Quantitative ^{13}C n.m.r. characterization of aqueous formaldehyde resins:
1. Phenol–formaldehyde resins*

D. D. Werstler
GenCorp, Research Division, 2990 Gilchrist Road, Akron, Ohio 44305, USA
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Phenol–formaldehyde (PF) resins which had experienced a variety of reaction conditions and/or ageing conditions were quantitatively characterized by ^{13}C n.m.r. Under the specific conditions of this study, the phenol para position was favoured for reaction over the ortho position on a per site basis, particularly for condensation reactions. Increasing the reaction temperature from 23°C (14 days reaction) to 80°C (3 h reaction) did not alter the type of resin structure. Ageing PF resins resulted in extensive condensation and a drastic reduction in para-substituted methylol and hemiformal groups. This apparently contributes to a sharp reduction in the reactivity of these resins for reactions requiring methylol substituents on the ring.

(Keywords: ^{13}C n.m.r.; phenol–formaldehyde; condensation reactions; structural characterization)

INTRODUCTION

The reaction products of formaldehyde with phenol and also resorcinol have been useful polymers for many years. Improvements in these products have necessitated a more complete understanding of how these resins function. The ability to analyse the structure of these resins is very important because the resin structure is closely related to resin function. Characterization of these resins has been very difficult in the past owing to the complexity of these systems and to inherit limitations of the methods of analysis[1-9].

^{13}C n.m.r. has been the most successful analytical tool used to characterize phenol–formaldehyde (PF) resins, and to a much lesser extent resorcinol–formaldehyde (RF) resins[10-14]. These n.m.r. studies have been very informative but not totally comprehensive, especially in relation to RF spectral assignments and quantitative applications to both PF and RF resins. Some of the ^{13}C assignments are also not specific and were not proven rigorously.

This paper discusses a ^{13}C n.m.r. study of PF resins with particular emphasis on quantitative applications. Some PF assignments determined from this study are also discussed because they are new, different from, or more detailed than existing assignments, or were arrived at by different means to those discussed in the literature. A comprehensive ^{13}C n.m.r. study of RF resins which complements this study is discussed in an accompanying paper[15].

Up till now detailed ^{13}C n.m.r. characterization of formaldehyde resins has been applicable only to aqueous systems, but it does provide an extensive data base for solid-state n.m.r. studies. Although solid-state study is the ultimate goal for many resin systems[16-18], detailed solution data of formaldehyde resins is often invaluable in predicting or explaining how certain resins function.

EXPERIMENTAL

PF reactions were carried out using Mallinckrodt practical grade phenol in a formalin solution (35.5 wt% formaldehyde in water to which approximately 7% methanol had been added as a preservative). These resins were then diluted by $\approx 20\%$ with D_2O (Merck 99.7% purity) to obtain a deuterium lock. Various levels of NaOH were used for the base-catalysed reactions. 1% w/w ($[CH_3]_3SiCD_2CD_2CO_2Na$) was added as an internal standard in some of the resins.

The samples were run on a Varian FT-80 NMR Spectrometer using the 10 mm dual frequency insert set for ^{13}C. The operating parameters were: probe temperature = 36.5°C; sweep width = 4000 Hz; pulse width = 12 μs ($\sim 45°$ flip angle), pulse delay = 2.0 s, acquisition time = 2.047 s, and data points = 16 384.

Fast reacting samples were run for ≈ 30 min; slow reacting samples were run for 1.5–2.0 h when appropriate.

T_1 (spin-lattice relaxation) data and nuclear Overhauser enhancement (NOE) data were obtained to quantify the data. The pulse delay for T_1 data was 5 times longer than the longest T_1; the pulse delay for NOE data was 10 times longer than the longest T_1. An inversion recovery $180°–\tau–90°$ pulse sequence was used to obtain the T_1 data. The NOE data were obtained by comparing data from a typical decoupled n.m.r. spectrum and integral with that obtained from an NOE suppressed procedure (the decoupler was on only during the 90° pulse and acquisition time and off during the pulse delay).

A shift reagent $Eu(fod)_3$ [tris(1,1,2,2,3,3-heptafluroro-7,7 dimethyl-4,6-octanedione)europium (III)] was added to some of the resins to shift apart superimposed resonances in their spectra.

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RESULTS AND DISCUSSION

Formalin

It has been confirmed by de Breet *et al.* via ^{13}C n.m.r. chemical shift assignments that the structure of formaldehyde in formalin solution is not that of free formaldehyde, but rather of oligomers of oxymethylene and hemiformal (owing to the presence of methanol added as preservative)[12]. These oligomers then break down to free formaldehyde as the PF reaction proceeds. These assignments are shown in *Table 1* (peaks K and L for oxymethylene carbons and peaks E and P for hemiacetal carbons).

