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Phenolic resins:
4. Self-condensation of methylolphenols in formaldehyde-free media

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Using kinetic and mechanistic monitoring by high-performance liquid chromatography and ^{13}C nuclear magnetic resonance, we have shown that in formaldehyde-free conditions the reactivity of substituted phenols towards condensation reactions arises from several factors. In particular, the groups reacting among themselves may be of two types: either a non-substituted *ortho* or *para* aromatic carbon, or the methylene carbon of a hydroxymethyl group. In addition to the difference in the nature of the group, its position on the aromatic ring is predominant, and the reaction in the *para* position is favoured. Thus, a third factor participates in the mechanism and kinetics of reaction: the ionization constant of the phenol, which increases with the substitution of phenol and favoured the formation of phenate. We thus show that, in the conditions chosen, two reaction mechanisms participate and the reactivity of sites depends on ring substitution by hydroxymethyl groups.

(Keywords: phenolic resins; methylolphenols; self-condensation)

INTRODUCTION

Phenol/formaldehyde systems lead to the formation of thermohardening materials in a basic medium. The reactions involved are the addition of formaldehyde to the phenol ring and condensation reactions[1].

In order to determine the reactivity of the first products arising from the phenol–formaldehyde reaction in a basic medium towards condensation reactions, we followed their changes in the reaction mixture in the absence of formaldehyde in conditions of resol synthesis. Phenol monomers substituted with hydroxymethyl groups can react with themselves in the absence of formaldehyde in a basic medium and yield higher-order compounds by condensation reactions[2–10].

These reactions were simulated for each of the five substituted phenol monomers **2** to **5** (*Figure 1*) in determined conditions of temperature, pH and catalyst ($T = 60°C$, pH = 8 and catalysed by NaOH).

EXPERIMENTAL

Samples

Origin of products. 2-Hydroxymethylphenol (**2**) (99%) and 4-hydroxymethylphenol (**3**) (98%) were obtained from Aldrich and were used without further purification. 2,4-Dihydroxymethylphenol (**4**) and 2,6-dihydroxymethylphenol (**5**) were synthesized according to Freeman and Sprengling[11–13] and 2,4,6-trihydroxymethylphenol (**6**) according to Perrin *et al.*[15].

Procedure. The monomer was diluted in water at 60°C and the pH was adjusted to 8 with a titrated solution of sodium hydroxide.

Experimental techniques

Liquid chromatography (h.p.l.c.). Analyses were carried out with a Varian 5000 chromatograph equipped with a detector set to 273 nm. The columns were 25 cm long and packed with Spherisorb ODS-2 (5 μm). The mobile phase of methanol–water was used with an elution gradient of 10 to 100% methanol in 50 min. Samples were dissolved in methanol.

Nuclear magnetic resonance (n.m.r.). High-resolution liquid-state ^{13}C n.m.r. spectra were recorded with a Bruker AM 400 spectrometer. The conditions for recording spectra were pulse angle 90° (4.2 μs) and digital resolution 0.375 Hz/pt corresponding to a spectral range of 20 000 Hz for a memory space of 128 K.

Samples were dissolved in monodeuterated ethanol or deuterated dimethylsulfoxide. ^{13}C n.m.r. (CH_3CH_2OD): $\delta = 17.9$ and 57.3 ppm with respect to tetramethylsilane (TMS), ^{13}C n.m.r. (DMSO-d_6) : $\delta = 39.5$ ppm/TMS.

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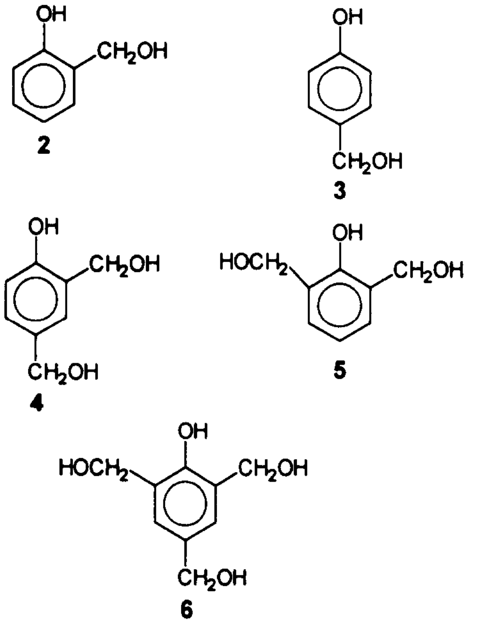
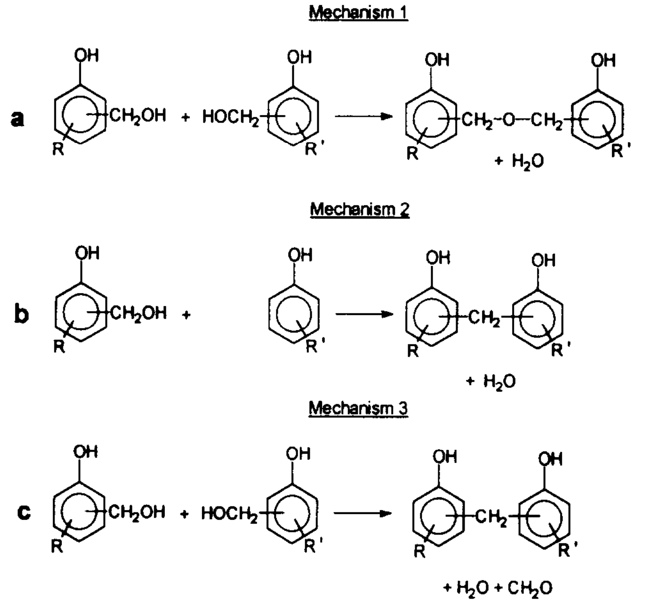


Figure 1 Phenolic monomers studied



R = R' = -H, -CH₂OH, -CH₂-Ar

Figure 2 Condensation reaction paths

ANALYSIS OF RESULTS

Review of condensation reaction mechanisms described in the literature

There are three possible condensation reaction paths for these systems, leading to the formation of a dimethylene ether or methylene chain (*Figure 2*). In the first case, the mechanism involves two hydroxymethyl groups and the release of one molecule of water (*Figure 2a*) with the creation of a dimethylene ether bridge. This mechanism occurs only in neutral or acid conditions and at temperatures less than 130°C. In the case of 2,4,6-trihydroxymethylphenol (**6**), however, it is observed in the molten state starting at 80°C[13–15]. The other two mechanisms involve a hydroxymethyl group with either a proton of the aromatic ring (*ortho* or *para*), with the release of one molecule of water (*Figure 2b*) or a hydroxymethyl group with the simultaneous release of one molecule of water and one molecule of formaldehyde (*Figure 2c*). In both cases, a methylene bridge is created.

