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Phenolic resins: 5. Solid-state physicochemical study of resoles with variable F/P ratios

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We have studied the reactions occurring in the solid state in phenol–formaldehyde systems crosslinked by a base. The results obtained with chemically defined models with Fourier transform infra-red spectroscopy and solid-state ^{13}C nuclear magnetic resonance spectroscopy (cross-polarization/magic angle spinning) applied the study of different resoles with variable formaldehyde/phenol ratios have shown that changes in the prepolymer can be followed after the gel point. Nevertheless, data obtained on the final structure of the system indicate that the fine characterization of the prepolymer before the gel point must be conducted in the study of these complex systems.

(Keywords: phenol–formaldehyde resins; crosslinking; kinetic studies)

INTRODUCTION

Phenol/formaldehyde prepolymers prepared using variable ratios of phenol and formaldehyde are highly crosslinked materials, whose final properties depend on synthesis and operating conditions.

To attribute and quantify the different groups present in such networks, we have carried out a fine structural study using two solid-state investigational tools: infrared absorption spectroscopy and solid-state ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy with cross-polarization and magic angle spinning (CP/MAS). Before the main study, a preliminary study was conducted on chemically defined reaction intermediates. The results obtained were applied to the kinetic monitoring of the crosslinking step of a model resole during base catalysis. Subsequently, we characterized several resoles in solution with variable formaldehyde/phenol (F/P) ratios before the crosslinking step in order to determine the influence of the chemical structure of the original resole on crosslinked resoles. The data gathered enable us to propose the chemical structures of the crosslinked resoles, as a function of operating conditions.

EXPERIMENTAL

Products

Synthesis of model compounds. Phenol (**1**; purity > 99%), 2-hydroxymethylphenol (2-HMP, **2**; purity 99%), 4-hydroxymethylphenol (4-HMP, **3**; purity 98%) and 4,4′-dihydroxydiphenylmethane (4,4′-DHDPM, **7**; purity 97%) were obtained commercially (Aldrich and Lancaster) and were used without further purification. 2,4-Dihydroxymethylphenol (2,4-DHMP, **4**) and 2,6-dihydroxymethylphenol (2,6-DHMP, **5**) were synthesized according to the method of Freeman and Sprengling[1,2] and 2,4,6-trihydroxymethylphenol (2,4,6-THMP, **6**) was synthesized following Perrin *et al.*[3].

Synthesis of resoles. The four batches of resoles referred to as A, B, C and D, were industrial samples with different and variable F/P ratios prepared with basic catalysts.

Experimental techniques

Liquid-phase n.m.r. High resolution liquid-phase ^{13}C n.m.r. spectra were recorded using a Bruker AM 400 spectrometer. The conditions used to record the spectra were pulse angle of 90° (4.2 μs) and digital resolution of 0.375 Hz/pt, corresponding to a spectral width of 20 000 Hz for a 128K memory space.

Samples were dissolved in monodeuterated ethanol, used as internal standard [$\delta\ ^{13}C\ (CH_3CH_2OD) =$ 17.9 ppm/TMS and 57.3 ppm/TMS, where TMS = tetramethylsilane], or in heavy water (D_2O).

Solid-state n.m.r. (CP/MAS). Solid-state ^{13}C n.m.r. spectra (CP/MAS) were obtained with a Bruker ARX300 spectrometer running under UNIX.

Samples (ground to a fine powder) were placed in a boron nitride sample holder. Contact time was 0.8 μs, the interval between sequences was 30 s and scattering was 5 kHz. Five hundred contacts were required to obtain an interpretable spectrum with a suitable signal/noise ratio. Chemical shifts were calculated from the line of polyoxymethylene (Delrin) at 80 ppm (internal standard).

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Fourier transform infra-red (FTi.r.) absorption spectroscopy. Spectra were recorded with a Bruker IFS 45 spectrometer and acquisition conditions were spectral width of 4000–400 cm^{-1}, 32 accumulations, 2 cm^{-1} resolution and signal processing by triangular apodization. Spectra of samples were recorded in the solid state as a KBr pellet.

High performance liquid chromatography (h.p.l.c.). Analyses were carried out using a Varian 9010 chromatograph equipped with an ultraviolet photodiode matrix detector set at 273 nm. The column was 25 cm long and packed with Spherisorb ODS-2 (5 μm). The acetonitrile–water mobile phase was used with an elution gradient of 10 min at 10/90 and then 70/30 in 50 min.

Differential scanning calorimetry (d.s.c.). The thermograms presented were obtained with a Setaram 111G DSC instrument with temperature programming (5°C min^{-1}). Samples were analysed in aluminium or steel capsules (resistant to moderate pressures).

ANALYSIS OF RESULTS

Study of model compounds

Compounds **2** to **7** were studied with solid-state ^{13}C n.m.r. (CP/MAS). This study was considered to be essential, since assignments of spectra are most often carried out from data obtained in solution. This study (*Table 1, Figures 1* and *2*) led to the following comments.

1. The products examined, perfectly defined chemically, were most often crystalline. Thus, spectra obtained in the solid state had fine lines that could be attributed with no particular difficulty by comparison with liquid-state spectra. In the special case of **2**, the resolution of the solid-state spectrum was such that all the lines of the benzene skeleton were represented, as in the liquid-phase spectrum (*Figure 1a*).
2. In the absence of crystalline structures, except in the case of **6**, certain line splittings are interpreted as conformational and structural effects in space, removing the degeneration of certain resonances. In particular, certain non-substituted carbons in *ortho* positions of **3** are not equivalent. The same is true for carbons 7 and 7′ of **5** and **6** and for the *ortho* and *meta* carbons of **7** (*Figures 1b, 2a, 2b* and *2c*).
3. The results obtained for **7** are consistent with those obtained for other compounds of the same series. We have shown that the non-equivalence of the lines observed between the two benzene rings results from a crystalline structure such that the two rings are out-of-plane by an angle of 35°, leading to a non-equivalence of the different *ortho* and *meta* carbons of the two rings[4].
4. The data obtained for carbons 2 and 2′ of **3** (*Figure 1b*), however, are more difficult to interpret, since the ring is flat. Only a spatial stacking effect of the different molecules, with preferential intramolecular associations, can explain this removal of degeneration of the *ortho* carbons.
5. Finally, the splitting of the hydroxymethyl lines in **4** and **6**, can be explained either by preferential intramolecular interactions of a hydroxymethyl group with the hydroxyl proton of the phenol group, or by preferential orientations in crystalline space, making them non-equivalent.

Nevertheless, analysis of all the data collected (*Table 1*) shows that, taking into account the width of the line observed in solid-state ^{13}C n.m.r., the following can be precisely followed with this method:

- changes in substitution of *ortho* and *para* carbons with a difference in chemical shift of $\Delta\delta_o$ (ns – s) = 7 ppm and $\Delta\delta_p$ (ns – s) = 10 ppm (here, ns refers to non-substituted carbons and s to substituted carbons);
- the formation and disappearance of hydroxymethyl groups (65–58 ppm). At this level, it is difficult to separate resole hydroxymethyl groups in *ortho* or *para* positions because of the small difference in chemical shift ($\delta_p - \delta_0$ = 2–3 ppm), and
- methylene groups simulating a *para–para* condensation and resonating at around 40 ppm.

All these solid-state results obtained with model compounds confirm previously published data[5–8] on systems in solution or of industrial crosslinked resole networks.

The interpretation of the *FT*i.r. spectra of compounds **1** to **7** was found to be more delicate, since this technique has been used little or not at all in the literature for the study of these crosslinked systems.

