Polymer Vol. 37 No. 6, pp. 939–953, 1996
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0032-3861/96/$15.00+0.00

Phenolic resins:
3. Study of the reactivity of the initial monomers towards formaldehyde at constant pH, temperature and catalyst type

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(Received 20 December 1994; revised 26 June 1995)

We have studied the addition of formaldehyde to the various phenolic monomers present in a phenol–formaldehyde system under conditions of constant temperature, pH and catalyst type. The techniques used, carbon-13 nuclear magnetic resonance and high-performance liquid chromatography, enabled us to show the effect of aromatic ring substitution on the reactivity of sites that can potentially react. We have shown from a mechanistic standpoint that the aromatic carbon in the *para* position is more reactive towards formaldehyde or a hydroxymethyl group than the aromatic carbon in the *ortho* position. Condensation reactions involving the *para* hydroxymethyl group preferentially lead to the formation of compounds with a *para–para* methylene bridge. From a kinetic standpoint, we have demonstrated that changes in each monomer as a function of time enable the order of reactivity of these compounds towards formaldehyde to be determined under the conditions of temperature, pH and concentration employed.

(Keywords: phenolic resins; reactivity; formaldehyde)

INTRODUCTION

Phenol–formaldehyde systems lead to the formation of a thermohardening material with good fire-resistance properties[1–5]. The synthesis of these systems is a two-step process. The first step (condensation reaction in aqueous medium) leads to a prepolymer in solution containing several compounds as a result of the synthesis process. In prior work[6] we described the physicochemical characterization of the major compounds in the prepolymer, as well as the influence of different synthesis factors on the composition of the resol. In the present work, we describe the reactivity of each of the phenolic monomers towards formaldehyde at constant temperature, molar ratio, pH and catalyst type, corresponding to the synthesis step preceding crosslinking.

The reaction between phenol (**1**) with functionality 3 and formaldehyde (F) with functionality 2 initially yields five monocyclic compounds polyfunctionalized by hydroxymethyl groups (*Figure 1*). The reaction mechanisms involved in these reactions have been proposed in our previous work[6].

The compounds formed contain positions that are reactive towards formaldehyde (non-substituted aromatic carbons in *ortho* or *para* positions) and towards condensation reactions (non-substituted aromatic carbons and hydroxymethyl groups), explaining the numerous reactions that are possible in the reaction medium. In order to determine the reactivity of the species present, we undertook a systematic study of each monomer in conditions of constant pH, temperature and catalyst type. The work involved monitoring the progress of equimolar monomer/formaldehyde systems, even though the number of reactive sites differs as a function of monomer substitution. In order to compare their reactivity towards formaldehyde in the same conditions as those of phenol, we initially studied phenol (**1**), then compounds **2** to **5** (*Figure 1*). Kinetics were followed in isothermal conditions at 60°C with an NaOH/phenol ratio close to 10^{-2} (pH = 8) in order to determine the kinetic laws governing these systems. In light of the low solubility of compounds **2** and **3** in water, however, the studies done in this second part required dilution of the reaction medium (monomer concentration close to $0.4\,\mathrm{mol\,l^{-1}}$).

EXPERIMENTAL

Synthesis of model compounds

Phenol (**1**) (>99%), 2-hydroxymethylphenol (**2**) (99%), 4-hydroxymethylphenol (**3**) (98%) and formaldehyde (F) (37% w/w solution) were commercial

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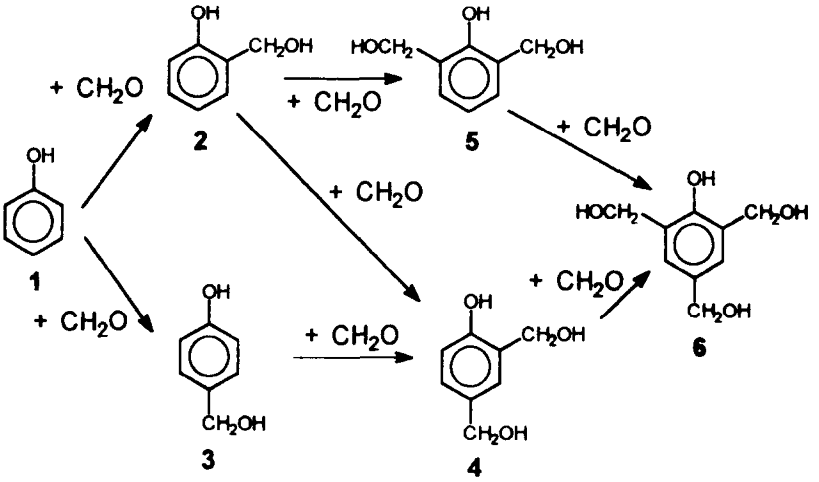


Figure 1 Reaction mechanism for addition of formaldehyde onto phenolic monomers

products (Aldrich and Lancaster) and were used without further purification. 2,4-Dihydroxymethylphenol (**4**) and 2,6-dihydroxymethylphenol (**5**) were synthesized according to Freeman and Sprengling[7,8].

Synthesis of resols

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

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

A Varian 5000 chromatograph equipped with a detector set to 273 nm was used. The columns were 25 cm long and packed with Spherisorb ODS-2 (5 μm). The mobile phase of methanol–water was used with two different elution gradients. The precise analysis conditions of each system are described in the figure legends.

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): δ(ppm) = 17.9 and 57.3 with respect to tetramethylsilane (TMS). ^{13}C n.m.r. (DMSO-d_6): δ(ppm) = 39.5 w.r.t. TMS.

ANALYSIS OF THE RESULTS

Study of the phenol (1)/formaldehyde system: T = *60°C, pH = 8*

Kinetic and mechanistic monitoring by h.p.l.c. As an example, *Figure 2* shows the h.p.l.c. traces of the kinetics of the phenol/formaldehyde reaction obtained over 48 h. After 4 h of reaction, monofunctional compounds **2** and **3** were formed in small quantities. The ratio of chromatographic peak surfaces of compounds **2** and **3** (S_2/S_3) was 1.8, showing a reactivity difference at the *ortho* and *para* positions of phenol. Phenol has two *ortho* sites and one *para* site, and so the order of magnitude of the ratio is consistent. If these positions had the same reactivity, however, the probability would lead to a ratio 2-HMP(**2**)/4-HMP(**3**) of 2. In spite of this, our results agree with published data[1].

After 48 h of reaction, the monomers present in the highest concentrations in the reaction mixture were **2**, **3** and **4** (*Figure 3*). In addition, there were a number of higher-order compounds (dimers on the curve). As a result of the high retention volumes of these compounds, it is consistent that there was a relatively low degree of substitution by hydroxymethyl groups[9,10]. The monomers present that could condense were primarily monofunctional 2-HMP (**2**) and 4-HMP (**3**) and difunctional 2,4-DHMP (**4**). Thus, these compounds have high reactivity even though present in the reaction medium in small quantities.

Analysis by ^{13}C n.m.r. The kinetics of the same samples were followed by liquid-state ^{13}C n.m.r., confirming the presence of bicyclic compounds in the reaction medium at $t = 24$, 32 and 48 h. In addition to resonance lines of phenolic monomers (compounds **1**, **2**, **3**, **4**, **5** and **6**), the 160–150 ppm region contained three resonance lines, at 154.9, 153 and 151.5 ppm, attributable to: (i) monosubstituted phenolic structures condensed in *ortho* or *para* position; (ii) disubstituted structures condensed in *ortho* or *para* position; and (iii) trisubstituted structures condensed in *para* position. These results agree with the data in *Figure 2* and with published results[9–13]. They are attributable to dimeric compounds with retention volumes included between 15 and 35 ml.

Two resonance lines were also present in the 45–30 ppm zone: around 40 ppm (methylene carbons in *para–para* ring joining) and at 35.2 ppm (methylene carbons in *ortho–para* ring joining), confirming the formation of dimeric or trimeric compounds in the reaction medium. In light of the slight progress of the reaction after 48 h and the low concentration of these lines, these results could not be used to deduce a mechanistic trend towards a given condensation reaction path.

