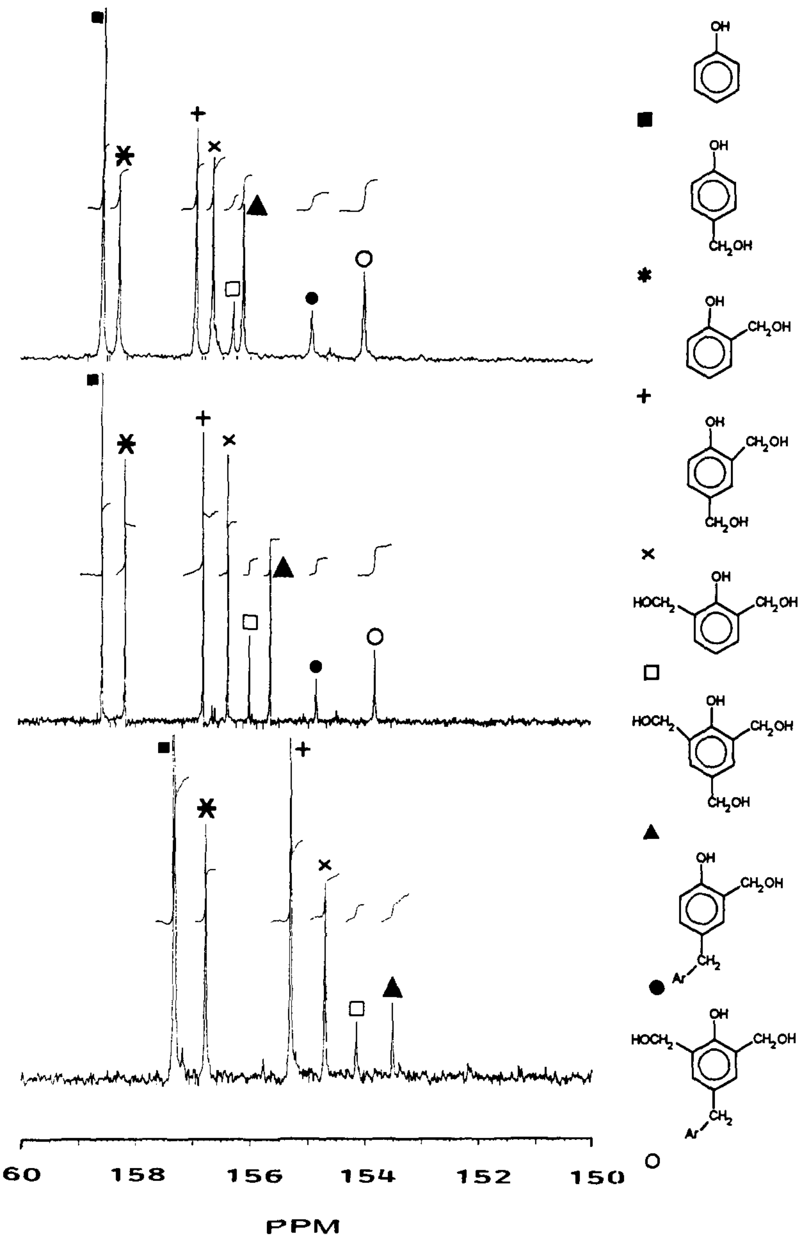


Figure 12 Monitoring kinetics and mechanism by ^{13}C n.m.r. in the 160–150 ppm region at constant stoichiometry and temperature: (a) pH = 9.25; (b) pH = 9; (c) pH = 8

side reactions on formaldehyde, as described in the literature[13].

We simulated the curves in *Figure 9*, for pH 8, 9 and 9.25, using second-order kinetic equations previously described. The rate constants as a function of the [NaOH]/[phenol] ratio (*Figure 10*) revealed a linear relationship of the two variables, showing that the reaction rate depends on the hydroxyl ion concentration, i.e. the pH of the reaction medium.

The h.p.l.c. analysis of reaction media after 8 h furnished interesting data on the products formed (*Figure 11*). After quantifying the different chemical species, it is seen that the level of phenol decreased considerably when the pH was increased from 8 (42% residual phenol) to 9 (16% residual). Similarly, there were more substituted compounds (57% at pH 8 and 68% at pH 9) and 16% dimers were detected at pH 9.

Varying the pH from 9 to 9.25, however, had no great effect on the species created, indicating that there may be a pH optimum for these systems.

The kinetics of these systems followed by ^{13}C n.m.r. (*Figure 12*) enabled the different chemical groups to be quantified and confirmed the h.p.l.c. results (*Table 4*).

CONCLUSIONS

Starting with the first intermediate reaction monomers in phenol–formaldehyde systems, we have shown their reactivity differences towards formaldehyde in conditions of constant stoichiometry and temperature. The kinetic and mechanistic results show that the reactivity of each unoccupied site (*ortho* or *para* to the hydroxyl group) is modified as a function of the number and the site of substitution on the benzene ring.

We have thus shown that the most important step in the disappearance of phenol monomers is the condensation reaction between formaldehyde and aromatic (*ortho*) carbons and/or the condensation of hydroxymethyl groups on the same carbons.

When applied to the study of F/P resoles synthesized in controlled conditions of pH, temperature and stoichiometry, these results indicate the influence of each parameter on the structures and the kinetics of reaction end-products. Thus, in the experimental conditions chosen for this work, the order of reactivity is: substituted dimers > substituted monomers > phenol.

These conclusions could be obtained only by the synthesis of perfectly defined models and by the use of the complementary techniques of h.p.l.c., chemical assay and ^{13}C n.m.r.

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