Phenol

The ^{13}C n.m.r. assignments for phenol carbons are also listed in *Table 1*. The reactive positions on the phenol ring are the 2, 4 and 6 positions. Reaction of formaldehyde with a phenol ring can result in the following structures where ϕ represents the phenol (hydroxyphenyl) ring.

$\phi\text{-CH}_2\text{OH}$ (Methylol) (1)

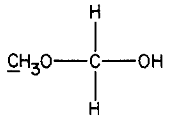
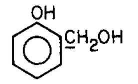
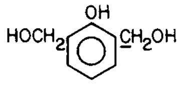
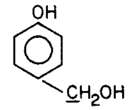
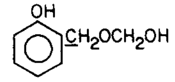
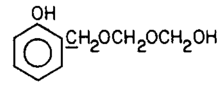
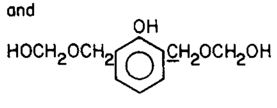
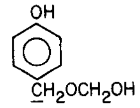
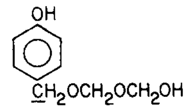
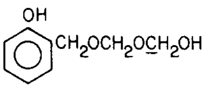
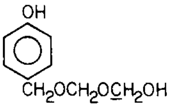
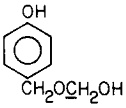
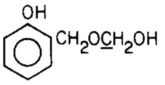
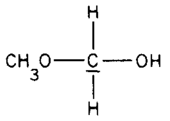
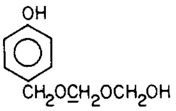
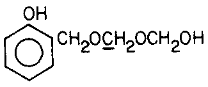
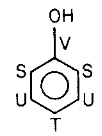
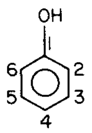
(a) (b) (c)
$\phi\text{-CH}_2\text{O(CH}_2\text{O)}_x\text{CH}_2\text{OH}$ (Hemiformal) (2)

$\phi\text{-CH}_2\text{-}\phi$ (3)
(Diphenyl methane methylene bridge; *p–p*, *o–p* or *o–o'*; these will be referred to as methylene bridges)

$\phi\text{-CH}_2\text{OCH}_2\text{-}\phi$ (Dimethylene ether bridge) (4)

The oxymethylene unit containing carbon (a) in structure (2) is stable. The other oxymethylene units, i.e. those containing carbons (b) and (c), are unstable. They

Table 1 ^{13}C n.m.r. assignments for phenol–formaldehyde resins

A	$\phi—\underline{C}H_2—\phi$	*o–o'* (ortho–ortho')	29.21
B	″	*o–p* (ortho–para)	34.93
C	″	*p–p'* (para–para')	39.67
D	$\underline{C}H_3OH$		50.70
E			56.29
F			61.4–61.5
F'			61.6–62.3
G			65.52
H			66.57
H'	 and 		67.10
I			70.57 (68.9)[a]
I'			71.16 (69.1)[a]
J	$\phi——\underline{C}H_2OCH_2——\phi$		70.77
K	$HO\underline{C}H_2OH$		83.73
L	$HOCH_2O\underline{C}H_2OH$		87.29
M	 		(87.3)[a]
N			89.27 (90.6)[a]
O			89.59
P			91.30
Q			92.21 (93.9)[a]
R			92.87
S T U V			115.5 121.0 128.8 157.6
W	 Phenolic carbons 2 to 6 on a reacted phenolic ring		
X	Phenolic carbon 1 on a reacted phenolic ring		

[a] Calculated value using the parameters in *Table 2*

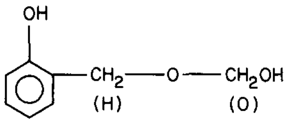
[b] Was not observed due to superimposition on peak L

can cleave from the structure and react with other phenol rings.

Figure 1 is the complex ^{13}C spectrum of a 1/3 mole ratio phenol/formaldehyde PF resin. This will be referred to as the PF (1/3) resin. The assignments of the reaction product carbons shown in *Figure 1* resulting from this study are detailed in *Table 1*. The means by which some of these assignments were determined are discussed below.