However, based on our model compounds and on

Table 1 CP/MAS ^{13}C n.m.r. chemical shifts of compounds **2** to **17**

	Carbon chemical shifts									
Compounds	C1	C2	C3	C4	C5	C6	$-CH_2OH$ *ortho*	$-CH_2OH$ *ortho′*	$-CH_2OH$ *para*	$Ar-CH_2-Ar$
2-HMP (**2**)	155.5	125.3	133.3	119.4	129.9	116.7	62.4			
4-HMP (**3**)	156.0	117.2 115.2	131.3	131.3	131.3	115.2 117.2			63.9	
2,4-DHMP (**4**)	156.7	125.2	130.9	132.4	130.9	117.0	62.5		64.9	
2,6-DHMP (**5**)	150.9	126.4	123.0	120.7	130.0	126.4	62.6	59.3		
2,4,6-THMP (**6**)	150.7	124.6	127.4	130.2	127.4	124.6	62.8	58.5	66.3	
4,4′-DHDPM (**7**)	152.8	117.8 116.3	132.3 129.4	135.4	129.4 132.3	116.3 117.8				40.8

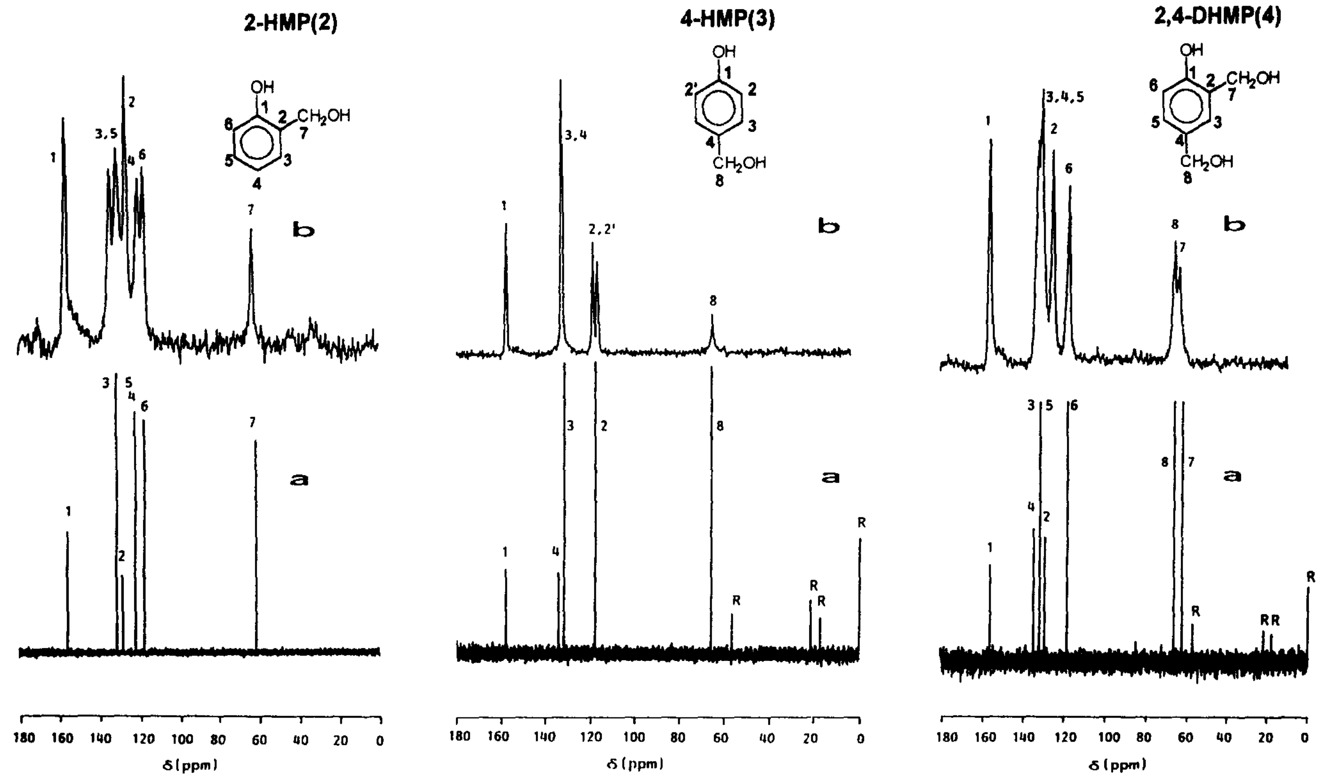

Figure 1 ^{13}C n.m.r. spectra of model compounds **2**, **3** and **4**: (a) liquid [solvent = D_2O, R = Na $SO_3(CH_3)_3Si(CH_3)_3$]; (b) solid

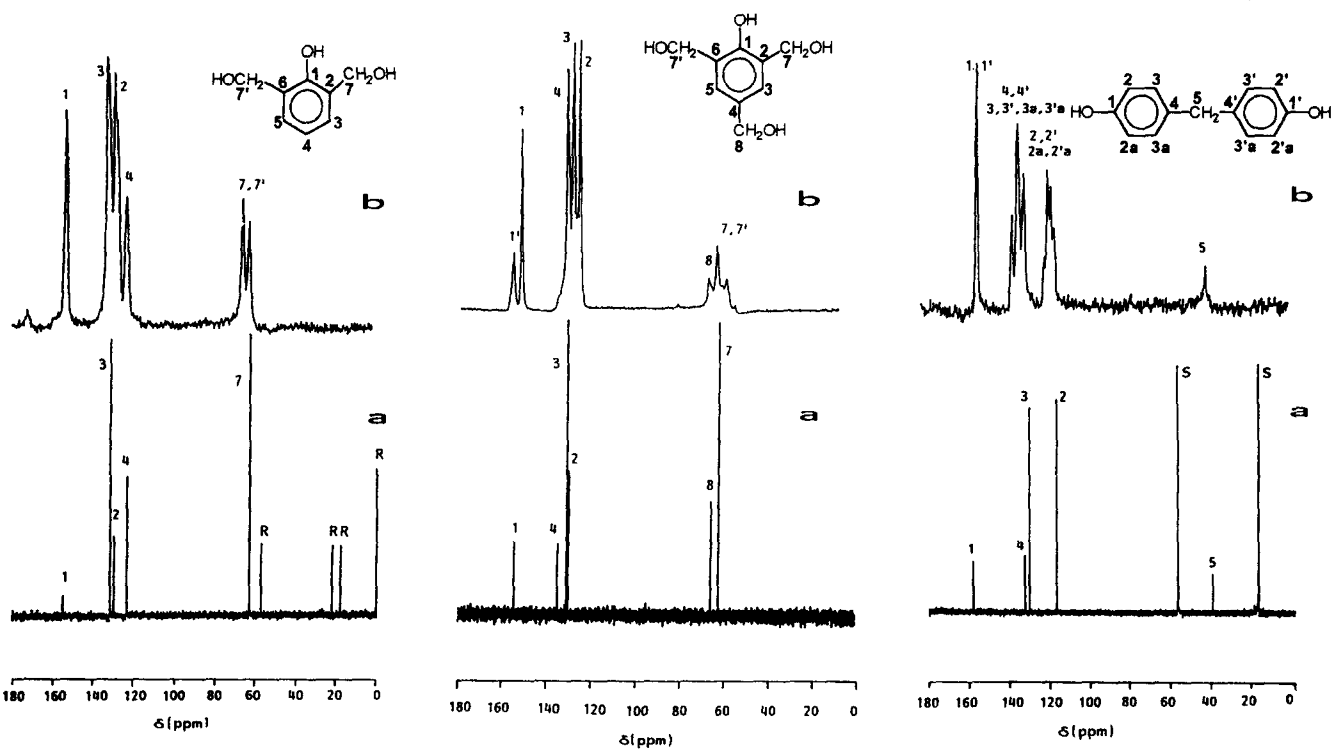

Figure 2 ^{13}C n.m.r. spectra of model compounds **5**, **6** and **7**: (a) liquid [solvent = D_2O (**5** and **6**) and monodeuterated ethanol (**7**), R = $NaSO_3(CH_3)_3Si(CH_3)_3$]; (b) solid

spectroscopic studies of substituted benzenes[9], we have succeeded in assigning the different wavelengths in the spectra of compounds **1** to **7**.

The results obtained show that two spectral zones, 4000–2500 cm^{-1} and 1800–400 cm^{-1}, are interesting for the study of these compounds (*Figures 3* and *4*, *Table 2*). Two types of modifications were observed: substitution of the benzene ring led to a splitting and shift of certain characteristic wavelengths and a splitting of the line at 1600 cm^{-1} [characteristic of the elongation of the aromatic ethylene bond (C=C)] has been observed with monosubstituted compounds **2**, **3** and **7**. Similarly, the characteristic frequencies of deformation of the hydroxyl group and of elongation of the C–O bond in primary alcohols (1050 cm^{-1}) were also affected by the structural change of the molecule. This was noted around 991 cm^{-1} for **3** which has few intermolecular hydrogen bonds. The presence of one or several hydroxymethyl groups in the *ortho* position, however, favours intermolecular hydrogen bonding. In this case, this vibration is split and there is a shift towards higher wavelengths (*Table 2, Figure 3*) in the case of compounds **2**, **4**, **5** and **6**.