Study of systems of functionalized monomer (2 and 3)/ formaldehyde (1/1): T = *60°C, pH = 8*

The same study was carried out on the monosubstituted

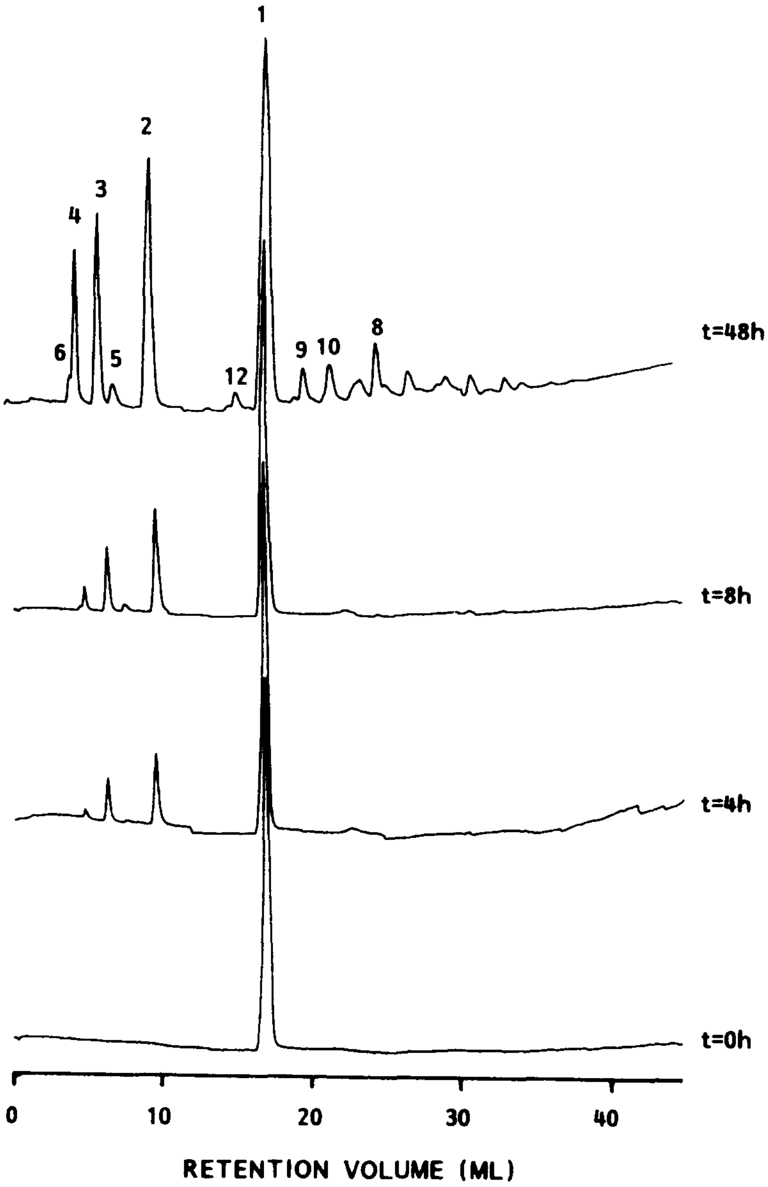


Figure 2 Kinetics of the phenol/formaldehyde system followed by h.p.l.c. (Programming: 0/100 to 100/0 methanol/water in 50 min; $T = 60°C$, pH = 8, $R = 1$.) See *Figure 6* for the identification of peaks

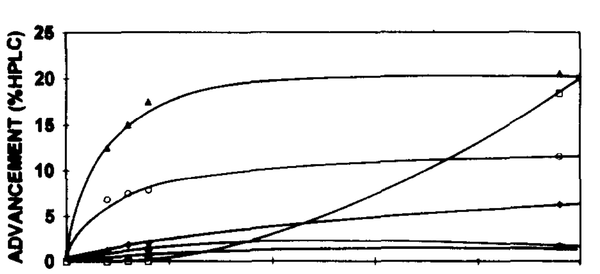


Figure 3 Quantification of chemical species in phenol/formaldehyde systems by h.p.l.c.: (▲) 2-HMP (**2**); (○) 4-HMP (**3**); (◆) 2,4-DHMP (**4**); (●) 2,6-DHMP (**5**); (■) 2,4,6-THMP (**6**); (□) dimers

compounds 2-HMP (**2**) and 4-HMP (**3**). The first reactions considered for these compounds were disubstitution and trisubstitution of the phenol ring (*Figure 1*). In the case of 2-HMP (**2**), two difunctionalized compounds were expected (**4** and **5**), while for 4-HMP (**3**), only compound **4** can form; in both cases, 2,4,6-THMP (**6**) forms. The compounds formed thus contained a high concentration of hydroxymethyl groups, leading to a number of condensation possibilities.

Kinetic and mechanistic monitoring of reaction mixtures by h.p.l.c. The above data were confirmed by h.p.l.c. kinetic monitoring (*Figure 4*). Substitution of the aromatic ring was shown by the presence of chromatographic peaks of di- and trisubstituted monomers with retention volumes less than $V_R = 15$ ml. We also detected the rapid appearance of dimeric compounds with retention volumes $V_R > 15$ ml starting at 4 h of reaction in the case of 2-HMP (**2**) (*Figure 4A*) and at 2 h in the case of 4-HMP (**3**) (*Figure 4B*). Starting at the onset of kinetics, there was competition between condensation reactions and formaldehyde addition reactions.

Figure 5 shows the changes in species created in the reaction mixtures with time. In the case of the two monosubstituted compounds **2** and **3**, disubstituted

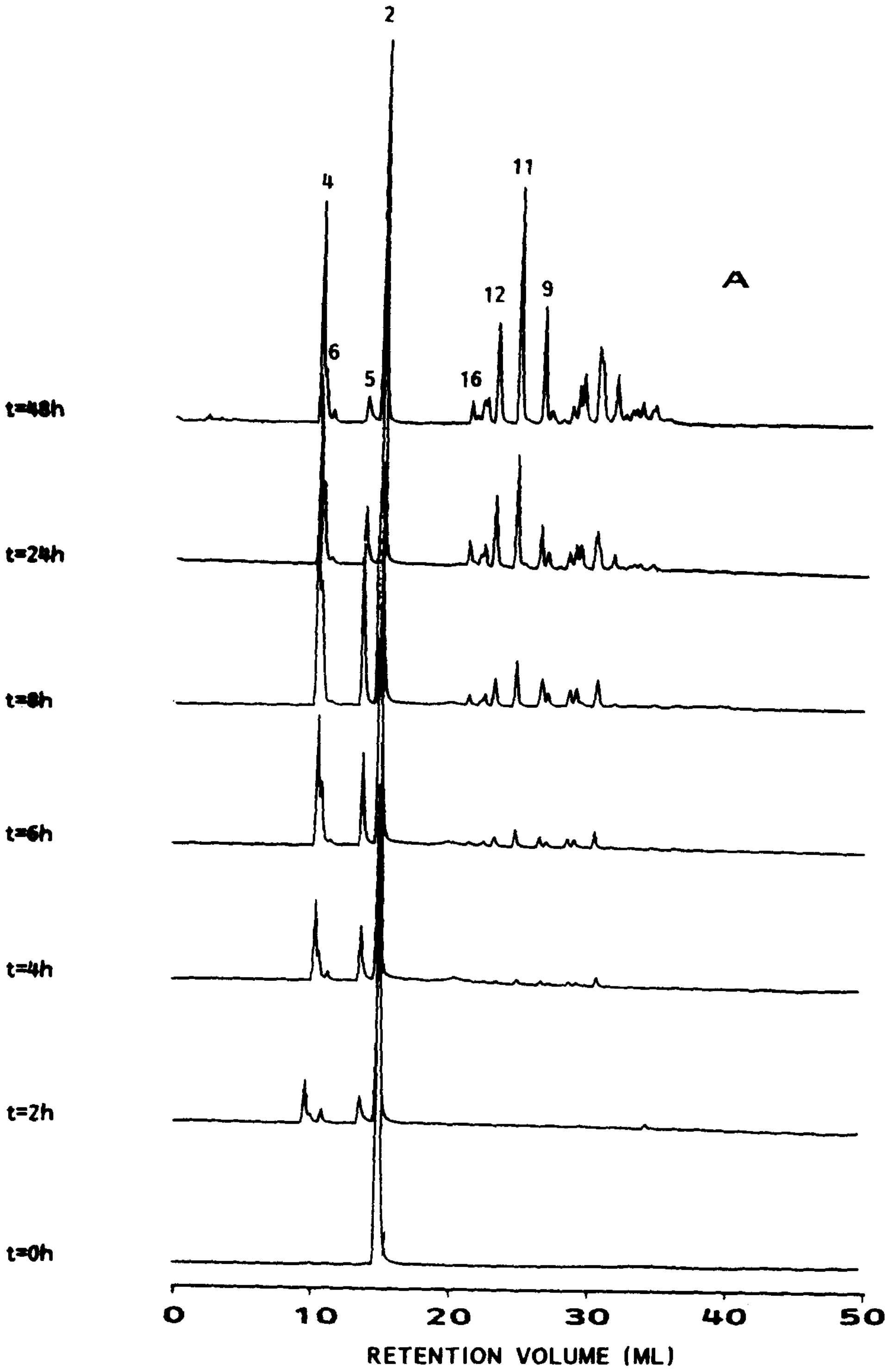


Figure 4 Kinetics of systems of monomers (**2** and **3**)/formaldehyde followed by h.p.l.c. Programming: 10/90 to 100/0 methanol/water in 40 min; $T = 60°C$, pH = 8, $R = 1$. (A) 2-HMP (**2**)/formaldehyde system; (B) 4-HMP (**3**)/formaldehyde system. See *Figure 6* for the identification of peaks

species **4** and **5** formed, followed by trisubstituted compound **6** in lower quantities. In the case of 2-HMP (**2**), however (*Figure 5A*), compounds **4** and **5** formed with similar rates and then compound **5** decreased to the benefit of compound **6** and dimers, whereas compound **4** reached a plateau. It disappeared as rapidly as it formed, suggesting a constant concentration in the medium. The same comment can be formulated for the change of 4-HMP (**3**).