Hemiformal

The hemiformal resonances were assigned by comparing predicted (calculated) and observed chemical shift values of known structures. Study of known hemiformal structures was lacking in the literature, and in general the hemiformal assignments were vague[12]. Predicted values are based on *o*-hydroxybenzyl alcohol (OHBA), *p*-hydroxybenzyl alcohol (PHBA), and formaldehyde oligomers (with water) as reference compounds in conjunction with the shift parameters of Carmen[19] and Strothers[20] given in *Table 2*. For example, the predicted values for carbons (H) and (O) in structure **I**



I

were calculated as follows:

$$\delta(\mathrm{H}) = \mathrm{OHBA\ ref.} + \beta\,\mathrm{CH_2\ effect} + \gamma\ \mathrm{oxygen\ effect}$$
$$= 61.5 + 9.5 - 6.2 = 64.8\ \mathrm{ppm}$$

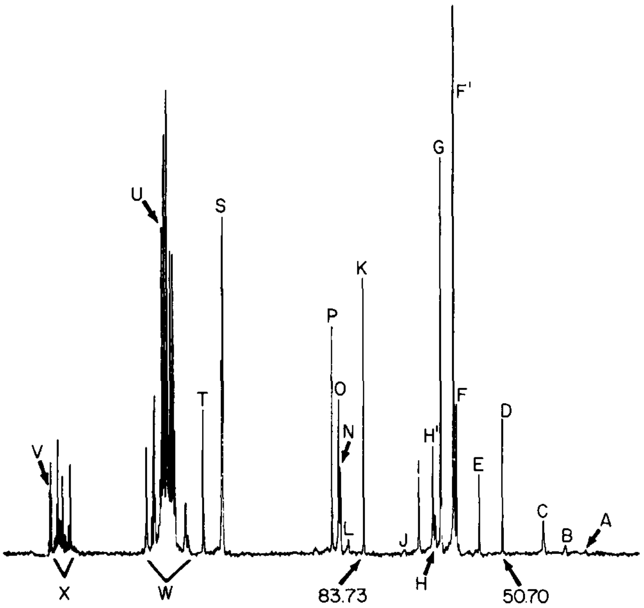


Figure 1 ^{13}C n.m.r. spectrum of a PF (1/3) resin

Table 2 Parameters for ^{13}C n.m.r. assignments in formalin (35.5% CH_2O in water, 7% CH_3OH added)

	Parameters				
	Chemical shift effect (ppm)				
Substituent	α	β	γ	δ	ε
–C	8.9	9.5	−2.3	+0.3	+0.1
–H	0.0	0.0	0.0	0.0	0.0
–O	49.0	10.1	−6.2	0.0	0.0
$–C_6H_5$	22.1	9.3	−2.6	0.3	0.0

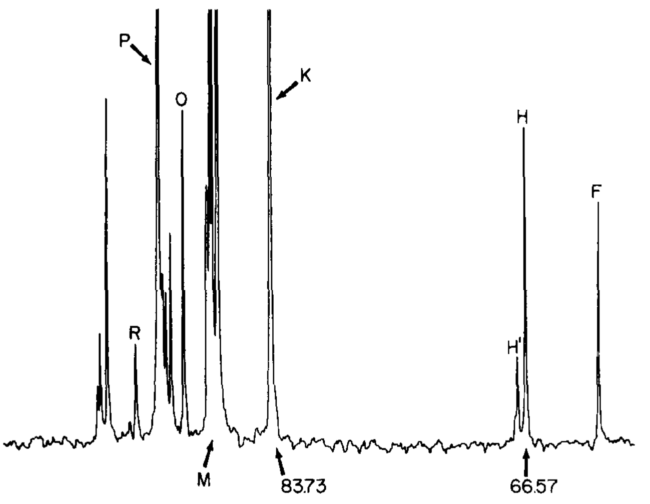


Figure 2 ^{13}C n.m.r. spectrum of 1/3 mole *o*-hydroxybenzyl alcohol/formaldehyde

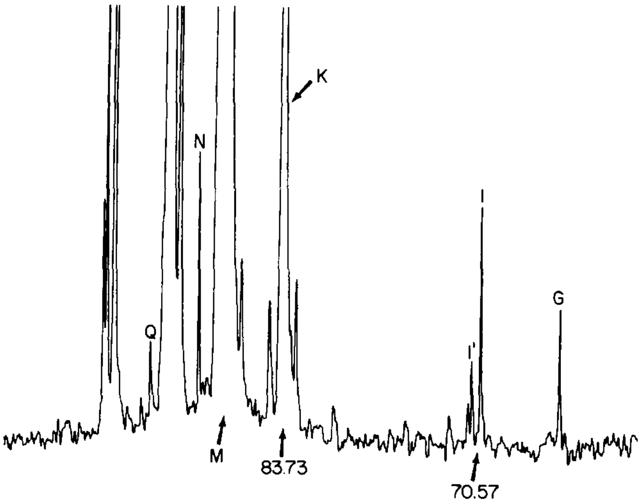
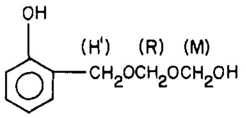