In addition, the 950–650 cm^{-1} spectral region—characteristic of deformations of the C–H bond out of the plane of the benzene ring[9]—enabled the different types of substitution to be characterized. Depending on the number and position of hydroxymethyl substituents on the ring, we could identify between one and seven lines specific to the structure of the benzene ring.

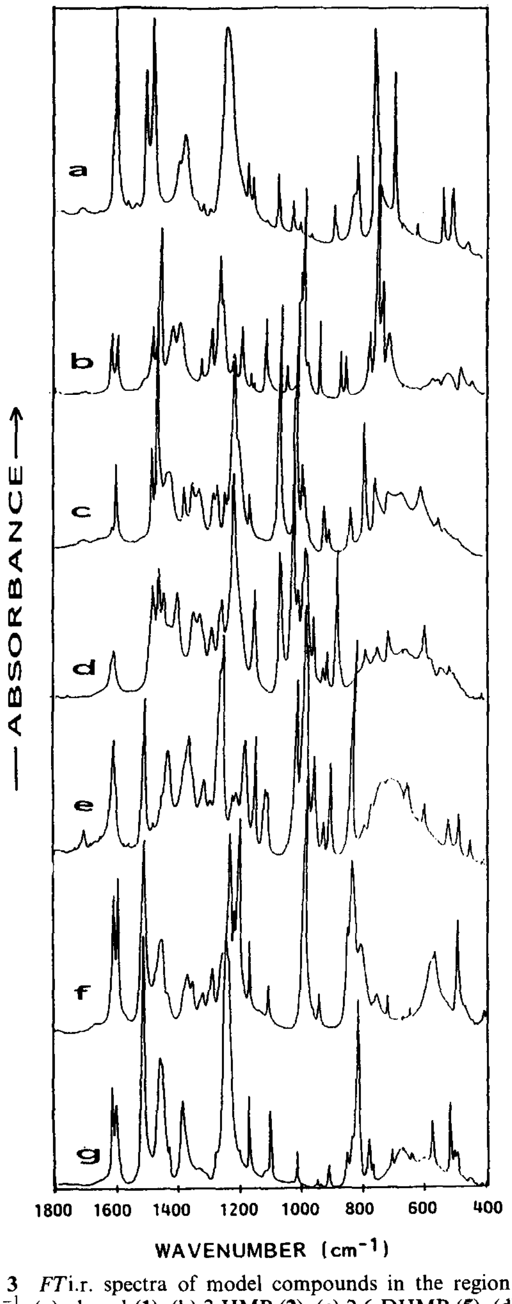

Figure 3 *FT*i.r. spectra of model compounds in the region 1800–400 cm^{-1}: (a) phenol (**1**), (b) 2-HMP (**2**), (c) 2,6-DHMP (**5**), (d) 2,4,6-THMP (**6**), (e) 2,4-DHMP (**4**), (f) 4-HMP (**3**) and (g) 4,4′-DHDPM (**7**)

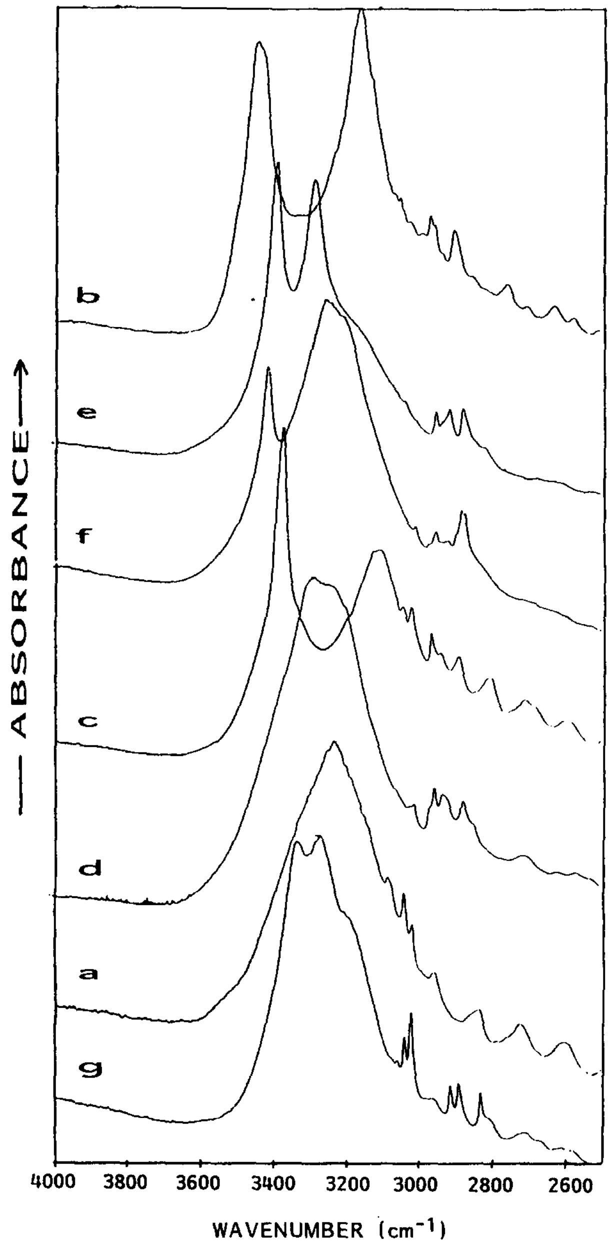

Figure 4 *FT*i.r. spectra of model compounds in the region 4000–2500 cm^{-1}: (a) phenol (**1**), (b) 2-HMP (**2**), (c) 2,6-DHMP (**5**), (d) 2,4,6-THMP (**6**), (e) 2,4-DHMP (**4**), (f) 4-HMP (**3**) and (g) 4,4′-DHDPM (**7**)

Several rare lines led to the selective characterization of certain structures. In particular, the line at a wavelength of ~690 cm^{-1} is characteristic of the monosubstituted ring (**1**). Similarly, those lines noted around 735 and 757 cm^{-1} corresponded to a monosubstituted and 1,2-disubstituted rings (**1** and **2**, respectively), lines at 813 and 837 cm^{-1} were noted for compounds **3**, **4** and **7** and are attributable to 1,4- and 1,2,4-substitutions, respectively, and the line at 890 cm^{-1} is characteristic of 1,2,4,6-tetrasubstitution (**6**). The disappearance of the vibration around 758 cm^{-1} reveals a structure that is or is not substituted in the *ortho* position subsequently becoming substituted in the *para* (*Figure 5A*), while the disappearance of the vibration at 826 cm^{-1} reflects a structure substituted in *para* and *ortho* positions that becomes substituted in *ortho* only (*Figure 5B*).

In addition, we were able to establish rules of incremental additivity by comparing different wavelengths as a function of the position and number of

Table 2 *FT*i.r. wavenumbers (ν exp in cm^{-1}) of compounds **1** to **7**

Compounds	Phenol (**1**)	2-HMP (**2**)	4-HMP (**3**)	2,4-DHMP (**4**)	2,6-DHMP (**5**)	2,4,6-THMP (**6**)	4,4′-DHDPM (**7**)
Benzenic cycle substitution							
ν (O–H)	3248	3438 3157	3382 3115	3291 3228	3400 3295	3421 3266	3336 3273
ν (C=C arom.)	1595	1616 1595	1610 1596	1614	1595	1609	1613 1599
ν (C=C arom.)			1518	1515			1513
δ(O–H) ν (C–O) primary alcohol		1003 995	991	1020 996 990	1063 1010	1028 1011 995	
ν (C–H) out-of-plane	690 758 735	869 852 757 735	850 837 829 805	906 838	833 786	958 881	813

substitutions. There was a 61 cm^{-1} shift for *ortho* substitution and a 150 cm^{-1} shift for *para* substitution compared with the absorption of phenol (690 cm^{-1}).

Other frequencies were usable in this series of compounds. Thus, monosubstitution of the phenol ring in the *para* position (**3** and **7**) was also characterized by a line of wavelength around 1236 cm^{-1}, while monosubstitution in the *ortho* position presented a weak line around 1044 cm^{-1}.