These results clearly show a difference of reactivity in the reaction mixture between the two disubstituted species. Since the starting products were already functionalized with a hydroxymethyl group, the condensed compounds appeared rapidly in the reaction medium (starting at 2 h). The structures formed initially contained two aromatic rings (dimers) and beyond 24 h compounds of order higher than 2 appeared in very low quantities (retention volumes more than 30 ml (*Figure 4*)).

Nevertheless there was a large number of compounds formed by condensation reactions in each case; some compounds formed preferentially (**12**, **9**, **11**, **10**, **8**, ...)

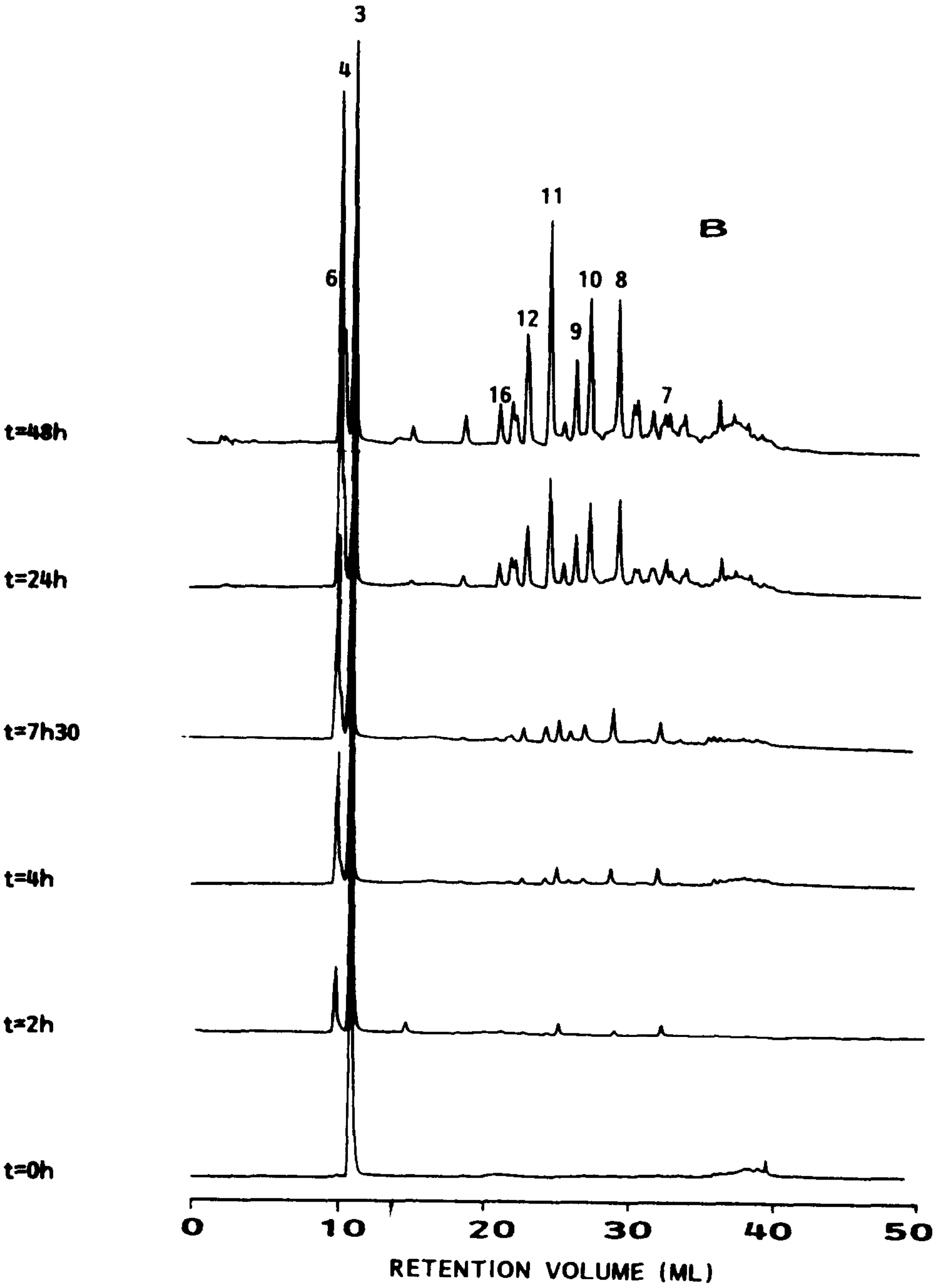


Figure 4 Continued

(*Figures 4* and *6*). Three of them were common to the two kinetics: **12**, **11** and **9**. They were dimers with *para–para* joining with a hydroxymethyl group functionality more than or equal to 2. In the study of 4-HMP (**3**), however, two other dimers, **10** and **8**, formed in large quantities. In light of the absence of *ortho* substitution on one of the two aromatic rings of these compounds, they were not obtained in the 2-HMP(**2**)/F system (*Figure 4A*).

Kinetic and mechanistic monitoring of reaction mixtures by ^{13}C n.m.r. As in our prior work, we studied two specific zones of the spectrum: (i) the 160–150 ppm region, corresponding to resonances of carbons bearing hydroxyl groups; and (ii) the 45–30 ppm region, characteristic of crosslinking in these systems.

These two regions seemed to be the most interesting for the study of the reaction mechanisms and kinetics of these systems. The results obtained in the 160–150 ppm and 45–30 ppm regions (*Figures 7* and *8*) are in agreement with h.p.l.c. data. Thus, in the case of 2-HMP (**2**), aside from the characteristic signals from monocyclic compounds (**2**, **4**, **5** and **6**), there were also several additional peaks, around 154.7, 153.0 and 151.5 ppm (*Figure 7A*), which were attributed to bicyclic compounds condensed in the *para* position. Structures condensed in the *ortho* position ($\delta = 152.4$ and 151.1 ppm) contained several lines but of weak intensity. Finally, the 45–30 ppm region (*Figure 8A*) contained resonance lines at 35.2 and 40 ppm, corresponding to *ortho–ortho* and *para–para* condensations, the latter being in the majority.

The results obtained with 4-HMP (**3**) (*Figure 7B*) were similar to those with 2-HMP (**2**), except for the band at 154.7 ppm, which was more intense and attributed to slightly condensed structures. In the 45–30 ppm region (*Figure 8B*), signals from *para–para* joinings (at 40 ppm)

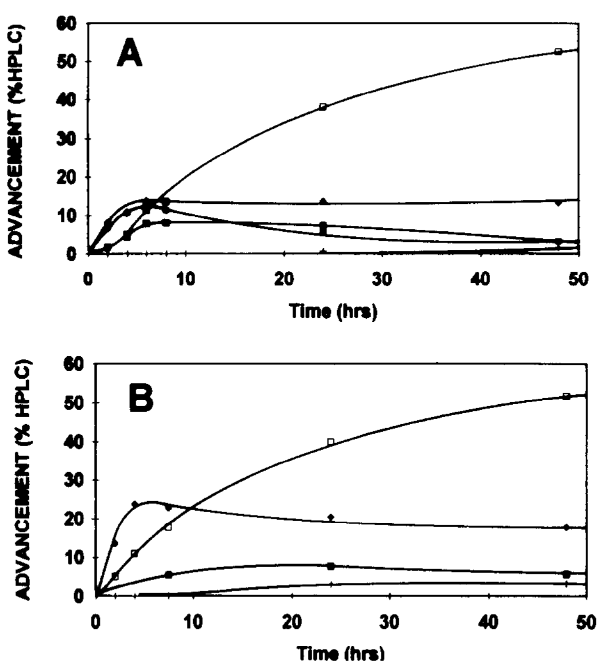
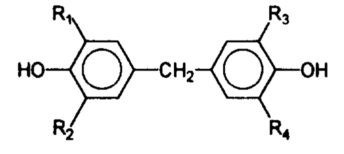
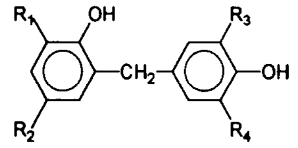


Figure 5 Quantification of chemical species by h.p.l.c. for various systems. (A) 2-HMP (**2**)/formaldehyde system: (◆) 2,4-DHMP (**4**); (●) 2,6-DHMP (**5**); (■) 2,4,6-THMP (**6**); (□) dimers; (+) trimers. (B) 4-HMP (**3**)/formaldehyde system: (◆) 2,4-DHMP (**4**); (■) 2,4,6-THMP (**6**); (□) dimers; (+) trimers



compound 7	$R_1=R_2=R_3=R_4=H$
compound 8	$R_1=CH_2OH$; $R_2=R_3=R_4=H$
compound 9	$R_1=R_3=CH_2OH$; $R_2=R_4=H$
compound 10	$R_3=R_4=CH_2OH$; $R_1=R_2=H$
compound 11	$R_1=R_3=R_4=CH_2OH$; $R_2=H$
compound 12	$R_1=R_2=R_3=R_4=CH_2OH$



compound 13	$R_2=R_3=CH_2OH$; $R_1=R_4=H$
compound 14	$R_1=R_2=R_4=CH_2OH$; $R_3=H$
compound 15	$R_2=R_3=R_4=CH_2OH$; $R_1=H$
compound 16	$R_1=R_2=R_3=R_4=CH_2OH$
compound 17	$R_1=R_2=R_4=CH_2OH$; $R_3=H$

Figure 6 Identification of dimer compounds

were slightly more intense than those from *ortho–para* joinings (at 35 ppm), confirming the presence of large quantities of compounds with *para–para* methylene bridge, of the type **8**, **9**, **10**, **11** and **12**.