Figure 3 ^{13}C n.m.r. spectrum of 1/3 mole *p*-hydroxybenzyl alcohol/formaldehyde

Similarly,

$$\delta(\mathrm{O}) = \delta\,\mathrm{HOCH_2OH} + \beta\,\mathrm{CH_2\ effect} + \gamma\ \mathrm{phenyl\ effect}$$
$$= 83.7 + 9.5 - 2.6 = 90.6\ \mathrm{ppm}$$

These assignments are supported by the observation that the non-catalysed 1/1 addition of OHBA/formaldehyde at RT, expected to result in structure **I** above[6], produces new resonances at 66.6 and 89.6 ppm, in good agreement with the predicted values. If the ratio of OHBA/formaldehyde is changed to 1/3, new peaks occur at 67.1 and 92.9 ppm, *Figure 2*. These are assigned to carbons (H′) and (R), respectively, in structure **II**.



II

These agree well with calculated values of 65.1 (H′) and 93.0 ppm (R). The resonance for carbon (M), calculated to resonate at 87.6 ppm, superimposes on an oxymethylene resonance and cannot be isolated.

The assignments for para-substituted hemiformal structures were made in similar fashion. Observed and predicted values are compared in *Table 1* and examples are demonstrated in *Figure 3*.

Ortho-substituted methylol group

The methylol carbon in a group substituted in the position ortho to the phenol OH group (designated as *o*-methylol group) resonates at 61.5–62.2 ppm depending on its environment. The monosubstituted *o*-methylol carbon assignment (peak F, *Figure 1*) is apparent in that the *o*-hydroxybenzyl alcohol methylol carbon resonates at 61.54 ppm. As verification, ^{13}C and ^{1}H n.m.r. data were compared on an acetone-soluble, acid-catalysed novolac resin and an acetone-soluble, base-catalysed *p*-chlorophenol resin. The ^{1}H n.m.r. data indicated the presence of methylol substituted in the ortho position on the ring in the base-catalysed resin, and the absence of such methylol in the novolac resin. Resonances were observed at 61.44 and 62.12 ppm in the ^{13}C n.m.r. spectrum of the base-catalysed resin, while no resonances occur in this region of the novolac ^{13}C n.m.r. spectrum.

Further study has shown that the 62.12 peak is due to the equivalent carbons in dimethylol *p*-chlorophenol. Addition of dimethylol *p*-chlorophenol to the *p*-chlorophenol (above) resulted in a sharp increase in the 62.12 ppm peak while the 61.44 ppm peak remained relatively constant. Therefore, peak F′ at ≃62.2 ppm in a PF resin spectrum (*Figure 1*) is assigned to the methylol carbons disubstituted in the 2 and 6 positions on the phenol ring. Monitoring a base-catalysed PF (1/3) resin for 14 days indicated that only peak F was present during the first 12 h of the reaction. Peak F′ then appeared and increased throughout the remainder of the reaction while peak F decreased during the latter part of the reaction (≈ 13–14 days). These data are consistent with the above assignments.

Para-substituted methylol group

de Breet *et al.*[12] have assigned the peak at 65.52 ppm (G in *Figure 1*) to the α carbon in a hemiformal-type structure. It is more logical that peak G is due to a *p*-substituted methylol carbon in that the methylol carbon in *p*-hydroxybenzyl alcohol also resonates at 65.52 ppm. Further evidence that the literature assignment cannot be correct was provided by the examination of a base-catalysed PF (1/0.75) resin by ^{13}C n.m.r. Spectral data indicated that the formaldehyde had been entirely reacted. The presence of hemiformal is highly unlikely under these circumstances. A peak is present at 65.52 ppm, but there is no peak at or near 89.6 ppm (representing the β-hemiformal carbon) as there would be if the 65.52 peak were due to a hemiformal-type α carbon.

Bridge methylene groups

The assignments for these resonances are from the literature and are shown in *Figure 1* and *Table 1*. The author has found good evidence for supporting the ortho–ortho′ CH_2 bridge carbon resonance (29.21 ppm) but offers little evidence to support the para–para′ bridge in this sample is ortho–para, this datum supports the carbon assignments. A partially-condensed *p*-hydroxybenzyl alcohol sample was therefore examined by ^{13}C n.m.r. The bridge methylene groups resonated at 34.93 ppm. Since the predominant type of methylene bridge in this sample is ortho–para, this data supports the ortho–para assignment from the literature at 34.93 ppm. The 39.67 ppm peak must therefore arise from para–para′ methylene bridge carbons.