In the course of this work, only the formation of a methylene link was observed. In this case, it is possible to obtain three types of methylene bridges depending on the substituent on the aromatic ring: *para–para*, *ortho–para* and *ortho–ortho*.

Autocondensation of monosubstituted phenolic compounds (2 and 3)

We examined the autocondensation reactions of 2-HMP (**2**) and 4-HMP (**3**) in a basic medium. The chromatograms obtained after 8 h of reaction (*Figure 3*) show that the concentrations of reaction products in the reaction mixture were low (see *Figure 4* for identification of peaks).

Thus, with 2-HMP (**2**) there was a single compound present in a very low proportion. Simultaneous analysis of the same sample by ^{13}C n.m.r. enabled us to identify the structure of the compound, attributable to 3-hydroxymethyl-2′,4-dihydroxydiphenylmethane (**7**) (*Table 1*) by the characteristic resonance lines at 35.62 ppm (*ortho–para* methylene bridge) and at 157.52 and 158.51 ppm (aromatic carbons bearing hydroxyl groups on an aromatic ring substituted in *ortho* positions).

The same study with 4-HMP (**3**) indicated the presence of two compounds at low concentration in the reaction mixture.

Based on models described in our prior work[16], an incremental study by ^{13}C n.m.r. enabled the chemical structures of two products to be attributed to those of the following dimer: 4,4′-dihydroxydiphenylmethane (**8**) (*Table 2*) and 5-hydroxymethyl-2,4′-dihydroxydiphenylmethane (**9**) (*Table 1*). The presence of a small quantity of 2,4-DHMP (**4**) observed in ^{13}C n.m.r. reflects the formation of free formaldehyde in the medium (resonance line at 88.74 ppm in ^{13}C n.m.r.).

These results lead to several comments on the reaction mechanisms involved in these systems. Only mechanism 2 in *Figure 2* participates in the case of 2-HMP (**2**). Mechanisms 1 or 3 would have yielded a dimethylene ether bridge (resonance line around 70 ppm) or an *ortho–ortho* methylene bridge (resonance line at 30 ppm). In addition, only condensation on the *para* site was shown, since the reaction involving mechanism 2 with the *ortho* aromatic proton would have yielded *ortho–ortho* aromatic ring linking and we would have observed a signal around 30 ppm in ^{13}C n.m.r.[17–20].

The kinetics of the reaction mixture were followed by h.p.l.c. It was concluded that after 8 h of reaction, very little initial monomer **2** reacted (2%), indicating the low reactivity of 2-HMP (**2**) towards itself.

In the case of 4-HMP (**3**), the formation of compounds **8** and **9** indicates the simultaneous presence of mechanisms 2 and 3. Compound **8** was obtained by the condensation of two hydroxymethyl groups with the release of one molecule of formaldehyde (mechanism 3), while compound **9** formed by the condensation of one *para* hydroxymethyl group with one aromatic proton in the *ortho* position (mechanism 2) (*Figure 5*).

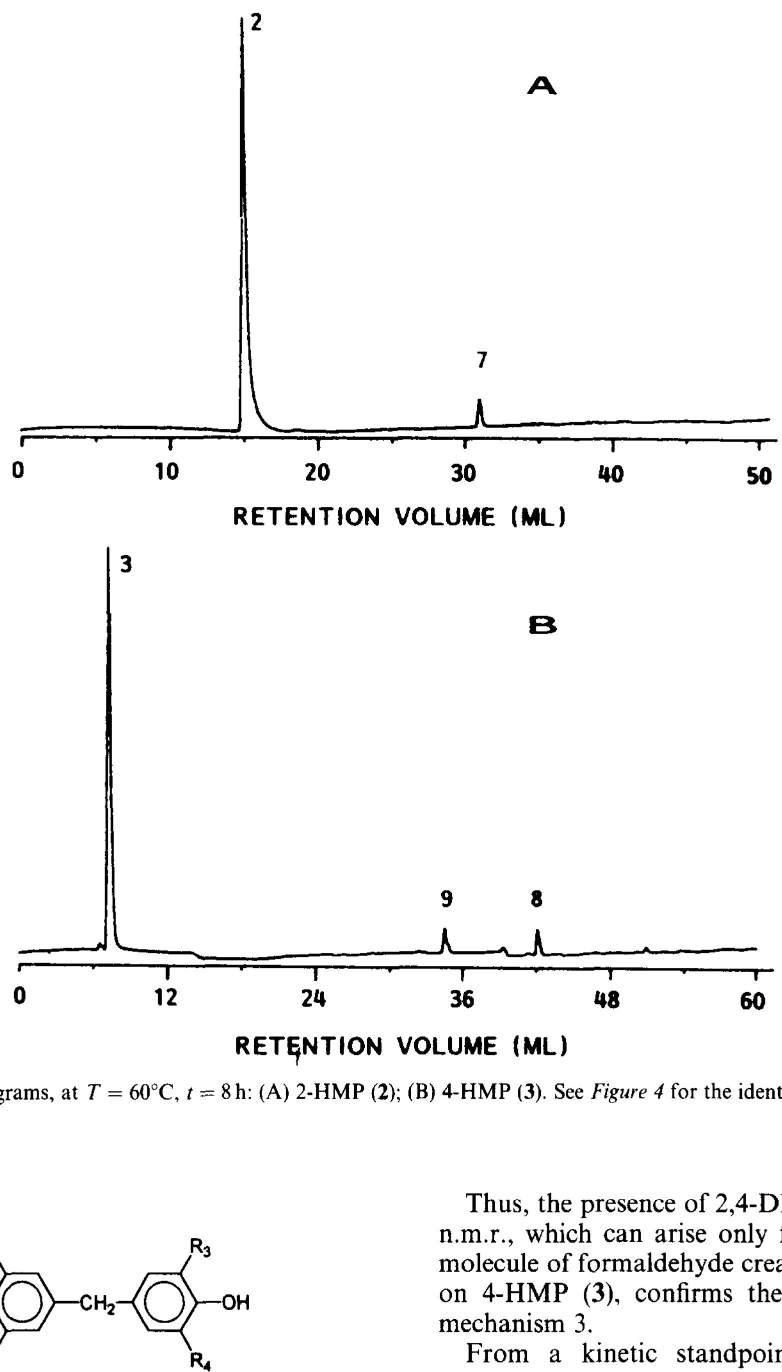
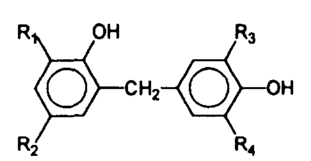
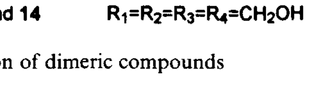