It is thus of interest to note that, regardless of the initial substitution of the phenolic monomer (*ortho* for **2** and *para* for **3**), the dimeric majority compounds resulted from the condensation of groups in *para* position.

These results give rise to several comments concerning the kinetics of these systems based on 2-HMP (**2**) and 4-HMP (**3**):

(i) The disappearance of monomers was similar, regardless of the position of the hydroxymethyl substituent, indicating that reactivity of both products towards formaldehyde was very similar in the conditions adopted in this work.

(ii) A large number of dimeric compounds that formed were common to the two kinetics.

(iii) The proportion of bicyclic compounds was fairly close, although *para–para* methylene bridge was favoured in both cases.

Study of systems of difunctionalized monomer (4 and 5)/formaldehyde (1/1): T = *60°C*, *pH* = *8*

As above, we studied the reaction of 2,4-DHMP (**4**) and 2,6-DHMP (**5**) with formaldehyde in the same conditions of temperature and pH ($T = 60°C$ and pH = 8). For each of these compounds, a single aromatic carbon (*ortho* for compound **4**, *para* for compound **5**) can participate in electrophilic addition on the aromatic ring.

For each of these compounds, the following reactions can be predicted: (i) trifunctionalization (production of compound **6**); and (ii) condensations involving the mechanisms in *Figures 9* and *10* and formation of bicyclic compounds and those of order higher than 2, as we indicated in prior work[6]. *Figures 9* and *10* summarize the first compounds expected for these systems.

Kinetic and mechanistic monitoring of reaction mixtures by h.p.l.c. The two systems, 2,4-DHMP(**4**)/F and 2,6-DHMP(**5**)/F, were followed kinetically by h.p.l.c., enabling the reaction paths depicted in *Figures 9* and *10* to be confirmed. H.p.l.c. kinetic monitoring of the reaction mixture of 2,4-DHMP(**4**)/F (*Figure 11A*) indicated the presence of new chromatographic peaks appearing in small proportions starting at 2 h of reaction: compound **6** (retention volume $V_R = 16.5$ ml) formed first as expected.

At 8 h, the chromatogram contained seven new chromatographic peaks attributable to the seven dimers predicted in *Figure 9*. Two of them, **9** and **11** (*para–para* joinings) were in the majority. There was also a compound of order higher than 2 with a retention volume $V_R = 34.3$ ml.

At $t = 24$ h, dimeric compounds became predominant; even though the initial monomer was still present in relatively high levels (34%), higher-order compounds were present, but in small proportions (13%) (*Figure 12A*).

In the 2,6-DHMP(**5**)/F system (*Figure 11B*), two additional chromatographic peaks appeared after 2 h of reaction ($V_R = 10.5$ and 27 ml). One was attributed to the monomer **6** as expected and the second was probably the first dimer formed **17** (*ortho–para* joining).

Subsequently at $t = 8$ h, two additional chromatographic peaks appeared, whose retention volumes ($V_R = 22$ and 25 ml) correspond to those of compounds **16** and **12**. In addition, compounds of order higher than 2 were already present.

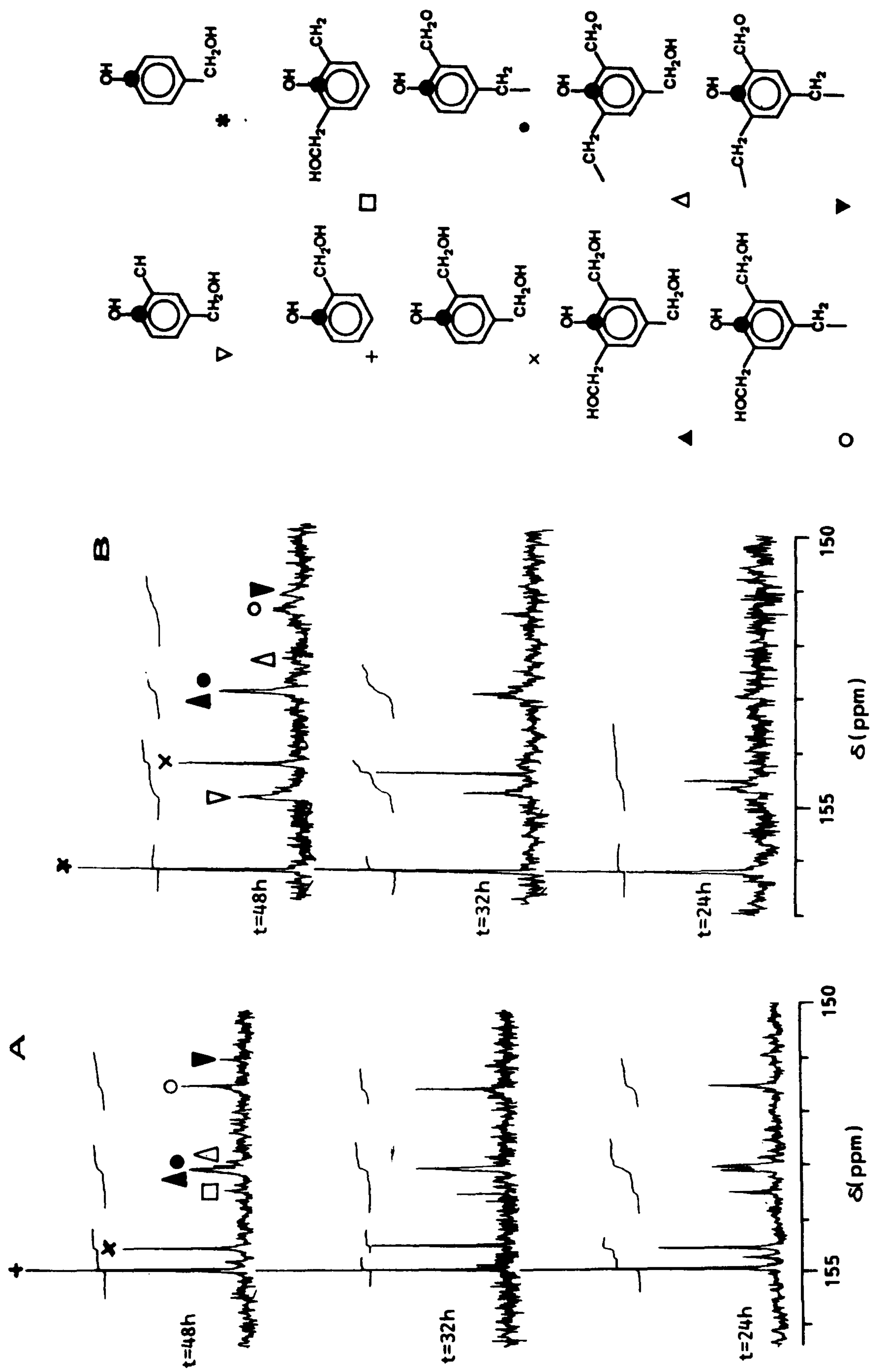


Figure 7 Kinetics followed by ^{13}C n.m.r. in 160–150 ppm region: (A) 2-HMP (**2**)/formaldehyde system; (B) 4-HMP (**3**)/formaldehyde system