In the 4000–2500 cm^{-1} region (*Figure 4*), we could show the presence of hydrogen bonds that may be intramolecular, as in the case of **2**, **5** and **6**, and intermolecular in the case of **3**. Despite this, the region is difficult to utilize in the study of resoles, where only a broad band containing all the wavelengths is expected as a result of the complexity of these systems.

Based on these data, it became possible to carry out kinetic and mechanistic monitoring of phenol ring substitution, and subsequently of the crosslinking of the products formed, as a result of the disappearance and appearance of wavelengths characteristic of rings substituted by hydroxymethyl groups.

Application to the study of a model resole

This study involved a resole prepared in basic medium, with an F/P ratio of 1.5. The progression of crosslinking was followed by mixing the resole with a fixed quantity of 50% (w/w) sodium hydroxide solution. The mixture was dispensed in tubes that were heated in an oven ($\Delta T = \pm 1$°C). Samples were removed at regular intervals and stored at −20°C before being ground and analysed.

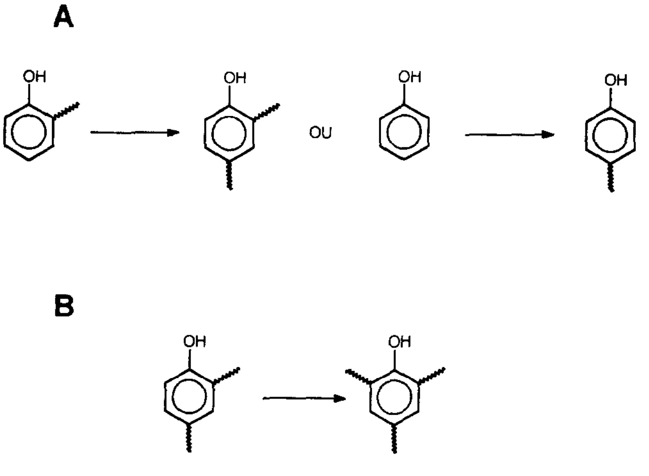

Figure 5 Substitution in *ortho* position (A) and in *para* position (B)

Physicochemical characterization of the initial resole in solution. The prepolymer studied was characterized by h.p.l.c., liquid-state ^{13}C n.m.r. and *FT*i.r., and was analysed on the basis of our previously published results (Parts 1 to 4 of this series of papers)[10–13].

The h.p.l.c. chromatogram and the ^{13}C n.m.r. spectrum (*Figure 6*) show that phenol was the major compound in the reaction mixture (10%) and that there were numerous dimers, since their retention volumes were included between 25 and 35 ml. In addition and based on prior results, it can be concluded that these dimers are relatively non-substituted.

A broad peak in the h.p.l.c. chromatogram beyond the retention volume of 35 ml corresponds to three, four and higher order ring compounds. In ^{13}C n.m.r., the presence of these compounds is shown by a broadening of the base of resonance lines in the zone between 160 and 150 ppm, characteristic of the condensed and stereosensitive structure of the compounds[10].

This industrial resole thus presents a relatively high degree of reaction advancement to tri-, tetra- and pentameric entities, although the quantity of monomers and phenol remains in the majority. This state of advancement was taken as reference at time $t = 0$ for the following crosslinking studies.

In light of the results obtained in the structural study of resoles in solution, where we showed that parameters such as the quantity of catalyst and temperature were important for these systems, we investigated the influence of these parameters on the crosslinking of the systems in the solid state.

Influence of the quantity of catalyst. The d.s.c. results, presented in *Figure 7* for the resole with variable concentrations of NaOH catalyst (0, 2 and 5%), were obtained in the temperature range of 60 to 360°C with temperature

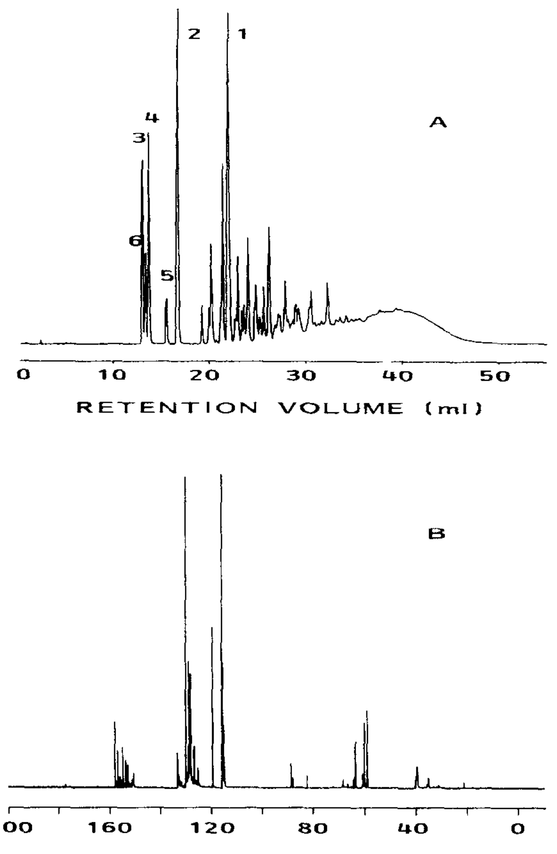

Figure 6 H.p.l.c. chromatogram (A) and liquid-state ^{13}C n.m.r. spectrum (B) of the resole studied

programming at 5°C min^{-1}. All the thermograms show a reaction exotherm of varying width, the reaction onset temperatures (T_{onset}) of which were affected by the presence of the catalyst (*Table 3*). As expected, the presence of sodium hydroxide in the resole catalyses the different reaction mechanisms from the standpoint of both the reaction onset temperature and the temperature range.

Kinetic and mechanistic monitoring of the same resole in isothermal conditions at 80°C for 50 h showed that wavelengths characteristic of various products are observed in the 1800–700 cm^{-1} region of the *FT*i.r. spectra (*Figure 8*). Thus, monitoring of wavelengths around 1010 cm^{-1}, attributable to deformation of the O–H bond and elongation of the C–O bond in primary alcohols ($-CH_2OH$ groups) or ethers ($-CH_2-O-CH_2-$), was found to be of value in these systems.

Similarly, in the region 970–740 cm^{-1}, the wavelengths of 756, 826 and 888 cm^{-1} were specifically followed. Resole crosslinking by condensation mechanisms caused a change in the absorbance of bands around 756 and 826 cm^{-1} (decrease in signal strength resulting from substitution of the aromatic ring).

Using a reference band (1610 cm^{-1}, corresponding to the elongation of C=C bonds of the aromatic ring) which seemed to be invariant during the heat cycle, we were able to follow changes in the structures present in the reaction medium (*Figures 9, 10* and *11*) as a function of catalyst concentration.

The kinetics of disappearance of the band at 1010 cm^{-1} in the absence of catalyst was relatively slow up to 50 h (*Figure 9*). The presence of catalyst (2 and 5%) accelerated the reactions involving dimethylene ether bridges or hydroxymethyl groups after 20 h of reaction and the curves tended towards a plateau with a high residual value.

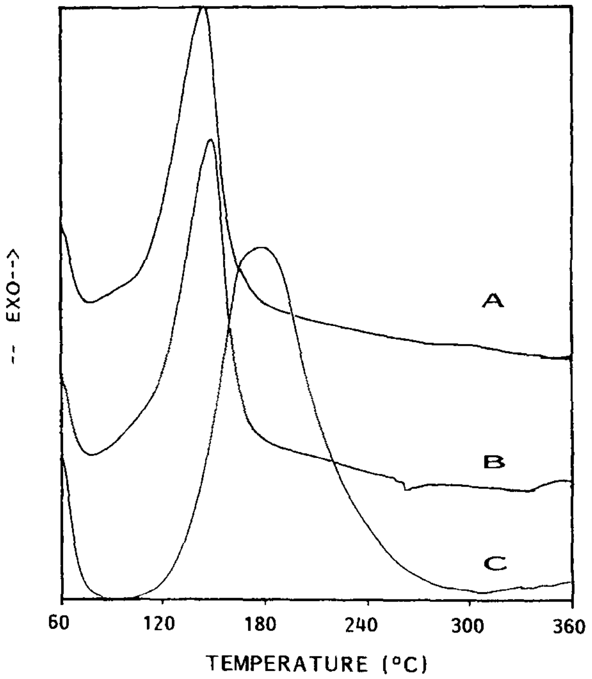

Figure 7 D.s.c. thermograms (temperature rise 5°C min^{-1}): (A) resole + 5% NaOH, (B) resole + 2% NaOH and (C) resole alone

Changes in vibration at 826 cm^{-1} (*Figure 10*), characteristic of *para*-substituted structures and mono- or non-substituted *ortho* structures, showed a clearcut effect of the catalyst concentration on *ortho* substitution. Catalysed systems no longer changed after 20 h. After 50 h of reaction, however, the 5% NaOH system contained 15% of structures that were non-substituted in the *ortho* position, while in the presence of 2% NaOH this value increased to 35%. These observations confirmed the results obtained in the first part of this work on the effect of pH on the reaction kinetics of resoles.