Figure 3 H.p.l.c. chromatograms, at $T = 60°C$, $t = 8$ h: (A) 2-HMP (**2**); (B) 4-HMP (**3**). See *Figure 4* for the identification of compounds



compound 8	$R_1=R_2=R_3=R_4=H$
compound 10	$R_1=R_3=CH_2OH$; $R_2=R_4=H$
compound 13	$R_1=R_2=R_3=R_4=CH_2OH$



compound 7	$R_3=CH_2OH$; $R_1=R_2=R_4=H$
compound 9	$R_2=CH_2OH$; $R_1=R_3=R_4=H$
compound 11	$R_2=R_3=CH_2OH$; $R_1=R_4=H$
compound 12	$R_1=R_3=R_4=CH_2OH$; $R_2=H$
compound 14	$R_1=R_2=R_3=R_4=CH_2OH$

Figure 4 Identification of dimeric compounds

Thus, the presence of 2,4-DHMP (**4**), observed in ^{13}C n.m.r., which can arise only from the addition of one molecule of formaldehyde created during condensations on 4-HMP (**3**), confirms the reaction path involving mechanism 3.

From a kinetic standpoint, in light of the low concentrations of products obtained, it would seem that the two dimers formed at the same rate. The quantification of these data indicate that 10% of the initial monomer had reacted after 7 h of reaction, thereby showing that the hydroxymethyl group was more reactive in the *para* position than in the *ortho* position. In addition, the results enable us to conclude that the *ortho* aromatic proton was reactive only towards a hydroxymethyl group in the *para* position.

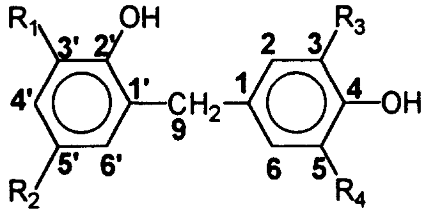
Autocondensations of disubstituted phenolic compounds (4 and 5)

In the case of compound **4**, h.p.l.c. analysis of the reaction mixture after 8 h of reaction indicated the formation of several compounds, one of which was in the majority; the others were present in low or very low concentrations (*Figure 6A*).

The ^{13}C n.m.r. study enabled the chemical structure of the major peak **10** to be identified and, with more

Table 1 Chemical shifts in ^{13}C n.m.r.

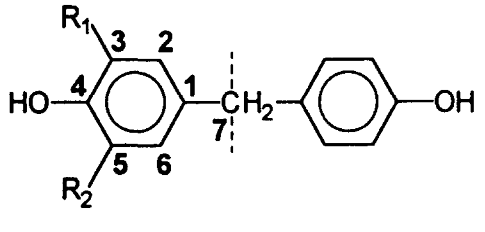
	Chemical shift (ppm)													
Samples	C1	C2	C3	C4	C5	C6	C1′	C3′	C3′	C4′	C5′	C6′	C9	$-CH_2OH$
7	131.1_2	130.1_2 130.0_7	128.6_0	158.5_1	118.2_3	130.0_7 130.1_2	128.0_3	157.5_2	117.1_8	130.4_6 130.4_1	119.4_3	130.4_1 130.4_6	35.6_2	62.1_6
9	132.1_8	130.5_1	116.4_8	156.5_1	116.4_8	130.5_1	128.4_4	155.5_4	116.4_0	130.3_9	131.9_5	130.3_9	35.1_9	64.6_0
11		129.2_7		153.1_0	115.9_8	129.3_6		154.4_5	115.9_5	129.6_0		129.5_0	35.2_0	60.5_5 64.4_2
12	132.8_4	127.8_2	128.7_6	151.8_3	128.7_6	127.8_2	126.9_0	153.1_8	127.7_1	130.3_3	120.8_1	129.9_0	35.2_2	61.3_1 62.0_1
14	133.8_9	128.4_1	127.7_6	151.6_4	127.7_6	128.4_1	127.6_9 127.6_7	152.5_6	127.6_7 127.6_9	128.6_4 128.5_9	132.8_0	128.5_9 128.6_4	35.2_5	61.2_8 64.3_9



$R_1 = R_2 = R_4 = -H$; $R_3 = -CH_2OH$ compound **7**
$R_1 = R_3 = R_4 = -H$; $R_2 = -CH_2OH$ compound **9**
$R_1 = R_4 = -H$; $R_2 = R_3 = -CH_2OH$ compound **11**
$R_2 = -H$; $R_1 = R_3 = R_4 = -CH_2OH$ compound **12**
$R_1 = R_2 = R_3 = R_4 = -CH_2OH$ compound **14**

Table 2 Chemical shifts in ^{13}C n.m.r.