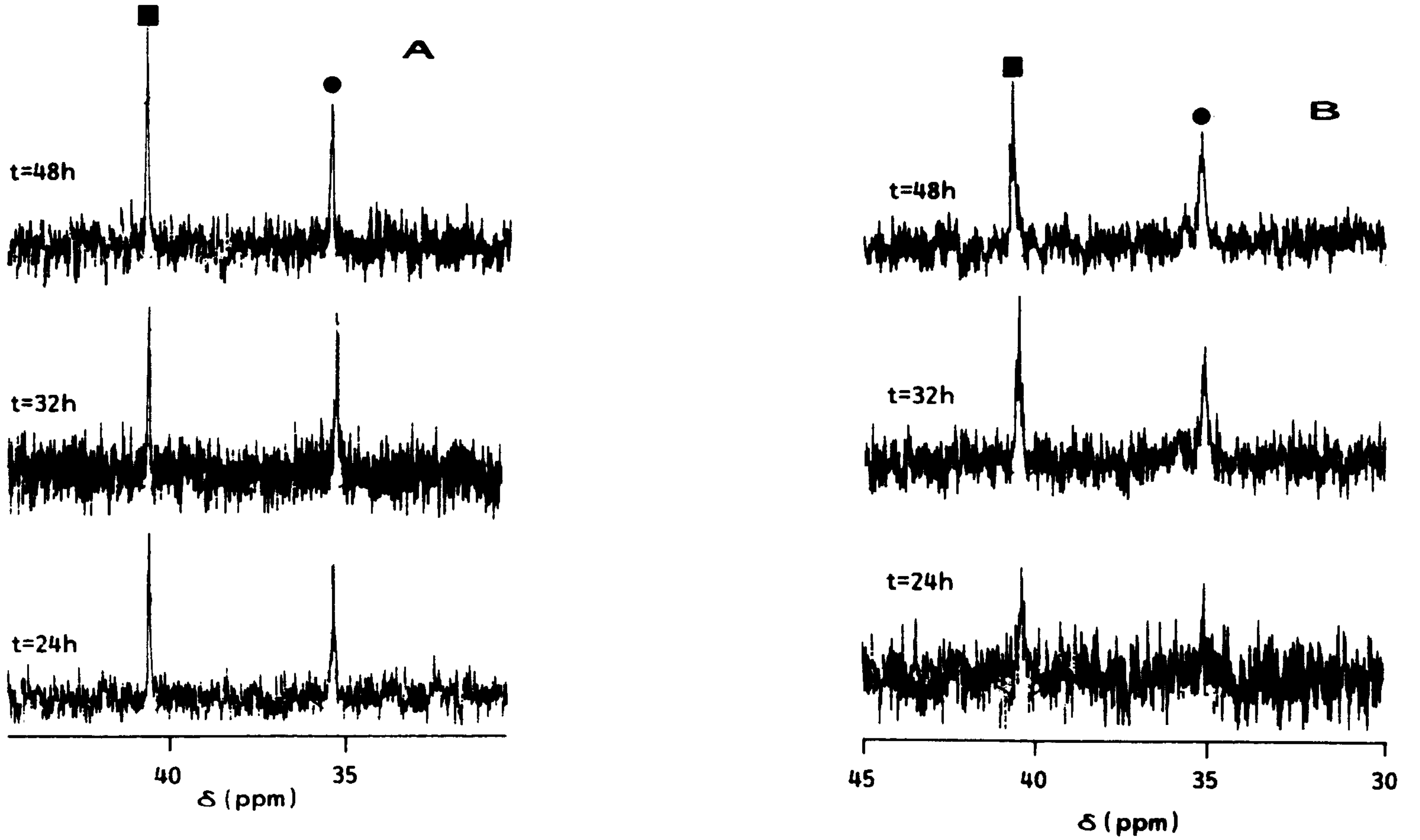


Figure 8 Kinetics followed by ^{13}C n.m.r. in 45–30 ppm region: (■) $-CH_2-$ (*para–para*); (●) $-CH_2-$ (*ortho–para*). (A) 2-HMP (**2**)/formaldehyde system; (B) 4-HMP (**3**)/formaldehyde system

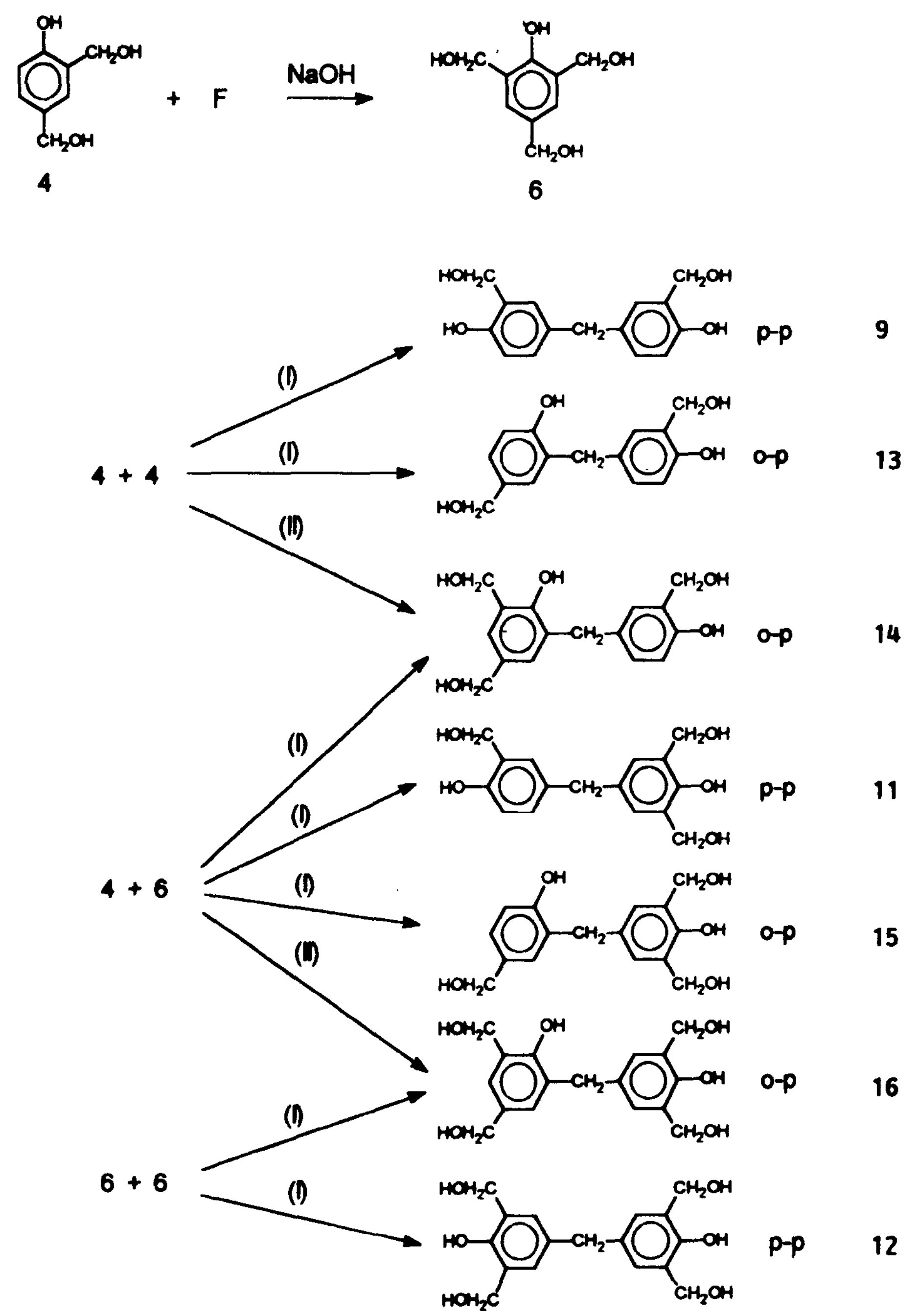
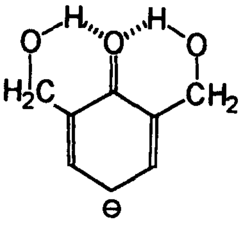


Figure 9 Reaction mechanism for addition of formaldehyde onto 2,4-DHMP (4): (I) condensation with loss of one molecule of water and of formaldehyde; (II) condensation with loss of one molecule of water

At $t = 24$ h, the concentration of the initial monomer was low (8%), while monomeric compound **6** and the dimeric compounds envisaged above were present in high concentrations. Dimeric compound **12** was the majority species and compounds of higher order became important (36%) (*Figure 12B*).