Changes in the kinetic curve of the band at 758 cm^{-1} (*Figure 11*) were similar for the two catalysed systems: the plateau appeared after 20 h for a reaction advancement of 0.4. In addition, the high value of residuals observed for this band was due to the superposition of different vibration bands between 810 and 740 cm^{-1}. It was thus not possible to adequately follow the disappearance of the band at 758 cm^{-1}. The absence of catalyst, however, inhibited any substitution in the *para* position.

As expected, these results show that the presence of catalyst in the systems considerably changes the reactions occurring. In particular, in the absence of catalyst,

Table 3 D.s.c. characteristics of exotherm reactions of the industrial resole—influence of the catalyst

	T_{onset} (°C)	ΔT (°C) (base width)
Resole 3	132	100
Resole + 2% NaOH	120	60
Resole + 5% NaOH	113	60

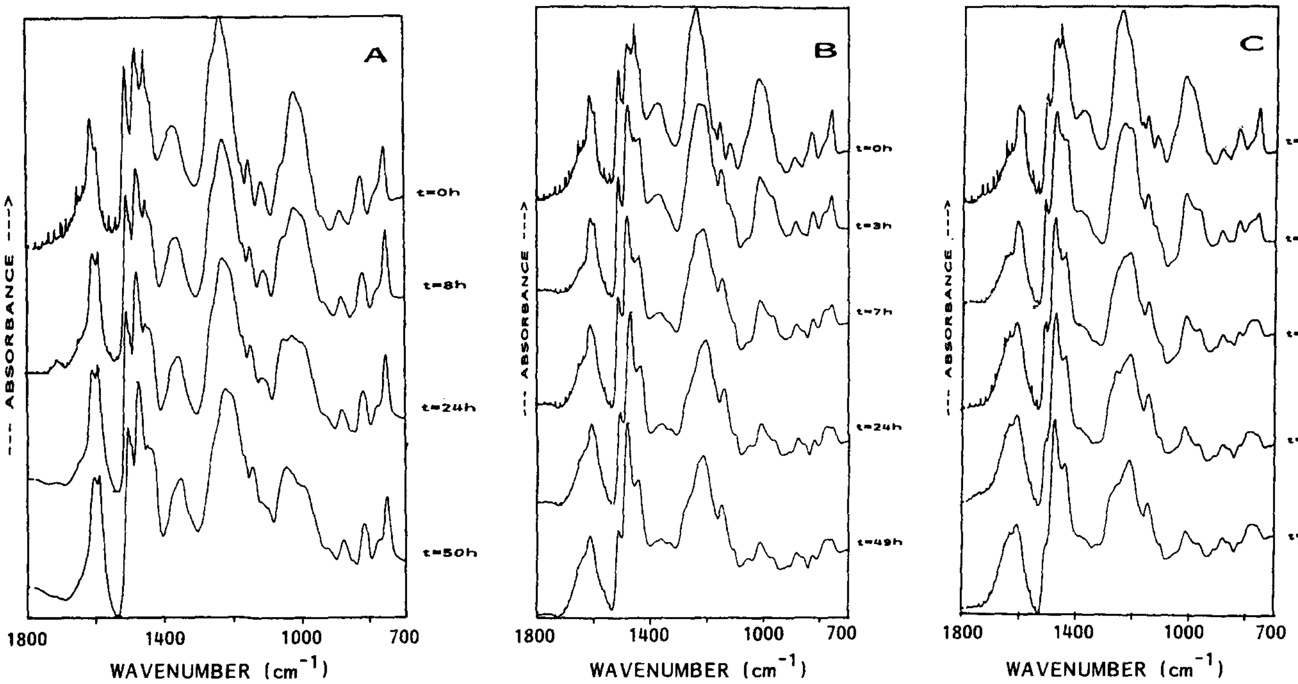

Figure 8 Kinetics of the resole followed by *FT*i.r., $T = 80°C$: (A) alone, (B) with 2% NaOH and (C) with 5% NaOH

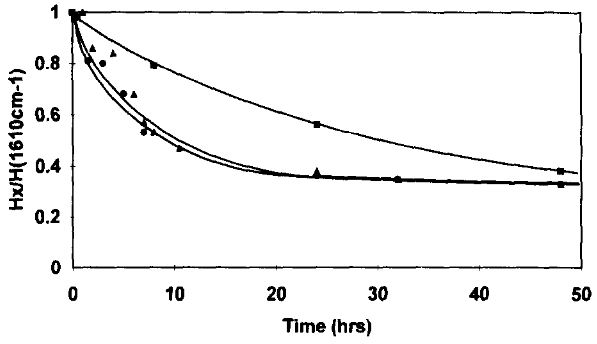

Figure 9 Changes in wavelength at 1010 cm^{-1}: ■, 0% NaOH; ▲, 2% NaOH; ●, 5% NaOH

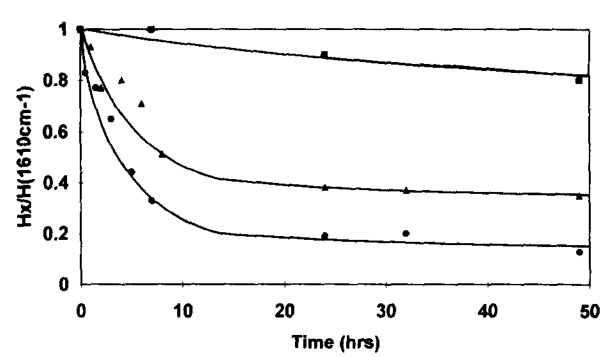

Figure 10 Changes in wavelength at 826 cm^{-1}: ■, 0% NaOH, ▲, 2% NaOH; ●, 5% NaOH

addition reactions on free *para* positions do not occur and those in *ortho* positions occur to a restricted extent, whereas hydroxymethyl groups undergo condensations. Thus hydroxymethyl groups in this system react preferentially among themselves in comparison with non-charged aromatic sites (no phenate ions form). *Ortho* substitution of these catalysed systems was favoured (*Figure 10*) as a function of catalyst concentration, confirming the role played by the catalyst in position addition reactions, as we had shown in the synthesis of resoles[11].

Reaction advancement did not become total at 80°C: the system was blocked and gelled.

The kinetics and mechanisms of the same systems were also followed using solid-state ^{13}C n.m.r. Considering the width of the line from 12 to 15 ppm in the spectra, only envelopes were obtained. Nevertheless, the spectral changes resulting from crosslinking were detectable.

The broad band at 45–25 ppm was characteristic of methylene bridges (*ortho–para* and *para–para* linkages), the band around 65 ppm was attributable to hydroxymethyl groups ($-CH_2OH$), that around 75 ppm to dimethylene ether bridges ($-CH_2-O-CH_2-$), the shoulder at 120–110 ppm was characteristic of non-substituted aromatic *ortho* carbons, while the band at 140–120 ppm contained the simultaneous resonance of aromatic *meta* carbons, *ortho*- and *para*-substituted aromatic carbons and non-substituted *para* aromatic carbons. When the latter were the major species, they could appear in the form of a slight shoulder around

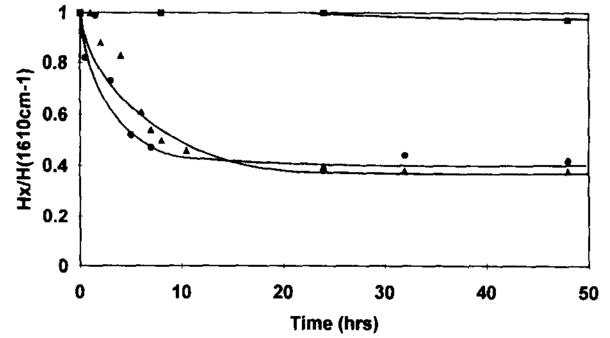

Figure 11 Changes in wavelength at 758 cm^{-1}: ■, 0% NaOH; ▲, 2% NaOH; ●, 5% NaOH

120 ppm. The broad band at 160–150 ppm, characteristic of all C_1 carbons bearing a hydroxyl group in the reaction medium, was used as internal standard.