Dimethylene ether bridges

A para–octyl, base-catalysed phenolic curing resin was examined by ^{1}H n.m.r. and was found to have *o*-substituted methylol groups and dimethylene ether groups. A shift reagent, $Eu(fod)_3$, was used to shift these resonances apart. In the ^{13}C n.m.r. spectrum of this sample, peaks were observed at 61.46 ppm (*o*-substituted methylol) and at 70.77 ppm, which was assigned to the methylene carbon of dimethylene ether bridges. This supports the literature assignment[12].

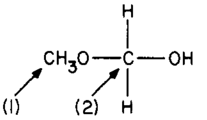
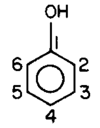
Nuclear Overhauser enhancement (NOE) factors

The nuclear Overhauser enhancement (NOE) factors of the relevant PF carbons determined from this study are shown in *Table 3*. These enhancement factors must be established to quantify intensity data. The accuracy of these values appears to be very good as evidenced by the following applications which demonstrate the usefulness of quantitative PF data.

Applications

A base-catalysed PF (1/3) resin reaction at RT was monitored by ^{13}C n.m.r. on a daily basis over a 14-day period. Primary interest was centered on obtaining information about the nature and kinetics of the reaction under these conditions, and the level of residual starting materials. A graph of the residual starting materials is shown in *Figure 4*. The phenol level had been reduced to

Table 3 NOE data on phenol–formaldehyde resins

Phenol–formaldehyde		
Structure		NOE
Formaldehyde (oxymethylene oligomer C's)		2.4
 $\underset{(1)}{CH_3}O-\underset{(2)}{\overset{H}{\underset{H}{C}}}-OH$	C_1 C_2	2.7 2.7
$o-\underline{C}H_2OH$		2.5
$p-\underline{C}H_2OH$		2.6
$o-\underset{\overset{\uparrow}{(1)}}{CH_2}O\underset{\overset{\uparrow}{(2)}}{CH_2}OH$	C_1 C_2	2.5 2.8
$p-\underset{\overset{\uparrow}{(1)}}{CH_2}O\underset{\overset{\uparrow}{(2)}}{CH_2}OH$	C_1 C_2	2.5 2.8
$\phi-\underline{C}H_2O\underline{C}H_2\phi$		2.7
$\underline{C}H_3OH$		2.0
$\phi-\underline{C}H_2\phi$	*o–p* *p–p* *o–o′*	2.4 2.4
	C_1 $C_{2,3,4,5,6}$	2.3 2.5

3.1 wt% after 7 days and to 1.6 wt% after 14 days. The formaldehyde had been reduced to 12.0 wt% after 7 days and to 9.4 wt% after 14 days.

Figure 5 indicates that the most dominant substituent is methylol in the ortho position, the level of which increases throughout the reaction. Methylol levels in the para position increase, but at a much slower rate than the ortho substituent. After an initial large increase, the hemiformal structures decrease as they break down for further reaction. The methylene bridges are *p–p'* and *o–p*. No *o–o'* methylene bridges or methylene ether bridges were observed.

The dominance of the para position in methylene bridge substitution is evident from *Figure 5*. After 14 days, 18% of the available para positions are involved in condensation of the phenol rings (methylene bridge substitution) while only 1.2% of the available ortho positions are involved. This is most likely due to steric hindrance at the ortho position.

Figure 6 demonstrates that although the total ortho substitution is larger than the total para substitution the para position is more reactive on a per site basis than the ortho position. After 14 days, 78% of the available para positions are reacted compared with only 60% of the available ortho positions. This is due to an obvious faster rate of reaction of para vs. ortho position during the first 2–3 days of reaction. After 3 days, 53% of the para positions are reacted, while only 33% of the ortho positions are reacted.

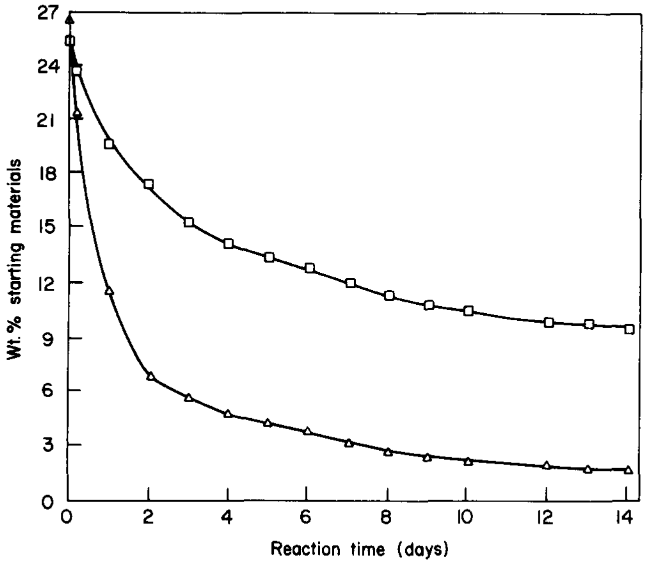


Figure 4 PF (1/3) resin reaction at room temperature. Residual starting materials (□) formaldehyde, (△) phenol