Considering the results obtained, it can be concluded that compounds **4** and **5** do not have the same reactivity towards formaldehyde. From a mechanistic point of view, this difference can be explained by taking into account the quinoid form of the species involved. Freeman and Lewis[14] in fact explained the higher reactivity of compound **5** from an electronic point of view, resulting from the stabilization of its resonance form by hydrogen bonds established in very basic aqueous medium between the phenolic hydroxyl group and the hydroxyl groups of hydroxymethyl:



This intramolecular stabilization would lead to a higher charge on the *para* carbon, thereby favouring electrophilic substitution. Nevertheless, this form depends on conditions of pH, temperature and concentration of the

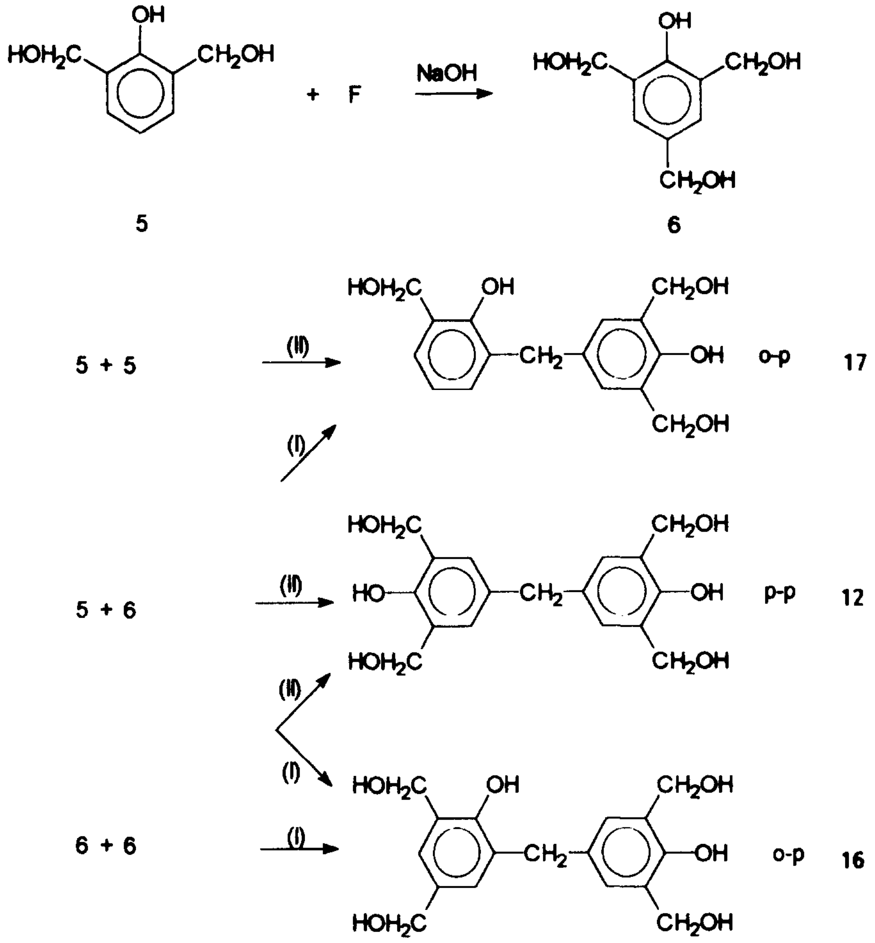


Figure 10 Reaction mechanism for addition of formaldehyde onto 2,6-DHMP (**5**): (I) condensation with loss of one molecule of water and of formaldehyde; (II) condensation with loss of one molecule of water

systems. It is considerably favoured in concentrated medium.

Similarly, other authors[4,15] have noted this reactivity difference between the two, thereby explaining the transitory presence of compound **5** in the reaction medium in the course of the addition reaction of formaldehyde onto phenol. In the case of compound **4**, on the other hand, this reasoning does not hold, as a result of its quinoid form, resulting in a reduced reactivity. These hypotheses proposed in the literature[4,15] are in agreement with our results.

Kinetic and mechanistic monitoring of reaction mixtures by ^{13}C n.m.r. Kinetics followed by ^{13}C n.m.r. are shown in *Figure 13*, in particular the changes in the 160–150 ppm spectral zone with time for compounds 2,4-DHMP (**4**) ($\delta = 154.5$ ppm) and 2,6-DHMP (**5**) ($\delta = 153.5$ ppm). *Table 1* lists the different groups of the condensed structures and the corresponding chemical shifts observed in the spectra. In spite of the high resolution of our equipment, the results include only one significant digit because of the high sensitivity of chemical shifts to the pH of the solution.

In the case of compound **4** (*Figure 13A*), h.p.l.c. data (*Figure 11*) showed that reaction progress was slow. The trisubstituted compound **6** ($\delta = 153$ ppm) formed at the same time as the *ortho* and *para* disubstituted species condensed in *para* position (M4) (attributable to compounds **9**, **17**, **22** and **11**). After this, the following species appeared: (i) trisubstituted, condensed in *para* position (M5) (compounds **11**, **12**, **15** and **16**); (ii) disubstituted in *ortho–para*, condensed in *ortho* (M3) (compounds **13** and **15**); and (iii) trisubstituted, condensed in *ortho* (M6) (compounds **14** and **16**).

The presence of all these fragments at $t = 8$ h agrees with the formation of each of these compounds predicted in *Figure 9*. Nevertheless, quantification of the chemical species by ^{13}C n.m.r. suggests that compounds **9** and **11** are majority species.

The parallel study of the 45–30 ppm spectral zone (*Figure 14A*) showed the presence of 55% *para–para* joinings and 45% *ortho–para* joinings at $t = 8$ h. These results confirm h.p.l.c. observations and enable the two major chromatographic peaks in the region of dimers at $t = 8$ h to be identified ($V_R = 28$ ml for compound **11** and $V_R = 29.6$ ml for compound **9**).

The analysis of the 160–150 ppm spectral zone in ^{13}C n.m.r. at $t = 24$ h showed the presence of small concentrations of compounds of order higher than or equal to 2, a result agreeing with the h.p.l.c. analysis described above.

Concerning compound **5**, *Figure 13B* shows the appearance of the trisubstituted monomer **6** ($\delta = 153$ ppm) as early as the onset of the reaction. After this and fairly rapidly, a large quantity of the trisubstituted species, condensed in *para* position (M5) appeared. It was present in each of the compounds considered and can be attributed to the structures of compounds **12**, **16** and **17**. Subsequently and up to 8 h of reaction, the chemical species disubstituted in *ortho* and *ortho'*, and condensed

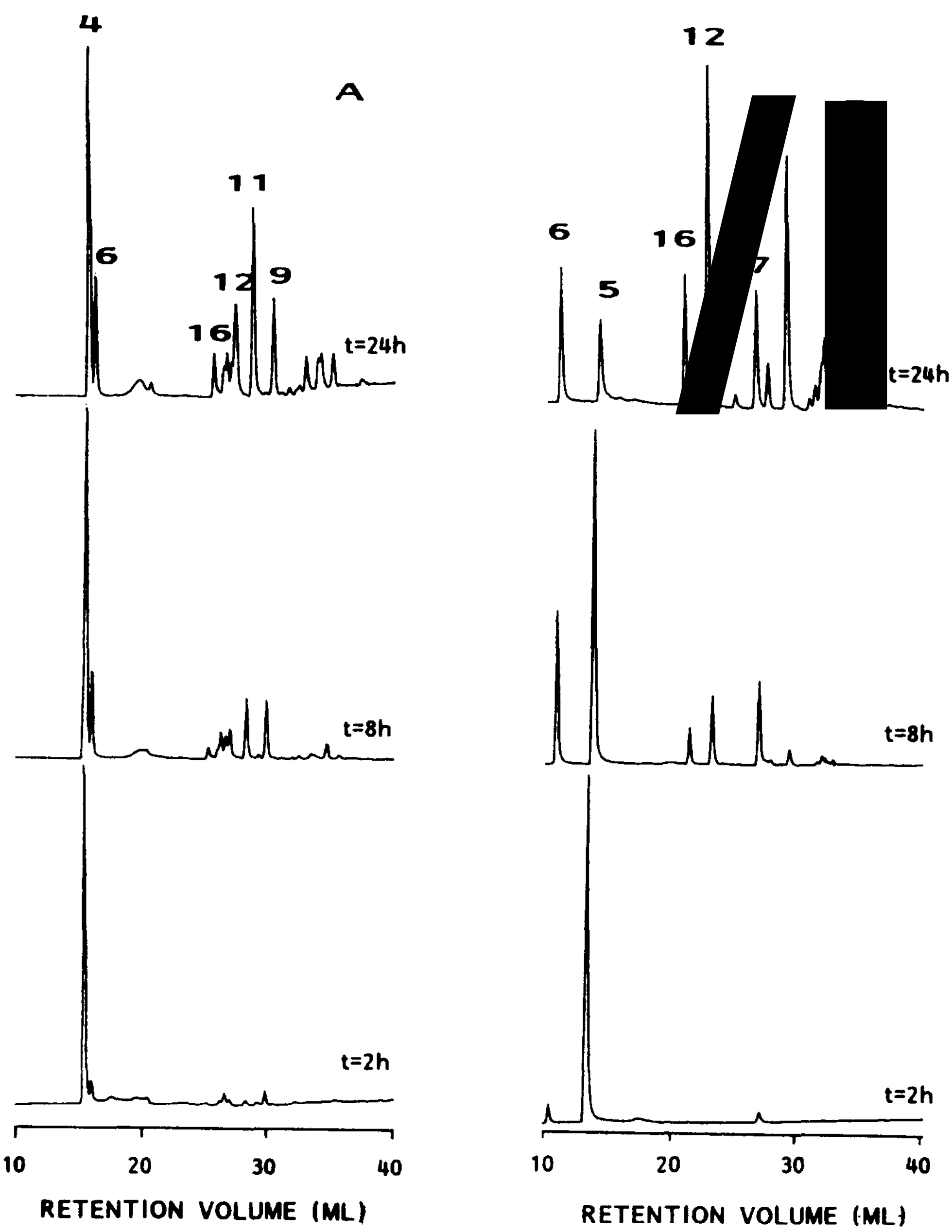


Figure 11 Kinetics of systems of monomers (**4** and **5**)/formaldehyde followed by h.p.l.c. Programming: 0/100 to 100/0 methanol/water in 50 min; $T = 60°C$, pH = 8, $R = 1$. (A) 2,4-HMP (**4**)/formaldehyde system; (B) 2,6-HMP (**5**)/formaldehyde system. See *Figure 6* for identification of peaks

in *ortho* position (M1), present for example in compound **17**, appeared, as did a small quantity of the trisubstituted structure condensed in *ortho* position (M6), attributable to compound **16**.