	Chemical shift (ppm)							
Samples	C1	C2	C3	C4	C5	C6	C6	$-CH_2OH$
8	133.0_8	130.2_3	116.5_3	156.6_8	116.5_3	130.2_3	40.4_7	
10	133.8_4	129.2_7	127.5_8	153.1_4	115.9_8	129.3_6	40.6_6	60.5_0
13	133.8_9	128.4_1	127.7_6	151.6_1	127.7_6	128.4_1	40.7_4	61.1_5



$R_1 = R_2 = -H$ compound **8**

$R_1 = -H$; $R_2 = -CH_2OH$ compound **10**

$R_1 = R_2 = -CH_2OH$ compound **13**

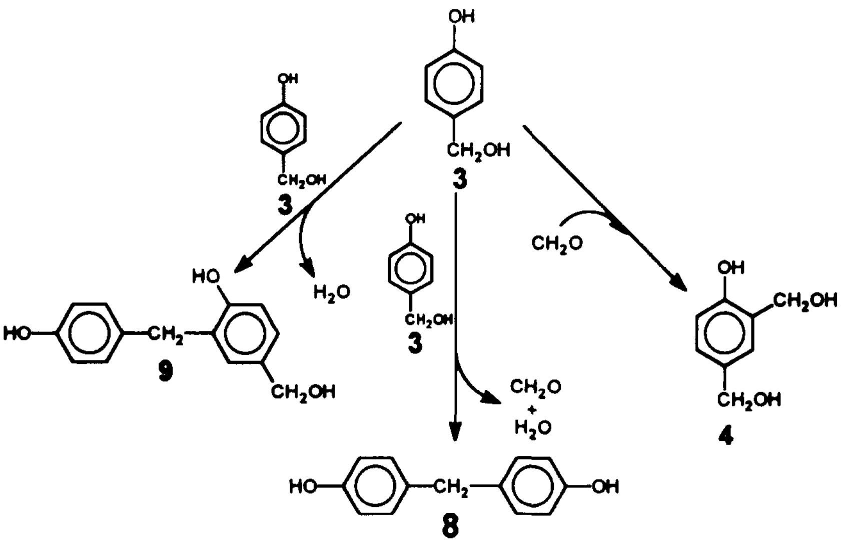


Figure 5 Autocondensation reaction paths of 4-HMP (3)

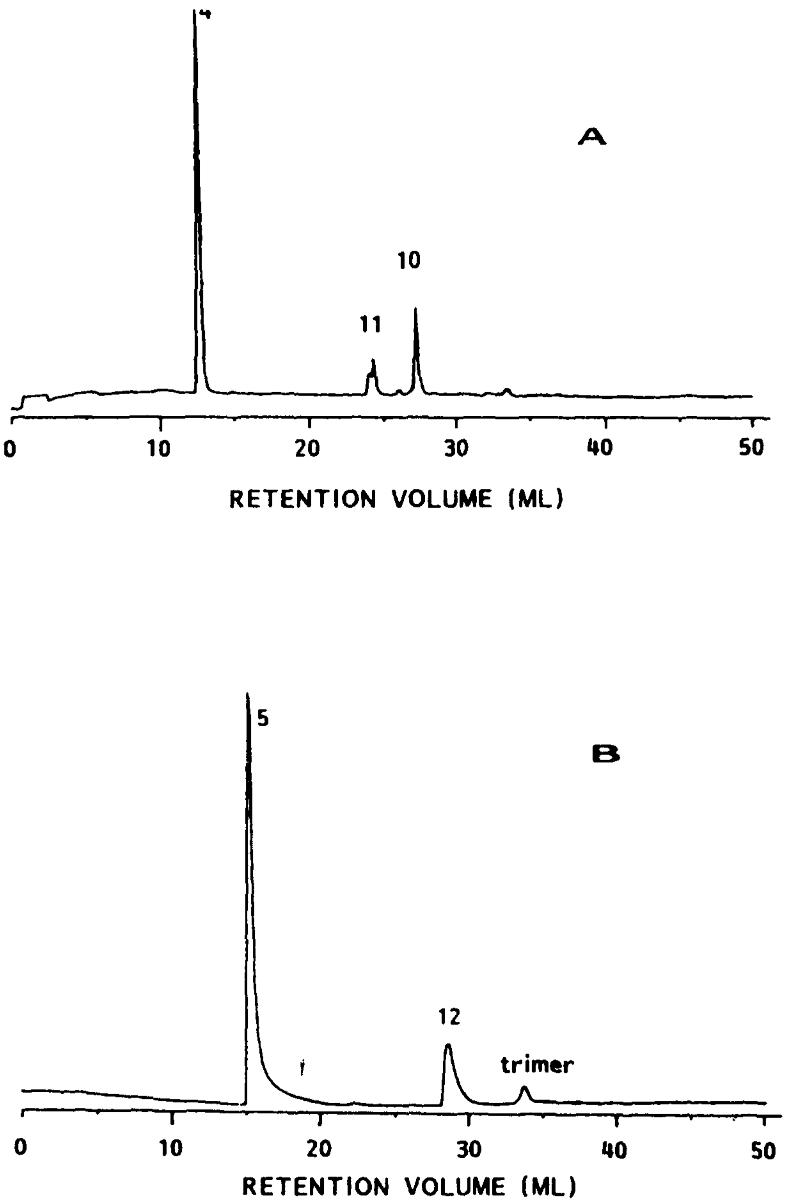


Figure 6 H.p.l.c. chromatograms, at $T = 60°C$, $t = 48$ h: (A) 2,4-DHMP (4); (B) 2,6-DHMP (5). See *Figure 4* for the identification of compounds

difficulty, that of peak **11**. Using the data gathered in the zones of 45–30 ppm and 160–150 ppm in ^{13}C n.m.r., the structures of compounds were attributed to 3,5-dihydroxymethyl-2′,4-DHMP (**11**) (*Table 1*) and 3,3′-dihydroxymethyl-4,4′-DHDPM (**10**) (*Table 2*).

In the case of compound **5**, two products were detected by h.p.l.c. after 8 h of reaction (*Figure 6B*). ^{13}C n.m.r. enabled us to identify the chromatographic peak at $V_R = 29$ ml as being a dimer. Since there was a resonance line at 35.22 ppm (methylene bridge with *ortho–para* linking) and resonance lines at 151.83 and 153.18 ppm (attributions to aromatic carbons bearing a hydroxyl group), the structure of this compound was attributed to 3,3′,5-trihydroxymethyl-2′,4-DHDPM (**12**) (*Table 1*). Because of the low concentration of the second compound, its structure could not be unequivocally identified. Nevertheless, its high retention volume ($V_R = 34$ ml), as well as the presence of new resonance lines in ^{13}C n.m.r., suggested that the compound was a higher-order oligomer with three aromatic rings. Faced with the number of expected isomeric structures, its chemical structure was not attributed.