Figure 12 shows the spectra of samples polymerized with 2 and 5% catalyst as a function of time. Comparison of the spectra reveals a decrease in the band 115 ppm, confirming the presence of condensation involving non-substituted *ortho* aromatic carbons, and of the band centred at 65 ppm, characteristic of hydroxymethyl groups. Changes in the band at 45–30 ppm, on the other hand, were slight.

The proportion of methylene bridges with *para–para* links remained practically identical throughout kinetic monitoring, in comparison with *ortho–para* linked methylene bridges. Since the mobility of entities in the medium was reduced, the envisaged reactions take into account the environment of the molecules rather than their affinities.

Changes in the areas of the different bands on the basis of the surface of the peak at 160–150 ppm (internal standard) are shown in *Figures 13* and *14*. The curves obtained confirm the *FT*i.r. results. In addition, supplemental data were obtained from the study of the lines characteristic of methylene bridges, which are the essential element of the network. The proportion of *ortho–para* or *para–para* linkages furnishes information of the reactivity of the functional groups having reacted. Furthermore, the rates of condensation increased with increasing percentage of catalyst, particularly in the case of *ortho* substitution, since after 7 h of reaction with 5% catalyst (*Figure 14*) the value was close to that obtained after 24 h of heat treatment with 2% catalyst (*Figure 13*). The same results were observed for the bands at 65 ppm and 40 ppm, showing that increasing the catalyst concentration accelerated network formation.

Since the resole contained more hydroxymethyl groups in the *ortho* position than in the *para* and the formation of oligomers requires the formation of *ortho–para* links, the latter were in the majority in the medium. As an example, deconvolution of the band around 45–30 ppm (8 h, 80°C, 5% NaOH) into basic lines indicates that the medium contained about 25% *para–para* links and 75% *ortho–para* links (*Figure 15*).

In the kinetic monitoring of resole formation in the absence of catalyst, we were only able to analyse samples obtained at 24 and 50 h because of the slight extent of reaction advancement during the first hours (results obtained by *FT* i.r.). Earlier samples were not sufficiently crosslinked to be studied with this technique.

Deconvolution of the ^{13}C n.m.r. spectrum from the sample obtained after 50 h (*Figure 16*) enabled the following conclusions to be reached:

- there were high proportions of non-substituted aromatic carbons in *ortho* (115 ppm) and *para* (125 ppm) positions;
- the formation of dimethylene ether bridges was much higher than in the presence of catalyst; and
- there was also the presence of methylene bridges always having the same preferential orientation towards the formation of *ortho–para* links.

We similarly processed the spectrum of the sample

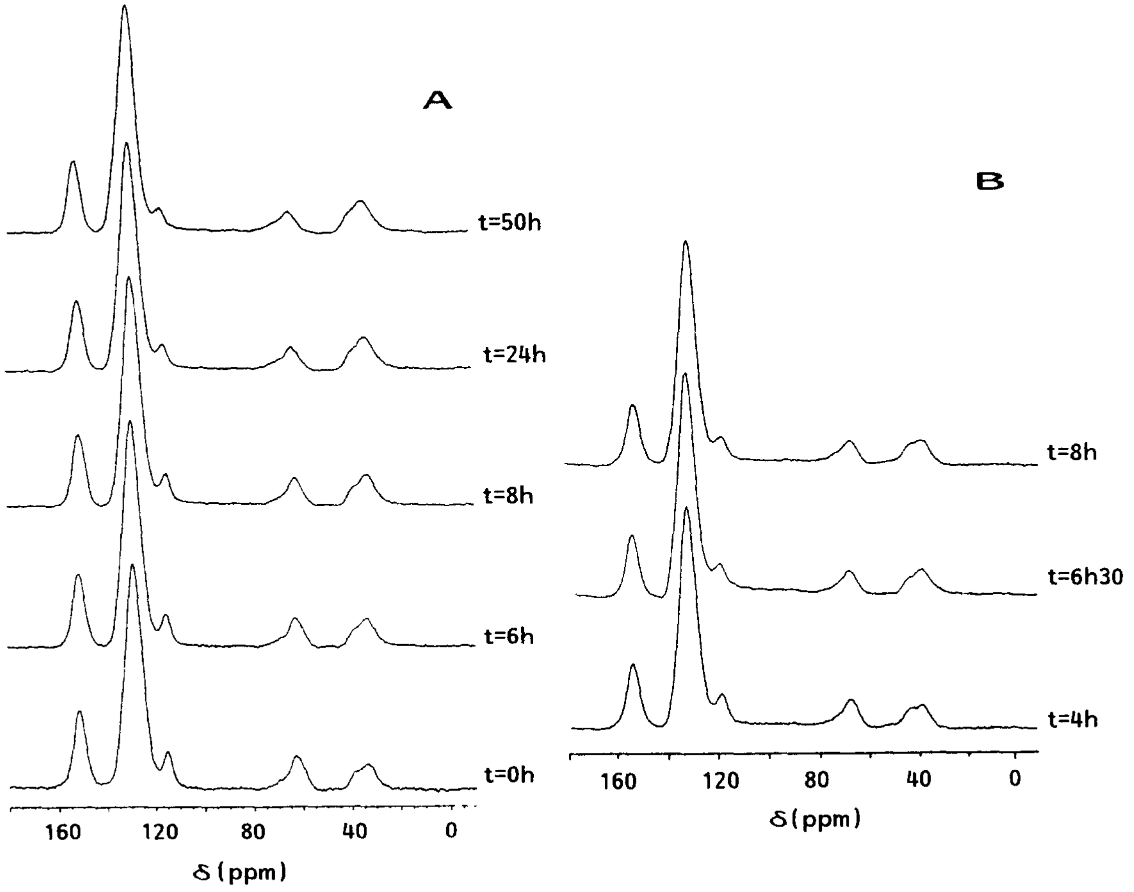

Figure 12 Kinetics followed by solid-state ^{13}C n.m.r., $T = 80°C$: (A) 2% NaOH and (B) 5% NaOH

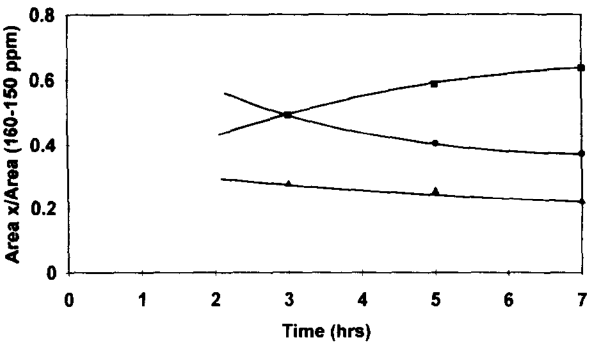

Figure 13 Changes in characteristic lines in solid-state ^{13}C n.m.r., 2% NaOH: ■, 45–30 ppm; ▲, 115 ppm; ●, 65 ppm

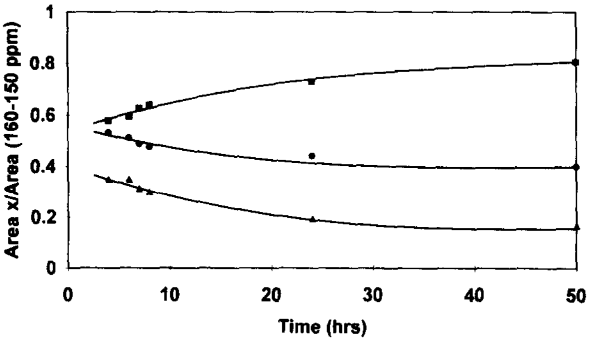

Figure 14 Changes in characteristic lines in solid-state ^{13}C n.m.r., 5% NaOH: ■, 45–30 ppm; ▲, 115 ppm; ●, 65 ppm

crosslinked with 2% catalyst for 50 h (*Figure 17*). By comparing this with the previous spectrum, it is seen that there was a small proportion of non-substituted aromatic carbons in *ortho* (115 ppm) and *para* (125 ppm) positions, as well as a low proportion of dimethylene ether bridges in the presence of catalyst. These observations show the very low reactivity of aromatic carbons in the absence of catalyst, in agreement with the *FT*i.r. results (*Figures 10* and *11*).