In parallel, the study of the 45–30 ppm spectral region (*Figure 14B*) is of interest from the standpoint of second- and higher-order ring structures. Thus, starting at 2 h of reaction, a resonance line was present at 35.2 ppm corresponding to an *ortho–para* methylene bridge. After 4 h, a new line appeared at 40.5 ppm, attributable to a *para–para* condensation. After 8 h, these two could be quantified and by direct integration of the signals we obtained a mixture of about 45% *para–para* joinings and 55% *ortho–para* methylene bridge.

The analysis of the reaction mixture at $t = 24$ h confirmed the h.p.l.c. results. New peaks were noted, indicating the presence of compounds of order higher than or equal to 2 (19%) (lines at 151.5 and 152 ppm). These compounds resulted from successive condensations occurring in the medium. The simultaneous study of the 45–30 ppm region indicates that *para–para* methylene bridges were favoured (50%) over *ortho–para* methylene bridges. The rate of *para–para* methylene bridge thus apparently increased as a result of the possibility of condensation with the free *para* aromatic carbon in compound **17** or the *para* hydroxymethyl group of compound **16**. It was not possible to choose between these two hypotheses.

The results obtained by ^{13}C n.m.r. enabled each of the dimeric compounds to be identified and to correlate them with those obtained from the chromatograms of *Figure 11*. Thus, the chromatographic peak at $V_R = 26.7$ ml was attributed to compound **17** and the two peaks at $V_R = 21$ and 22.6 ml corresponded to compounds **12** and **16**. In addition, we could confirm the presence of large quantities of compounds of order higher than 2 (trimers and tetramers).

Based on these data, we have represented (*Figure 15*)

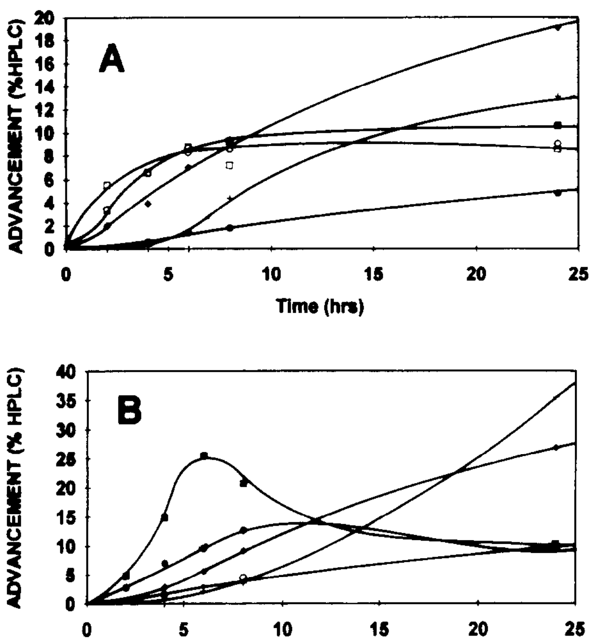


Figure 12 Quantification of chemical species by h.p.l.c. for various systems. (A) 2,4-HMP (**4**)/formaldehyde system: (■) compound **6**; (○) compound **9**; (◆) compound **11**; (●) compound **16**; (□) dimers; (+) trimers. (B) 2,6-HMP (**5**)/formaldehyde system: (■) compound **6**; (◆) compound **12**; (○) compound **16**; (●) compound **17**; (+) trimers

the disappearance of monomers (**1**, **2**, **3**, **4** and **5**) as a function of time. A reactivity difference was observed depending on the position and the substitution number on the aromatic ring. The rate constants obtained by simulating kinetic curves during the first hours, using a second-order equation of the type $dx/dt = kC_0(1-x)^2$ ($C_0 = 1$ and x = reaction advance) are listed in *Table 2*.

The monomers can thus be classified in the following order (in the conditions chosen for this work):

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

It is thus seen that 2,6-DHMP (**5**) disappeared rapidly from the reaction medium, whereas phenol and 2,4-DHMP (**4**) tended to accumulate in the medium.

Applications

In order to apply these basic results, we studied several industrial resols (prepared in different conditions of pH, concentrations and catalyst type) using different physicochemical techniques developed in this work. As an example, we present the results obtained for four industrial resols A, B, C and D prepared in different conditions of pH, catalyst type and F/P concentrations.

H.p.l.c. analyses of the four resols in *Figure 16* show that all the major chromatographic peaks in the medium could be attributed. Non-attributed peaks are mainly dimeric compounds with *ortho–para* methylene bridge.

Since the four resols analysed resulted from industrial syntheses in basic medium whose operating conditions of R = F/P, pH and catalyst type are very different, we expected that analysis results would be specific for each, from the point of view of reaction products and their chemical structure. It was thus seen that resol A contained a high monomer content, in particular phenol and 2-HMP (**2**), as well as a large number of dimers. In addition, there was a broad peak beyond 35 ml, corresponding to oligomers with $n > 2$.

Resol B presented a fairly low degree of reaction advance as a result of the high proportion of monomers (**1** and **2**) and dimers. Resol C was composed of more highly substituted species (**4**, **6**, **11**, **12** and **16**) and had a small number of dimers with a low degree of substitution. Concerning resol D, it was composed almost exclusively of entirely substituted species (**6** and **12**). The proportions of mono- and disubstituted monomers was very low and there was a very small number of dimers.

Additional analyses by ^{13}C n.m.r. confirmed these results. The study of the probe zones 160–150 ppm and 45–30 ppm led to the same comments as formulated for the h.p.l.c. analysis. These data show the validity of a basic study for the examination of these complex systems.

CONCLUSIONS

We have investigated the addition of formaldehyde onto phenol and the initial monocyclic phenolic compounds formed. The use of h.p.l.c. and ^{13}C n.m.r. enabled us to demonstrate the simultaneous formation of bicyclic compounds, obtained principally by a condensation reaction between the different monomers in the reaction mixture.

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:

(i) From a mechanistic standpoint, the aromatic carbon in the *para* position is more reactive towards formaldehyde or a hydroxymethyl group than the aromatic carbon in the *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 (*Figure 16*) enable the order of reactivity of these compounds towards formaldehyde to be determined under the conditions of temperature, pH and concentration employed.

In light of the greater reactivity of phenol (**1**) in the reaction medium, its disappearance is delayed once the substituted phenolic monomers become involved. There is a competition between the products formed and the phenol that has not yet reacted.

Thus, the operating conditions for the synthesis of the resol should be oriented towards a more rapid disappearance of phenol (**1**) starting in the first hours, by favouring the phenol/formaldehyde reaction and towards a reorganization of reaction paths in order to avoid the formation of 2,4-DHMP (**4**) that accumulates in the medium.