These results show that only mechanism 2 is involved in the case of 2,6-DHMP (**5**), as in that of 2-HMP (**2**). The absence of resonance lines around 30 and 89 ppm (resonance line characteristic of the methylene carbon of dimethylene glycol) excludes mechanism 3.

Autocondensations of 2-HMP (**2**) and 2,6-DHMP (**5**) involved the same mechanism and in each case only one dimer formed. Given the structure of the dimers formed (presence of one aromatic carbon in non-substituted *para* position), chain elongation was possible and a trimer was observed in the case of 2,6-DHMP (**5**). The fact that no trimer was observed with 2-HMP (**2**) indicates that either the aromatic carbon in the *para* position or the hydroxymethyl group in the *ortho* position is less reactive. It should also be noted that the reactivity of sites depends on the substitution of the aromatic ring.

In the case of 2,4-DHMP (**4**), the presence of hydroxymethyl groups and the formation of free formaldehyde in the medium (resonance line at 88.74 ppm) indicates that condensation reactions occurred according to mechanism 3 (*Figure 7*). Furthermore, the absence of a signal at 30 ppm confirms that the

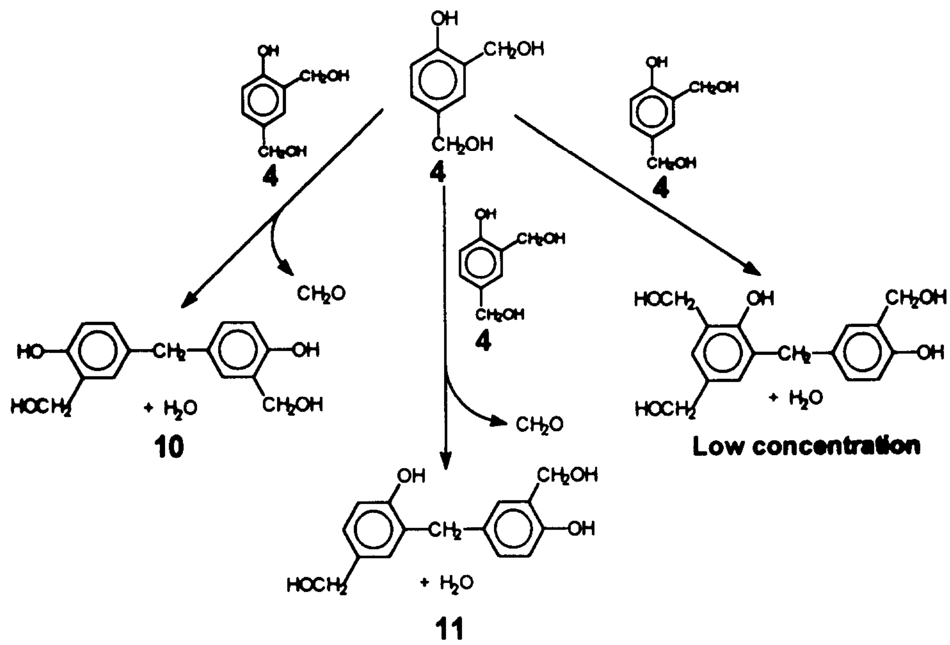


Figure 7 Autocondensation reaction paths of 2,4-DHMP (4)

ortho hydroxymethyl group did not condense with the other substituents in the *ortho* position in the conditions adopted for this study.

The formation of minor compounds is due either to condensations involving mechanism 2, or to the addition of formaldehyde into the compounds present. The trisubstituted compound 2,4,6-THMP (**6**) was not observed.

The quantification of the chemical entities shown in *Figure 8* indicates a slight reactivity difference at the level of condensations of 2,4-DHMP (**4**) (62% residuals) in comparison to 2,6-DHMP (**5**) (76% residuals), in spite of the higher number of condensation possibilities in the case of 2,4-DHMP (**4**). These data taken together indicate the high reactivity of 2,6-DHMP (**5**) among all the monomers studied in this work.

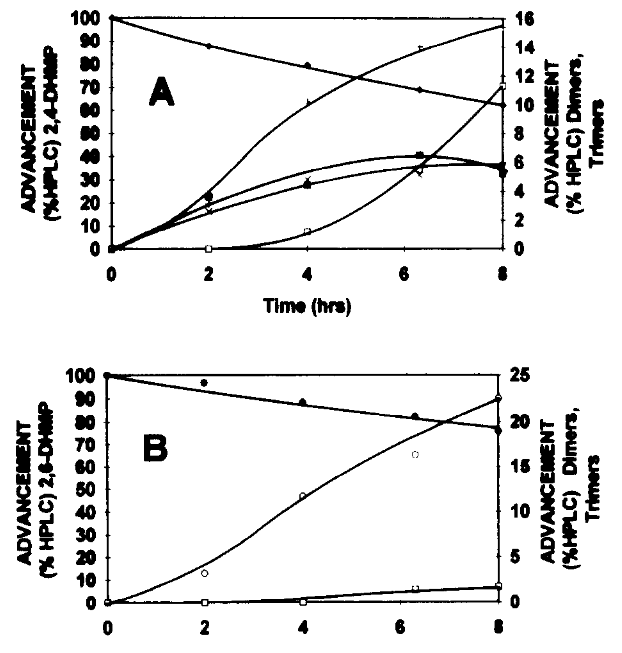


Figure 8 Quantification of chemical entities by h.p.l.c. (A) 2,4-DHMP (4): (◆) 2,4-DHMP (4); (+) dimer 10; (×) dimer 11; (■) dimers; (□) trimers. (B) 2,6-DHMP (5): (●) 2,6-DHMP (5); (○) dimer 12; (□) trimer

These results also indicate that the number of hydroxymethyl groups was greater in the case of disubstituted phenolic compounds; in each case, trimers appeared after 8 h of reaction. The overall advancement of the reaction was greater.

Autocondensation of the trisubstituted phenolic compound (6)

Mechanism 2 can be eliminated as a result of the chemical structure of 2,4,6-THMP (**6**), since all the reactive aromatic carbons are already substituted.