From a mechanistic and kinetic standpoint, these results reveal the role played by the catalyst in the reaction medium. It participates: (1) from the point of view of reaction mechanism, by making possible condensation reactions with non-substituted *ortho* and *para* carbons; and (2) from the kinetic point of view, by accelerating all condensation reaction kinetics (reactions between hydroxymethyl groups and reactions between hydroxymethyl groups and aromatic protons).

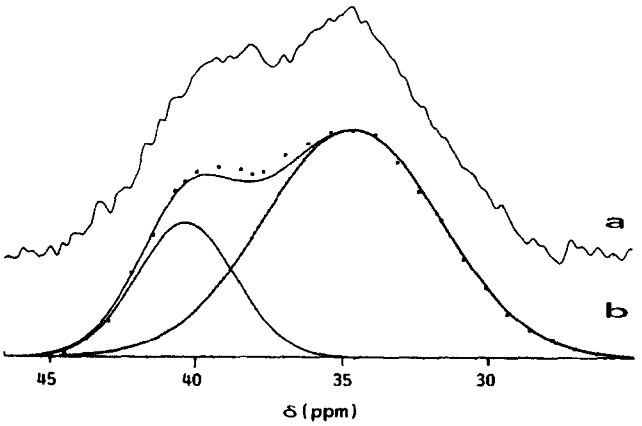

Figure 15 Deconvolution of the band at 45–30 ppm into basic lines: (a) experimental spectrum and (b) mathematical deconvolution

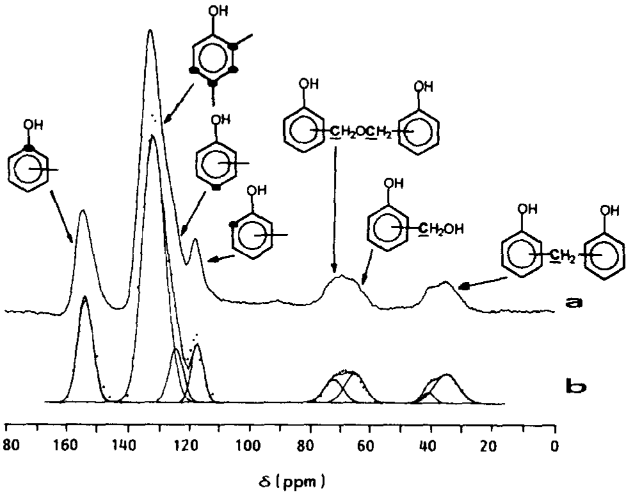

Figure 16 Deconvolution of the solid-state ^{13}C n.m.r. spectrum, $T = 80°C$, $t = 50 h$, 0% NaOH: (a) experimental spectrum and (b) mathematical deconvolution

These data obtained in the solid state confirm results obtained in solution: the condensation mechanism is predominant at basic pH.

APPLICATION TO THE STUDY OF INDUSTRIAL RESOLES

In order to apply these results, we investigated three industrial resoles prepared with different F/P ratios and catalyst concentrations. For optimal control of these parameters, they were characterized in solution. We also wanted to determine if the fingerprint of these resoles before heat treatment was important during their crosslinking.

Characterization of batches of industrial resoles in solution

The batches were analysed by h.p.l.c. and ^{13}C n.m.r. in

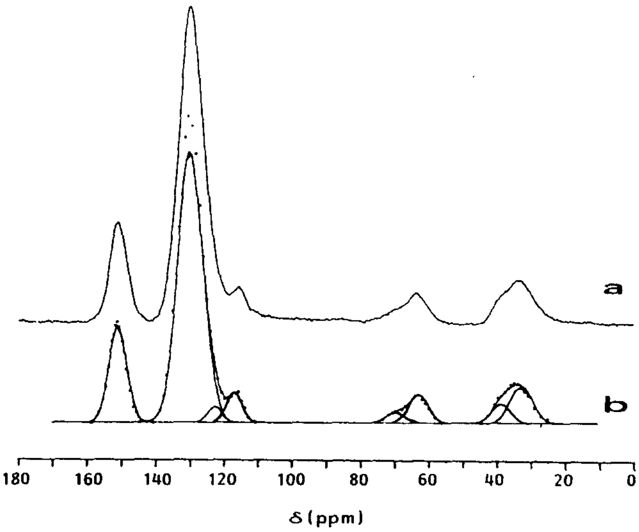

Figure 17 Deconvolution of the solid-state ^{13}C n.m.r. spectrum, $T = 80°C$, $t = 50 h$, 2% NaOH: (a) experimental spectrum and (b) mathematical deconvolution

solution. The principal compounds (monomers and several dimers) were identified by h.p.l.c. (*Figure 18*).

In ^{13}C n.m.r., the zone from 200 to 0 ppm (*Figure 19*) of resoles A, B and C confirmed the results obtained by h.p.l.c. Resole C was thus found to contain a number of lines between 100 and 80 ppm (hemiformal carbons), indicating that the F/P ratio was high. Similarly, non-substituted *ortho* and *para* aromatic carbons (at 118 and 124 ppm, respectively) are present in a lower proportion than in resoles A and B.

There is also a significant difference in the 160–150 ppm zone. The major peaks of resole A in this zone resonate between 160 and 155 ppm (region of relatively unsubstituted and little condensed phenol groups) while the major resonance lines in resole C are in the 155–150 ppm region, characteristic of condensed and substituted phenol groups.

All these data indicate that the degree of advancement of the three resoles is different, due to their different conditions of synthesis.

Study of resoles after heat treatment

Resoles A, B and C were subjected to a 6 h treatment at 120°C. After solidification, the samples were ground and analysed by ^{13}C n.m.r. CP/MAS. Comparison of the spectra obtained at the end of the heat cycle (*Figure 20*) shows that resole A has a high number of non-substituted *ortho* sites, few residual hydroxymethyl groups and a higher proportion of *ortho–para* links than *para–para*. Resole B has fewer free *ortho* sites than resole A, residual hydroxymethyl groups, methyl groups around 20 ppm arising from oxidation by oxygen in the air, and a higher proportion of *ortho–para* links than *para–para*. In resole C, the band of free *ortho* sites around 115 pm is very weak. The band at 90 ppm indicates the presence of polyoxymethylene chains due to a high initial F/P ratio. This was confirmed by the high proportion of hydroxymethyl and hemiformal groups around 70–50 ppm in solution.

The *FT*i.r. study of the resins after heat treatment confirms the above results. *Figure 21* shows the 1800–700 cm^{-1} spectral zone of each batch of crosslinked products studied. Wavelengths around 756 and 826 cm^{-1} are important in the case of resole A and agree with the presence of the resonance line at 115 ppm (non-substituted *ortho* sites). In addition, the system no longer contains hydroxymethyl groups (1010 cm^{-1}). In the case of resole B, the intensities of these bands are weak and characterize an incompletely crosslinked structure. In resole C, there is a band corresponding to deformations of C–O bonds, present in large numbers because of the presence of polyoxymethylene chains, masking the 1150–820 cm^{-1} region. The weak intensity of the band at 756 cm^{-1} confirms the substituted phenolic structure of the network.