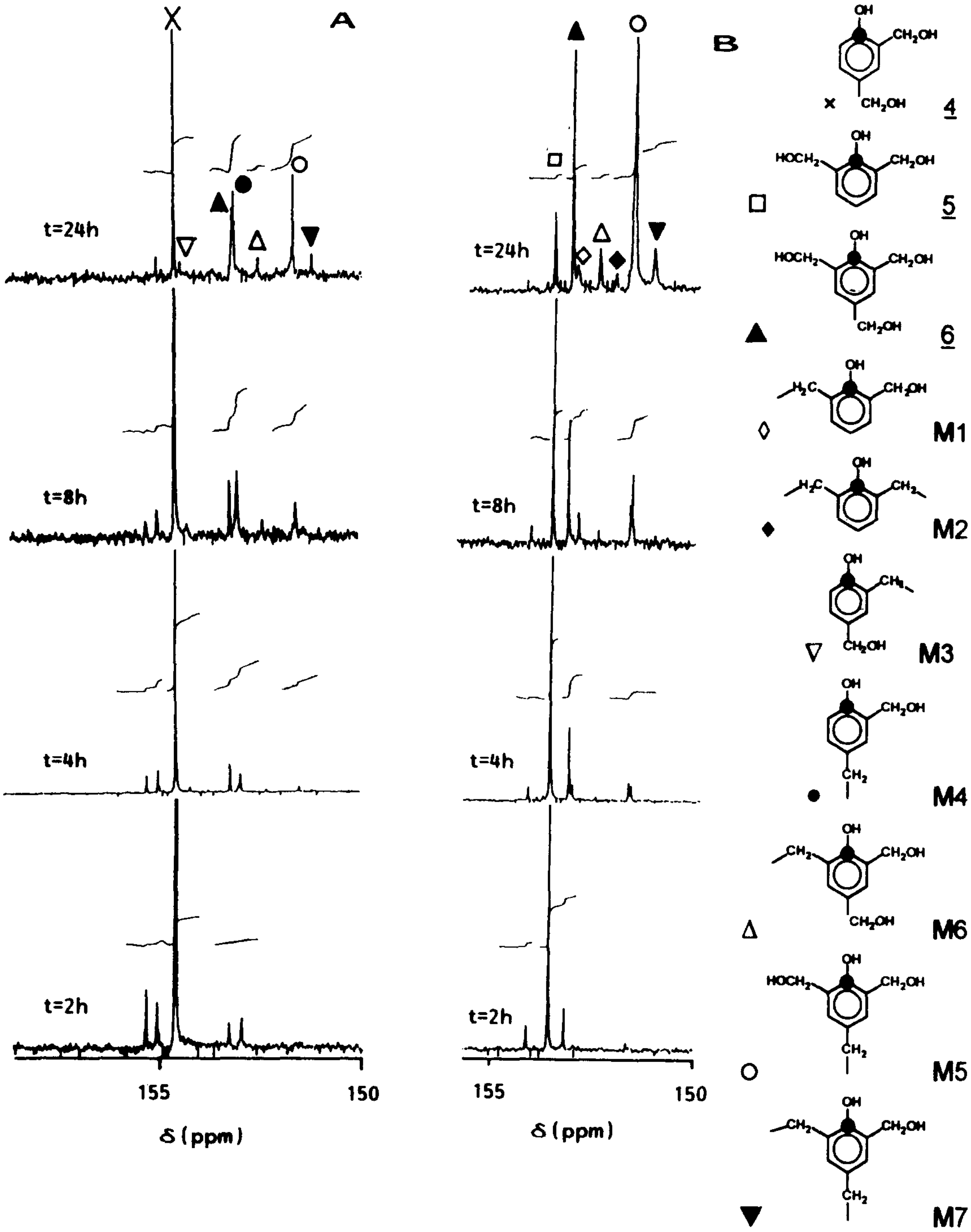
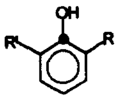
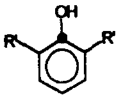
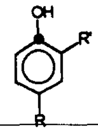
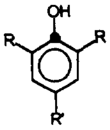
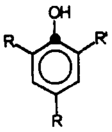
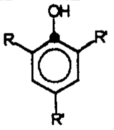


Figure 13 Kinetics followed by ^{13}C n.m.r. in 160–150 ppm region: (A) 2,4-HMP (4)/formaldehyde system; (B) 2,6-HMP (5)/formaldehyde system

Table 1 Chemical shifts of aromatic groups (●) in ^{13}C n.m.r. (liquid state, 100 Mhz). Solvent: monodeutrerated ethanol

Chemical structure[a]							
^{13}C n.m.r. δ (ppm)	153.0	152.0	154.4	153.0	151.5	152.4	151.1
Indexation	M1	M2	M3	M4	M5	M6	M7

[a] $R = -CH_2OH$, $R' = -CH_2-Ar$

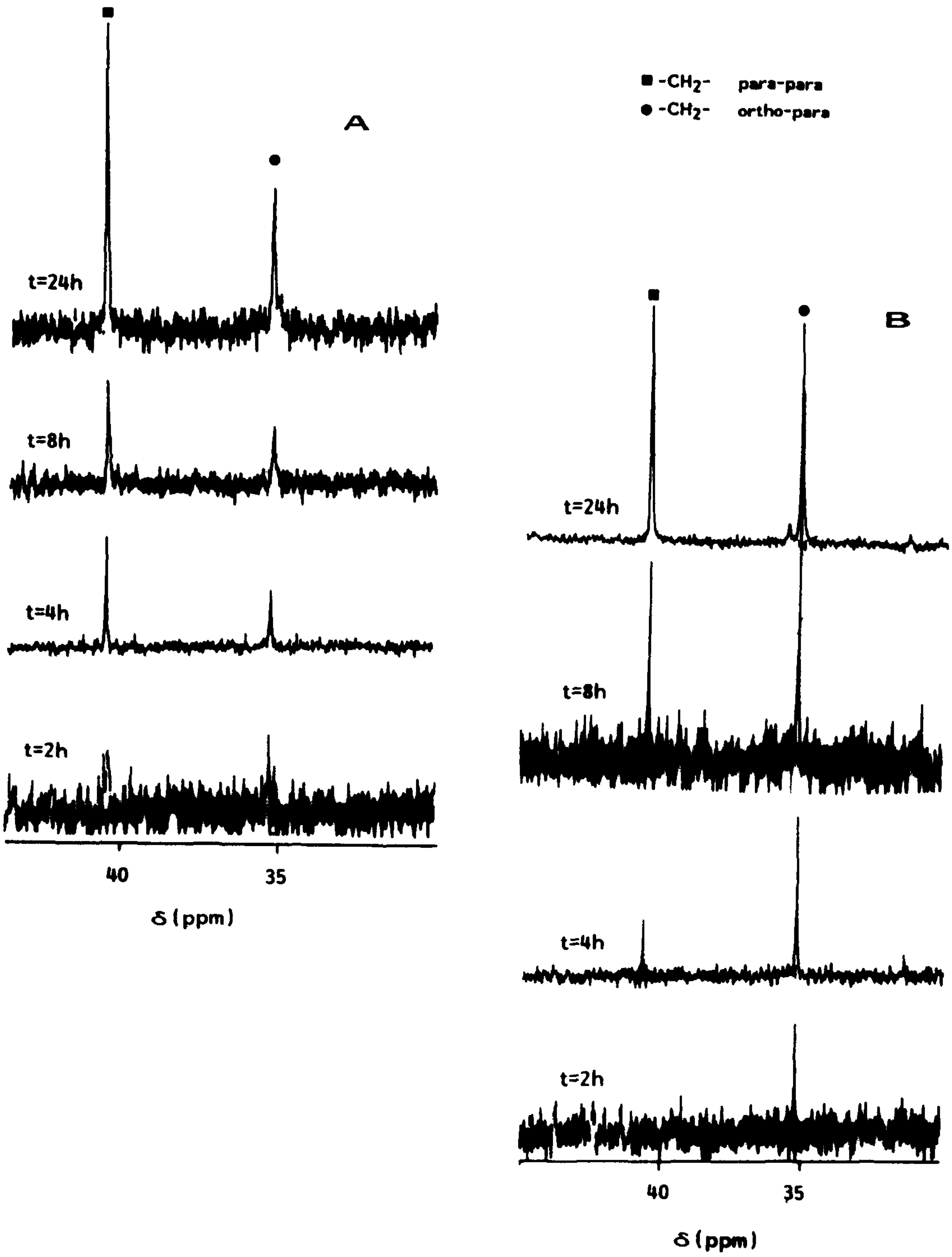


Figure 14 Kinetics followed by ^{13}C n.m.r. in 45–30 ppm region: (■) –CH$_2$– (*para–para*); (●) –CH$_2$– (*ortho–para*). (A) 2,4-HMP (**4**)/formaldehyde system; (B) 2,6-HMP (**5**)/formaldehyde system

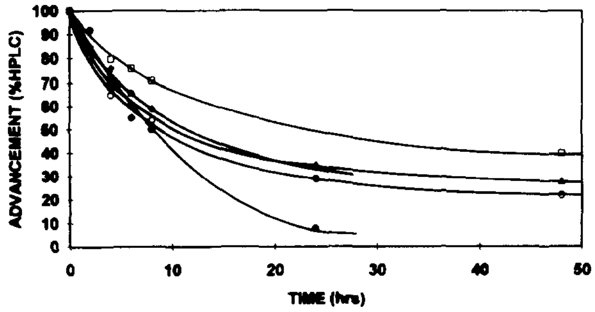


Figure 15 Disappearance of monomers followed by h.p.l.c.: (■) phenol (**1**); (▲) 2-HMP (**2**); (○) 4-HMP (**3**); (◆) 2,4-DHMP (**4**); (●) 2,6-DHMP (**5**)

Table 2 Second-order rate constants of phenolic monomers towards formaldehyde

Compound	k (l mol^{-1} h^{-1}) × 10^2
Phenol (**1**)	5.1
2-HMP (**2**)	9.9
4-HMP (**3**)	10.7
2,4-DHMP (**4**)	8.6
2,6-DHMP (**5**)	13.0

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