After 8 h of reaction, the h.p.l.c. chromatogram (*Figure 9*) shows that residual initial monomer and three products were present in the reaction medium and that two were majority species (**13** and **14**). ^{13}C n.m.r. enabled these two compounds to be identified. The chemical shifts noted in their spectra enabled peaks **13** and **14** to be attributed to the following compounds:

3,3′,5,5′-tetrahydroxymethyl-2,4′-DHDPM (**14**) (*Table 1*)

3,3′,5,5′-tetrahydroxymethyl-4,4′-DHDPM (**13**) (*Table 2*)

There was also a resonance line at 151.30 ppm characteristic of an aromatic carbon bearing a hydroxyl group on a phenol ring condensed in *ortho* and *para* positions. The attribution of this line to a trimeric structure was confirmed by h.p.l.c. analysis, in which the presence of a large chromatographic peak was detected. In light of its high retention volume ($V_R = 31$ ml), it was a compound of order higher than two. Jones[8] reported that the first trimer formed was composed of a link of *ortho–para/para–para* rings, which agrees with the structure presented in *Figure 10*. The chromatogram contained other peaks around the latter, suggesting the formation of other trimeric structures.

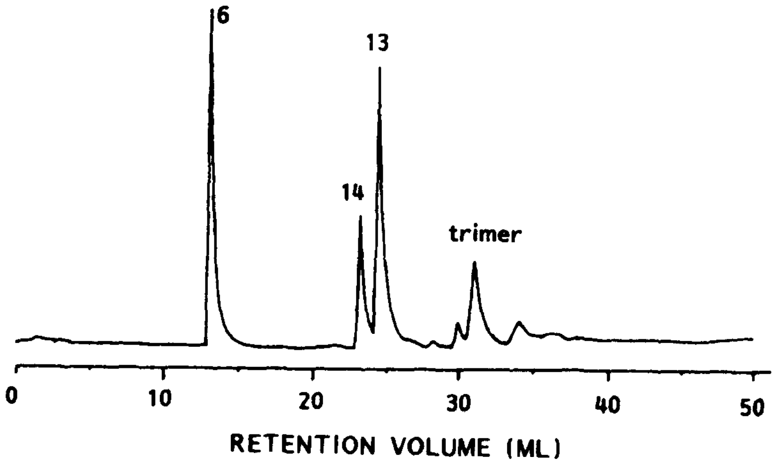


Figure 9 H.p.l.c. chromatograms at $T = 60°C$, $t = 8\,h$ for 2,4,6-THMP (**6**)

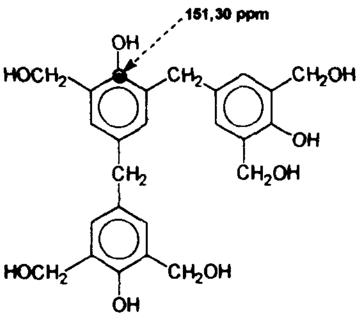


Figure 10 Chemical structure of the trimer obtained after condensation of compound **6** (according to Jones[8])

Only reaction mechanism 3 (*Figure 2*) was involved in the condensation of these products because of the trisubstitution of the aromatic ring of the monomer and the absence of a resonance line corresponding to ether bridges at 70 ppm in ^{13}C n.m.r. These condensation reactions were thus automatically accompanied by the formation of molecules of formaldehyde and water in the reaction medium, as a result of the absence of reaction sites permitting the addition of formaldehyde (*Figure 11*). ^{13}C n.m.r. showed two resonance lines, at 82.65 ppm (central carbon of methylene glycol) and at 88.73 ppm (carbons of the methylene glycol dimer), indicating that it accumulated in the medium.

In spite of the larger number of hydroxymethyl groups in the *ortho* position, however, the formation of compound **13** (*Figure 11*) involving condensation between two hydroxymethyl groups in the *para* position was favoured from the onset of the reaction.

Kinetic monitoring of products arising with time (*Figure 12*) shows that compound **13** was consistently the majority species among all the products formed. It is also seen that the concentration of compound **14** ceased to increase to the benefit of trimers. Given the structure of the two dimers, compound **13** contained relatively unreactive hydroxymethyl groups in the *ortho* position, while compound **14** enabled new condensations to occur as a result of the hydroxymethyl group in the *para* position.

This important result shows the reactivity difference of hydroxymethyl groups depending on their position on the aromatic ring (*ortho* or *para*). This may be due to intramolecular interactions between hydroxymethyl groups in position *ortho* and the hydroxyl group borne by the aromatic ring, or to a steric hindrance preventing the sites from reacting in the reaction medium in the conditions of synthesis and kinetic monitoring[9,10]. In order to compare the reactivity of each of the monomers, we have depicted the changes of each as a function of time (*Figure 13*).

It is clearly seen that two parameters affect the reactivity of hydroxymethyl groups: (i) the position of substituents on the aromatic ring—at equivalent func-

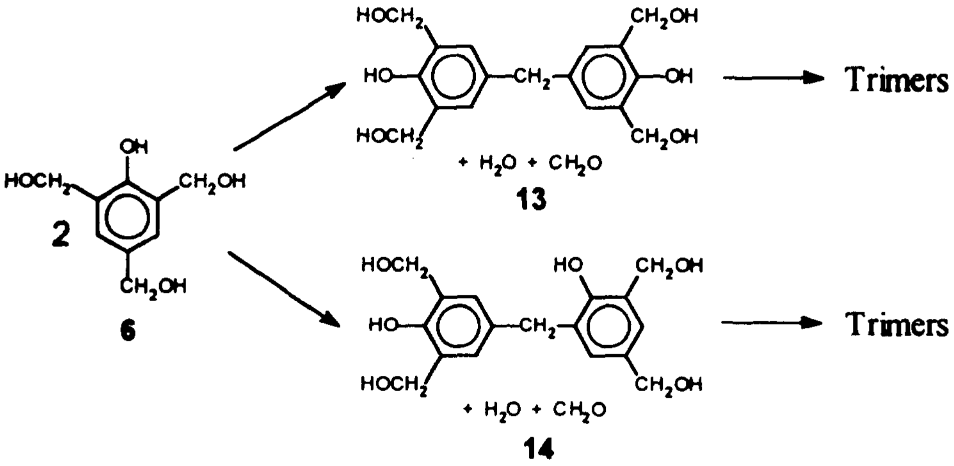


Figure 11 Autocondensation reaction paths of 2,4,6-THMP (**6**)