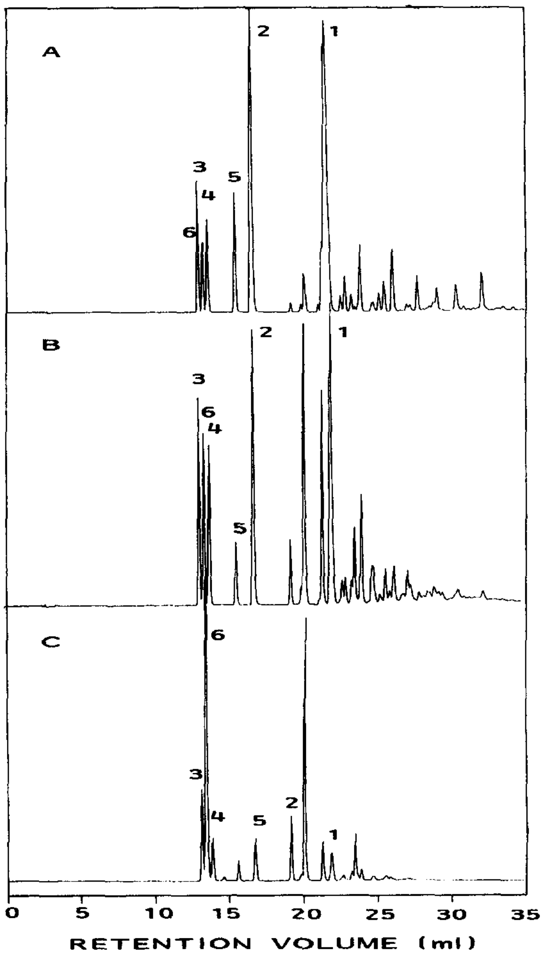

Figure 18 H.p.l.c. chromatograms of resoles A, B and C

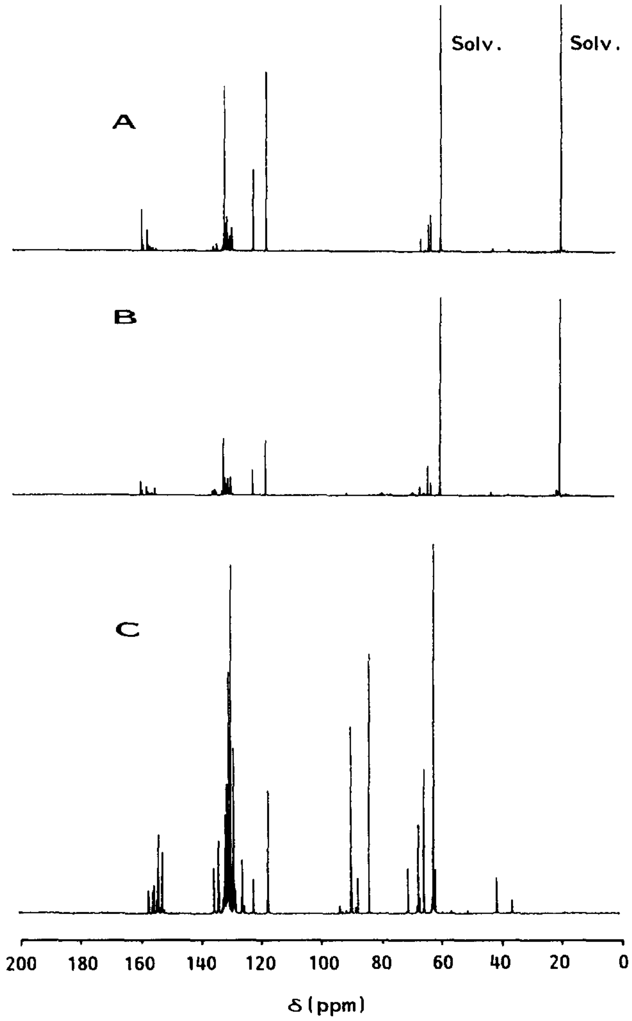

Figure 19 Liquid-state ^{13}C n.m.r. spectra of resoles A, B and C in the 200–0 ppm region. Solvents: monodeuterated ethanol (A and B) and D_2O (C)

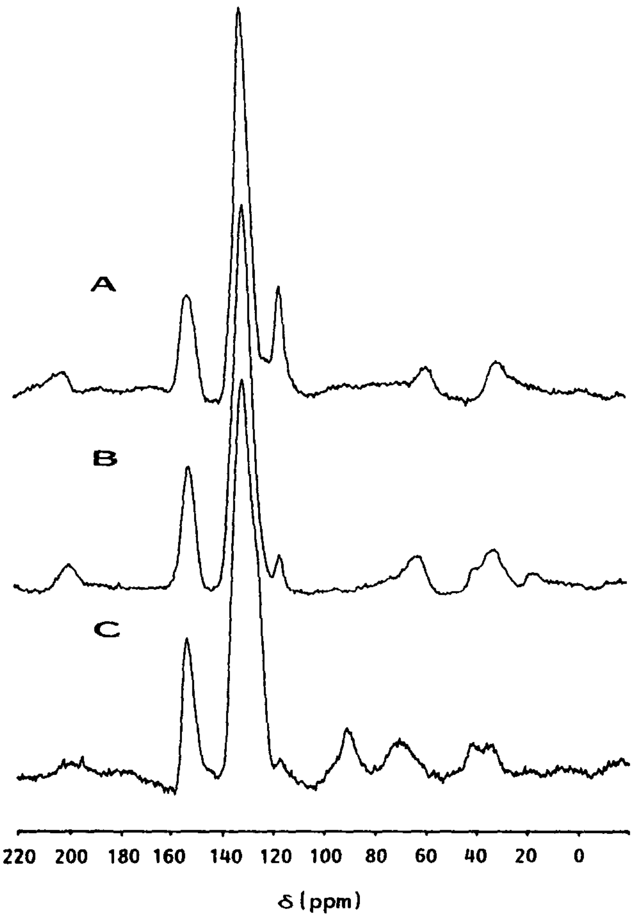

Figure 20 Solid-state ^{13}C n.m.r. spectra of resoles A, B and C at the end of heat treatment

The results obtained with ^{13}C n.m.r. CP/MAS and *FT*i.r. are in agreement and show to what point the chemical composition of a resole before crosslinking is important in the study of the crosslinked network.

CONCLUSIONS

The results obtained in this work are consistent with those of So and Rudin[6]. We have shown the influence of parameters of resole synthesis and their thermal treatment on the crosslinking of phenolic resins. Based on a solid-state study, we have found that increasing the crosslinking density [number of methylene bridges divided by the number of aromatic rings (CH_2/Ar)] depends on several determining factors, in particular:

1. the F/P ratio of the resole—ring substitution is favoured during resole synthesis at high F/P ratios, thereby causing the formation of methylene bridges during crosslinking;
2. the time of resole synthesis—we have shown that only condensation reactions participate during crosslinking. Thus it would be interesting to obtain a resole in which a maximum of formaldehyde has reacted, leading to considerable substitution of aromatic rings. A resole still containing considerable quantities of phenol and formaldehyde will form fewer methylene bridges than the same resole in a more advanced state of progression;
3. the chemical nature of the catalyst used in resole synthesis—the study in solution showed that the nature of the catalyst modifies the substitution of aromatic rings as well as the state of advancement of the resole. This result was confirmed by the solid-state study of crosslinked structures. It is also possible to increase the extent of crosslinking by modifying this parameter.
4. the catalyst concentration (pH during crosslinking)—increasing the pH in basic medium favours the formation of methylene bridges.

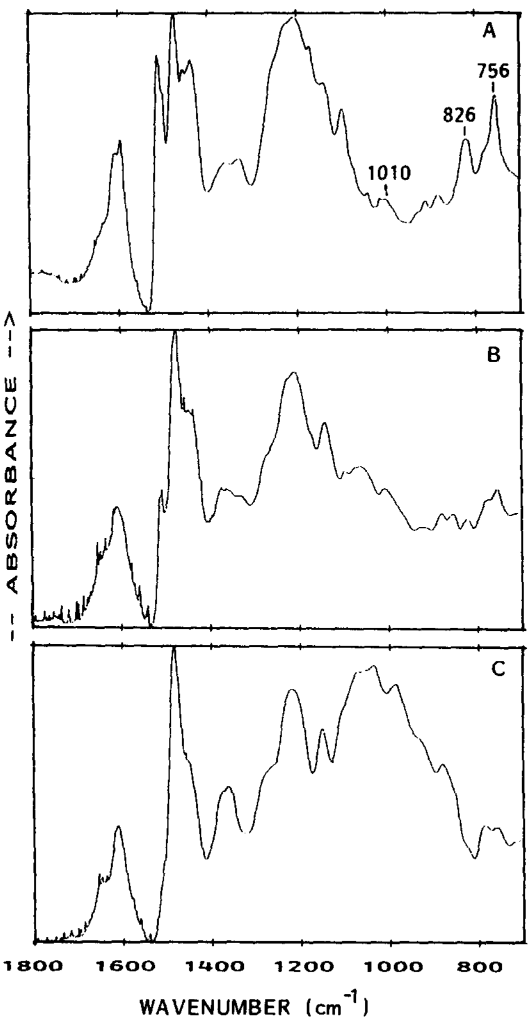

Figure 21 *FT*i.r. spectra of A, B and C after heat treatment in the 1800–700 cm^{-1} region

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