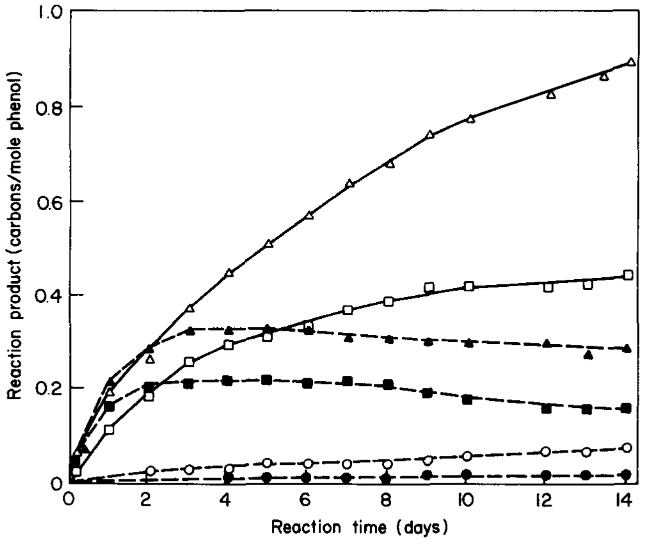


Figure 5 PF (1/3) resin reaction at room temperature. Reaction products (△) o-CH_2OH, (□) p-CH_2OH, (▲) o-$CH_2O(CH_2O)_xH$, (■) p-$CH_2O(CH_2)_xH$, (○) p-p' ϕ–CH_2–ϕ, (●) o-p ϕ–CH_2–ϕ

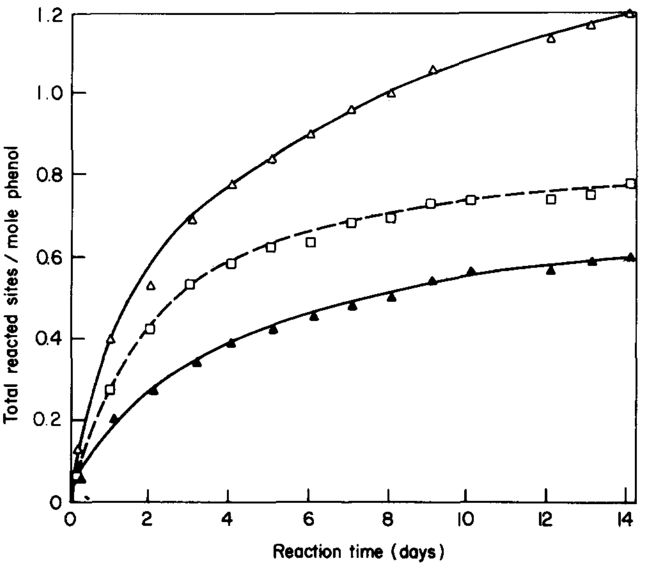


Figure 6 PF (1/3) resin reaction at room temperature. Reacted sites (△) ortho (total), (□) para, (▲) ortho (per site)

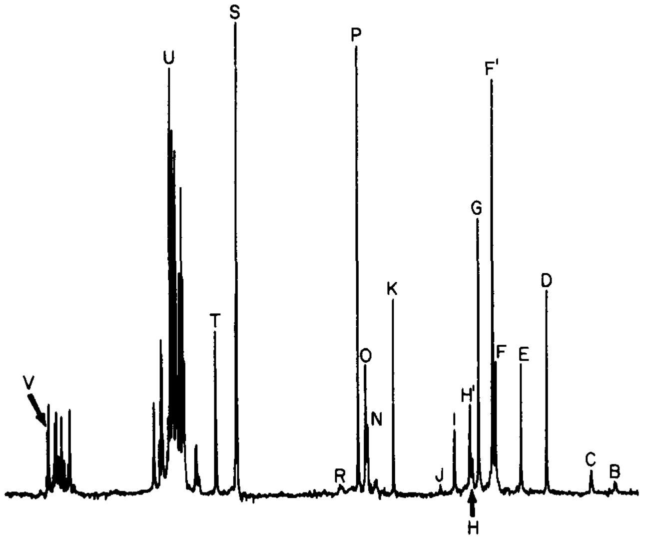


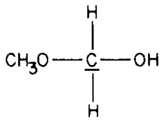
Figure 7 ^{13}C n.m.r. spectrum of a fresh PF (1/3) resin

The data in *Figures 4–6* were normalized to three total formaldehyde-type carbons per mole phenol for ease of comparison. The actual values ranged from 2.87–3.09 with an average of 3.03. This suggests that the quantitative data using the NOE factors from this study are accurate.