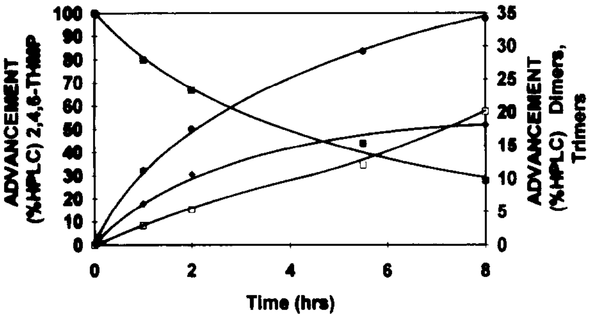


Figure 12 Quantification of chemical entities by h.p.l.c. 2,4,6-THMP (**6**): (■) 2,4,6-THMP (**6**); (●) dimer **13**; (◆) dimer **14**; (□) trimer

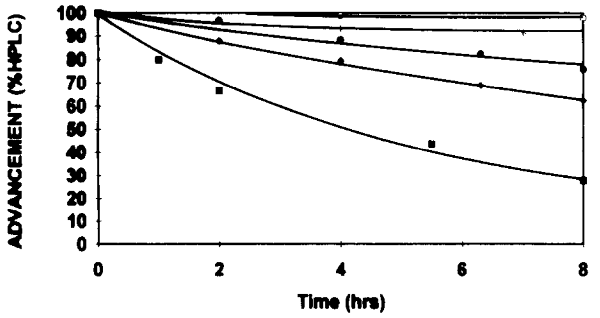


Figure 13 Disappearance of monomers by h.p.l.c. (autocondensation reactions): (○) 2-HMP (**2**); (+) 4-HMP (**3**); (◆) 2,4-DHMP (**4**); (●) 2,6-DHMP (**5**); (■) 2,4,6-THMP (**6**)

tionality, substitution in *para* position increased the reactivity of the molecule; and (ii) the number of substituents on the aromatic ring—the reactivity of monomers towards themselves increased with increasing substitution.

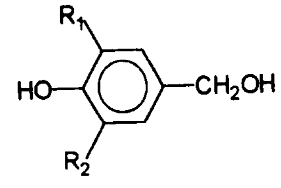
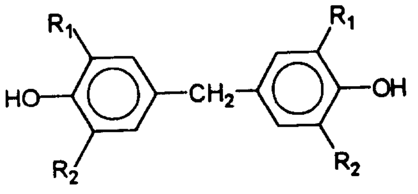
As an example and to support these observations, *Table 3* lists the proportion of *para–para* linked dimers resulting from the condensation of *para* hydroxymethyl groups for the three *para*-substituted monomers (**3**, **4** and **6**). It is obvious that the reactivity of the same group depends on the degree of substitution of the monomeric molecule present in the reaction medium.

CONCLUSIONS

Using kinetic and mechanistic monitoring, we have shown that, in formaldehyde-free conditions, the reactivity difference of substituted phenols towards condensation reactions arises from several factors: (i) The groups reacting among themselves may be of two types: either a non-substituted *ortho* or *para* aromatic carbon, or the methylene carbon of a hydroxymethyl group. (ii) In addition to the difference in the nature of the group, its position on the aromatic ring is predominant and we have shown that the reaction is favoured in *para* position. (iii) A third factor participates and enables the data of *Table 3* to be explained: the ionization constant of the phenol considered.

When the ionization constant increases (decrease of pK_A) with the substitution of phenol (**1**) the formation of the phenate form is favoured (intermediate required in the mechanism proposed by Jones[8]).

Table 3 Proportion of *para–para* linked dimers from condensation of *para* hydroxymethyl groups for three *para*-substituted monomers

Monomer	Concentration of dimer created
  	
$R_1 = R_2 = -H$ (**3**)	4% (**8**)
$R_1 = -H$; $R_2 = -CH_2OH$ (**4**)	11% (**10**)
$R_1 = R_2 = -CH_2OH$ (**6**)	29% (**13**)

Substitution of the aromatic ring by hydroxymethyl groups increases its reactivity towards condensation. Thus, the most highly substituted species have the highest probability of disappearing from the medium by condensation. Substituted dimers are thus formed, whereas little-substituted and thus unreactive dimers are less present in the reaction medium.

The results obtained concerning the reactivity of the initial monomers towards formaldehyde are very important for the synthesis of phenolic prepolymers.

We have thus shown the following in prior work[1]: (i) From a mechanistic standpoint, the aromatic carbon in *para* position is more reactive towards formaldehyde or a hydroxymethyl group than the aromatic carbon in *ortho* position. Condensation reactions preferentially involving *para* hydroxymethyl groups initially lead to the formation of compounds with *para–para* methylene bridge. Subsequent to this, *ortho* hydroxymethyl groups react and generate compounds with *ortho–para* methylene bridge. (ii) From a kinetic standpoint, changes in each monomer as a function of time enable the order of reactivity of these compounds towards formaldehyde to be determined in the conditions of temperature, pH and concentration employed:

$$k_{\text{phenol}} < k_{2,4\text{-DHMP}} < k_{2\text{-HMP}} < k_{4\text{-HMP}} < k_{2,6\text{-DHMP}}$$

Thus, 2,6-DHMP (**5**) disappears rapidly from the reaction medium, while 2,4-DHMP (**4**) and phenol tend to accumulate.

In light of the lower reactivity of phenol in the reaction medium, its disappearance slows down once the substituted phenolic monomers start participating. There is a competition between the products formed and unreacted phenol.

Thus, the operating conditions for the synthesis of the resol should be oriented towards a more rapid disappearance of phenol starting in the first hours, by favouring the phenol–formaldehyde reaction, and towards a reorganization of reaction paths in order to

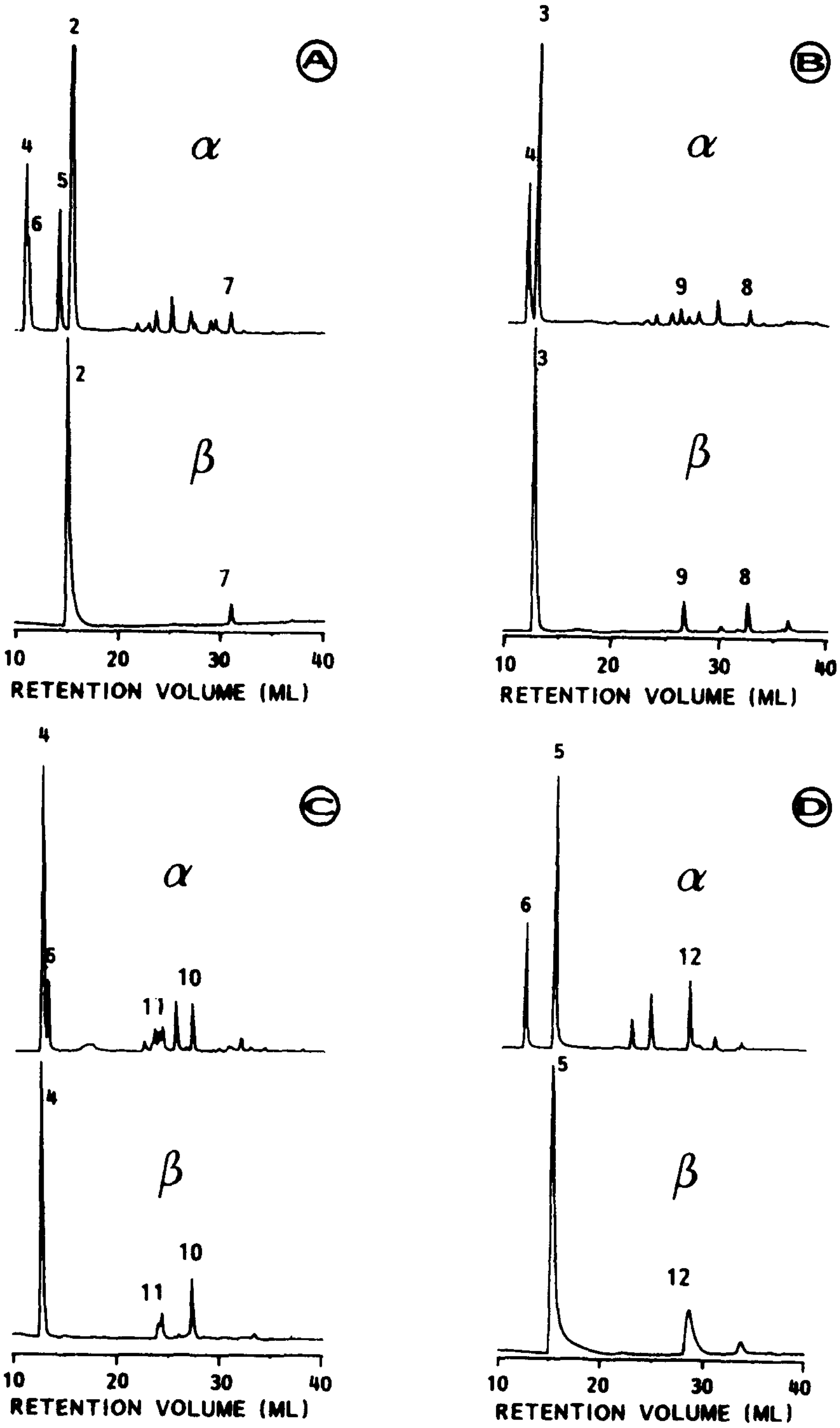


Figure 14 H.p.l.c. chromatograms at $T = 60°\mathrm{C}$, $t = 8$ h, (α) in presence of formaldehyde and (β) in absence of formaldehyde: (A) 2-HMP (**2**); (B) 4-HMP (**3**); (C) 2,4-DHMP (**4**); (D) 2,6-DHMP (**5**). See *Figure 4* for the identification of compounds

avoid the formation of 2,4-DHMP (**4**) that accumulates in the medium.

In order to extend these observations, we compared monomer residuals after 8 h of reaction in the case of autocondensation reactions and in the presence of formaldehyde. In each case, the presence of formaldehyde led to lower quantities of monomer residuals. The h.p.l.c. chromatograms obtained after 8 h of reaction confirm the presence of compounds arising from autocondensation reactions in the reaction medium in the presence of formaldehyde (*Figure 14*).

In the case of compound **2**, the autocondensation reaction is weak and the presence on a number of functionalized monomers leads to the formation of several dimers.

Autocondensation reactions for compound **3** are somewhat more important, but the amount of residual monomer in the presence of formaldehyde remains higher than in the case of compound **2**.

It is interesting to note that, in the case of compound **4**, residual monomers are similar in both cases. The chromatograms are different, however, since the dimers result from condensation with 2,4,6-THMP (**6**) formed by the addition of formaldehyde on **4**. Thus, autocondensation reactions are not favoured in the presence of formaldehyde.

Concerning compound **5**, it is not possible to conclude on the presence of autocondensation reactions with formaldehyde present, since the dimer **12** resulting from the autocondensation of **5** can also arise from the condensation of **5** and **6** formed in the medium.

The reactions studied in this work enable us to understand better the reaction mechanism operating in the reaction medium in our particular conditions.

In the case of condensation reactions, we observed that only methylene-type links are possible in the experimental conditions chosen for this study. In addition, *ortho* hydroxymethyl groups react only with substituents in *para* position, thereby never forming *ortho–ortho* methylene bridges. Concerning the hydroxymethyl groups in *para* position, they react with all substituents, but preferentially with hydroxymethyl groups in *para* position. The more the compound is functionalized, the more it reacts by a condensation reaction.

We have also established an order of disappearance of monomers in the reaction medium in the presence of formaldehyde. These results take into account the different reactions that may occur in the mixture (addition of formaldehyde, condensations and autocondensations) and indicate that 2,6-DHMP (**5**) and 2,4,6-THMP (**6**) disappear rapidly from the medium, while phenol and monofunctionalized compounds react more slowly.

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