The question arose as to the effect of reaction conditions on the resin structure; specifically, can one alter the branched type of condensation network by altering reaction conditions? A PF (1/3) resin was reacted at 80°C for 1, 2 and 3 h. The values in *Table 4* represent the observed amounts of formaldehyde-type carbons, either reacted or unreacted, per mole of phenol. These values were also normalized to 3.00. The observed totals were 2.95, 3.08 and 3.07, in good agreement with the expected values.

The data in *Table 4* indicate the following: approximately 2/3 of the formaldehyde was consumed

Table 4 N.m.r. data on resin (1/3) reacted for varying time intervals

	Structure	Sample		
		130–1[a]	130–2[b]	130–3[c]
1.	Formaldehyde (total)	1.06	0.93	0.89
	A. $HOCH_2OH$	0.17	0.20	0.16
	B.  $CH_3O\underline{C}H_2OH$	0.35	0.31	0.29
	C. Ortho- and para-substituted $CH_2O\underline{C}H_2OH$	0.35	0.29	0.27
	D. Other: dimer, trimer, etc. of A and B	0.19	0.13	0.17
2.	Ether	0.03	0.02	0.02
3.	o-Substituted CH_2OH	1.01	1.18	1.16
4.	p-Substituted CH_2OH	0.39	0.33	0.26
5.	ϕ—CH_2—ϕ			
	A. para–para′	0.08	0.13	0.21
	B. ortho–para	0.05	0.11	0.18
	C. ortho–ortho′	–	–	–
6.	o-Substituted $\underline{C}H_2OCH_2OH$	0.29	0.24	0.23
	p-Substituted $\underline{C}H_2OCH_2OH$	0.09	0.06	0.05
	Total Carbons	3.00	3.00	3.00

[a] Reacted for 1 h
[b] Reacted for 2 h
[c] Reacted for 3 h

Table 5 Involvement in condensation

Temperature	Reaction time	% of available positions involved in condensation		
		Ortho	Para	Total
80°C	1 h	2.5	21.0	8.7
80°C	2 h	5.5	37.0	16.0
80°C	3 h	9.0	60.0	26.0
Room temperature	22 days	1.7	20.6	8.0
Room temperature	28 days	1.9	23.3	8.7

during the first hour. During the second and third hours, relatively little reaction between phenol and formaldehyde occurred. The major reaction during this time was condensation of the phenol rings. This is evidenced by the significant increase in ϕ-CH_2-ϕ as the reaction proceeded. The data also indicate that the para position was definitely more involved in the condensation reactions than the ortho positions by a factor of over 3.

The data in *Table 5* compare the level of methylene bridge substitution in this resin with that in the resin made at room temperature. It shows that for a given level of para reaction (≈21%) there is only slightly more involvement in the 80°C resin (2.5% vs. 1.7%). The data also indicate that the total condensation in the 1 h resin reacted at 80°C is the same as that in a 28 day resin reacted at room temperature.

Certain PF resins become ineffective for specific reactions requiring methylol, and/or dimethylene ether bridge groups on the phenol ring after prolonged storage at ⩾30°C. *Figures 7* and *8* and *Table 6* compare a typical 'fresh' PF (1/3) resin which has been aged for 60 days at 33°C losing its effectiveness in the process. Although the ageing has resulted in further phenol–formaldehyde reaction, the major reaction mechanism is condensation, primarily at the para position. The extent of condensation is such that although 0.83 mole of unreacted formaldehyde remains, 91% of the reactive phenol positions have reacted including 97% of the para positions. This is clearly shown in *Figure 8* by peaks S and T which represent unreacted ortho and para positions, respectively. It is possible that the bulkiness of the condensed PF molecules hinders further reaction and is therefore a contributing factor to the ineffectiveness of the resin.

Table 6 also indicates that the level of potentially reactive substituted species (methylol + hemiformal) has declined slightly from 1.74 to 1.65 carbons/mole phenol as a result of ageing. This amount of reduction should have only a modest influence on the reactivity of the resin. The location of the reactive species on the ring has changed considerably, however. Methylol and hemiformal groups substituted in the ortho position (F, F′, H and H′ in *Figures 7* and *8*) have increased by 0.35 carbon/mole

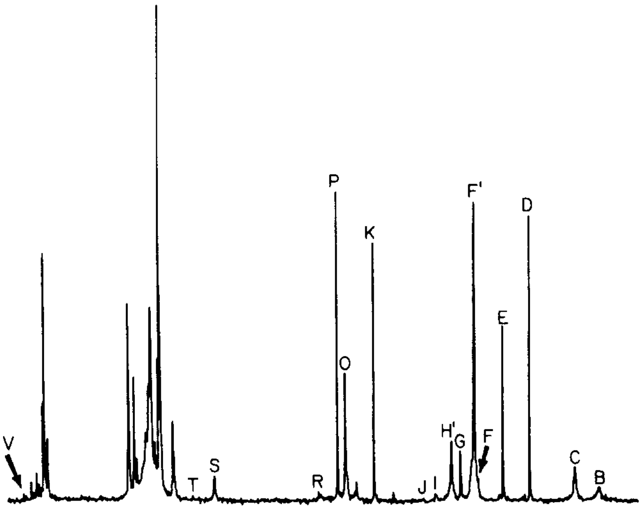


Figure 8 ^{13}C n.m.r. spectrum of a PF (1/3) resin aged for 60 days at 33°C

Table 6 ^{13}C n.m.r. structural data on fresh and aged PF (1/3) resin

		Fresh	Aged	Difference
1	$CH_3O\underline{C}$—	0.26	0.26	–
2	$HOCH_2OH$	0.21	0.23	+0.02
3	ϕ—$CH_2O(CH_2O)_xH$	0.43	0.29	−0.14
4	Dimer, trimer, etc. of 1 and 2	0.25	0.05	−0.20
	Total	1.15	0.83	−0.32
	p—$\underline{C}H_2O(CH_2O)_xH$	0.16	0.04	−0.12
	o—$\underline{C}H_2O(CH_2O)_xH$	0.28	0.28	–
	p—CH_2OH	0.43	0.11	−0.32
	o—CH_2OH	0.87	1.22	+0.35
	Total	1.74	1.65	−0.09
	p-$p'\phi$—CH_2—ϕ	0.07	0.29	+0.22
	o-p ϕ—CH_2—ϕ	0.02	0.22	+0.20
	o-$o'\phi$—CH_2—ϕ	–	0.02	+0.02
	Total	0.09	0.53	+0.44
	ϕ—CH_2OCH_2—ϕ	0.01	0.01	–
	Phenol (wt%)	1.5	0.1	−1.4
	Total % reacted ortho sites	58.5	88.0	+29.5
	Total % reacted para sites	77.0	97.0	+20.0
	Total % reacted sites	64.0	91.0	+27.0

phenol, while the sum of these groups substituted in the para position (G and I in *Figures 7* and *8*) has decreased by 0.44 carbon/mole phenol (i.e. reduced by a factor of 4). This redistribution of potentially reactive species may also contribute to the ineffectiveness of the resin since there is very little reactive species remaining in the more reactive para position and steric hindrance would discourage further reaction at the ortho position.

It should be noted that although rhe total percentage of reacted ortho sites increased relative to the total percentage of reacted para sites during this ageing, this does not reflect preferential reactivity at the ortho position. This is rather due to the lack of available unreacted para positions at this advanced stage of the reaction. The considerable amount of reaction that did take place in the para position largely involved changes in previously-reacted para positions (from methylol and hemiformal to methylene bridges). Reactivity in the para position, in fact, involved more positions than reactivity in the ortho position.

SUMMARY AND CONCLUSIONS

Some ^{13}C n.m.r. chemical shift assignments for PF reaction products have been made to supplement and/or verify the assignments in the literature. NOE factors have been determined from this study to allow quantification of the data. This capability allows one to monitor studies of PF reactions on a quantitative basis. It also allows the quantitative characterization of experimental PF resins, including determination of residual starting materials.

Under the specific conditions of the PF reactions in this study, the phenol para position was favoured for reaction over the ortho position on a per site but not collective basis. The para position was the markedly favoured position for condensation reactions. Increasing the reaction temperature to 80°C, and decreasing the reaction time to 1, 2 and 3 h (relative to the RT study) did not effectively alter the resin structure.

Ageing PF resins (33°C for 60 days) resulted in extensive condensation and a drastic reduction in para-substituted methylol and hemiformal groups. This apparently contributed to a sharp reduction in the reactivity of these resins.

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