Quantitative ^{13}C n.m.r. characterization of aqueous formaldehyde resins: 2. Resorcinol–formaldehyde resins*

D. D. Werstler

GenCorp, Research Division, 2990 Gilchrist Road, Akron, Ohio 44305, USA

(Received 5 May 1985)

^{13}C n.m.r. chemical shift assignments of resorcinol–formaldehyde (RF) reaction products have been made to fill many of the voids in the literature, particularly for base-catalysed RF resins and the aromatic carbons in acid-catalysed RF resins. Nuclear Overhauser enhancement (NOE) factors have been determined for relevant carbons. Quantitative results using these factors appear to be very accurate. Applications of these assignments and quantitative data to the structural characterization of commercial and experimental RF resins are discussed. The results of this study allow more accurate detailed studies of the nature of various RF reactions and provide an extensive data base for future solid-state n.m.r. studies.

(Keywords: ^{13}C nuclear magnetic resonance; resorcinol–formaldehyde; condensation reactions; structural characterization)

INTRODUCTION

The importance of formaldehyde resins and the necessity to characterize their structures are discussed in an accompanying paper[1]. A survey of the literature indicates that many relevant resorcinol–formaldehyde (RF) carbon assignments have not been made. ^{13}C n.m.r. assignments have appeared in the literature for various methylene bridge carbons in acid-catalysed RF resins[2,3]; however, very little data has appeared on specific ring carbon assignments. Also, little data has been presented for base-catalysed RF resins. Most hemiformal-related and methylol-related ^{13}C n.m.r. assignments have not been made or are vague and lacking in evidence[4]. These assignments have been made as a result of this study.

Nuclear Overhauser enhancement (NOE) data have been obtained to quantify the data. Applications demonstrating how these data are useful will also be discussed.

EXPERIMENTAL

Fisher's certified grade resorcinol was used in the RF reactions. Other experimental conditions including sample preparation and analysis are the same as those discussed in the previous paper[1] with one exception. Run times on the Varian FT-80 NMR Spectrometer were shorter, i.e. 30–60 min, for the monitored, base-catalysed RF reactions relative to the slower reacting PF reactions.

RESULTS AND DISCUSSION

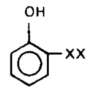
Resorcinol

The ^{13}C n.m.r. assignments for resorcinol carbons are listed in *Table 1*. The three reactive positions on the resorcinol ring are the 2, 4, and 6 positions. Data from this study support literature data showing that there is reaction in the 2 position[2,3]. The reaction of formaldehyde with resorcinol under basic conditions can result in the following substituents on the ring: $-CH_2OH$, $-(CH_2O)_xOH$, $-CH_2-\phi$, or $-CH_2OCH_2-\phi$. For brevity of terminology, resorcinol substituted in the 4 position, e.g. with CH_2OH, will be referred to as $4(-CH_2OH)$ in this paper. ^{13}C n.m.r. assignments of substituted resorcinol rings determined from this study are shown in *Figure 1* and *Table 1*. They were assigned in the following manner.

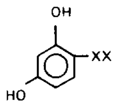
4-Substituted methylol and hemiformal

Figure 2 compares the aliphatic carbon regions in the ^{13}C n.m.r. spectra of a 1/3 mole ratio P/F resin [hereafter designated PF (1/3) resin] and an RF (1/1) resin, both base-catalysed. The data indicate that the peaks due to methylol and hemiformal substitution in the 2 position on a phenol ring [peaks F, F′, H, H′, N, and O in (A)] have almost identical chemical shift counterparts due to methylol and hemiformal substitution in the 4 position on a resorcinol ring [peaks F, F′, H, H′, K, and K′, respectively, in (B)]. The chemical shifts of the corresponding peaks agree within 0.1 ppm. The assignments in (B) are supported by the following data.

Structures I and II differ only in that the substituent XX is on a carbon para to a carbon substituted with a hydroxyl group,



I



II

where XX = either $-CH_2OH$ or $-CH_2O(CH_2O)_x$.

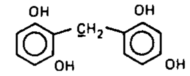
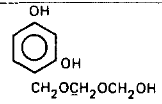
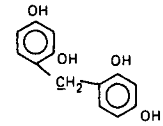
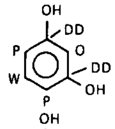
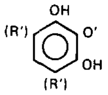
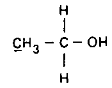
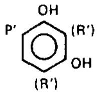
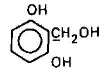
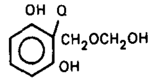
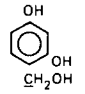
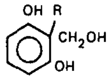
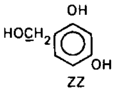
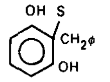
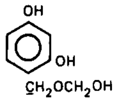
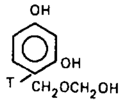
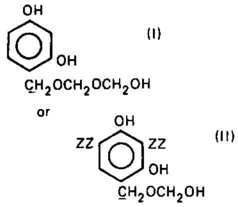
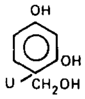
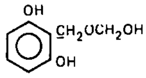
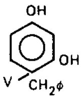
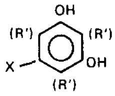
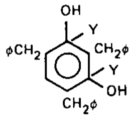
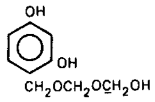
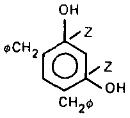
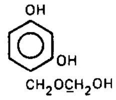
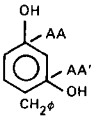
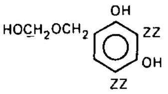
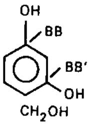
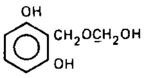
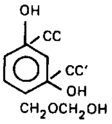
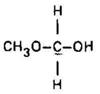
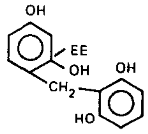
A study of ^{13}C n.m.r. spectra of comparably-substituted benzene, phenol, and resorcinol rings indicates that the effect of OH para substitution on the methylol or hemiformal carbon chemical shifts should be $\leqslant 1.0$ ppm.

---

* This paper was presented in part at the Akron Polymer Conference in May 1981

0032-3861/86/050757-08$03.00

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

Structure		Chemical shift[a]	Structure		Chemical shift[a]
A		24.29	N		92.51
B		29.93	O P W DD		104.25 109.18 132.04 158.27
C	$\underline{C}H_3OH$	50.70	O′		104.4–104.5
D	 $\underline{C}H_3-\overset{H}{\underset{H}{C}}-OH$	56.10	P′		108.8–108.9
E		57.8–58.8	Q		112.00
F		61.49	R		114.92
F′		62.36	S		116.16–116.81
H		66.50	T		117.05
H′		67.11	U		120.00
G		63.50	V		121.29
I	$HO\underline{C}H_2OH$	83.73	X		131.26–133.78
J	$HO\underline{C}H_2O\underline{C}H_2OH$	87.29	Y		151.52
J′		≈87.3 (calculated)	Z		153.43
K		89.27	AA and AA′		AA = 155.35 AA′ = 156.34
K′		89.65	BB and BB′		BB = 156.92 BB′ = 158.07
L		≈89.90	CC and CC′		CC = 157.26 CC′ = 158.47
M	 $CH_3O-\overset{H}{\underset{H}{\underline{C}}}-OH$	91.30	EE		154.23

[a] In ppm downfield relative to [$(CH_3)_3SiCD_2CD_2CO_2Na$], an internal standard

ZZ = Either $-CH_2OH$, $-CH_2O(CH_2O)_xH$ or $-CH_2\phi$

R′ = Reacted in any or all of these positions

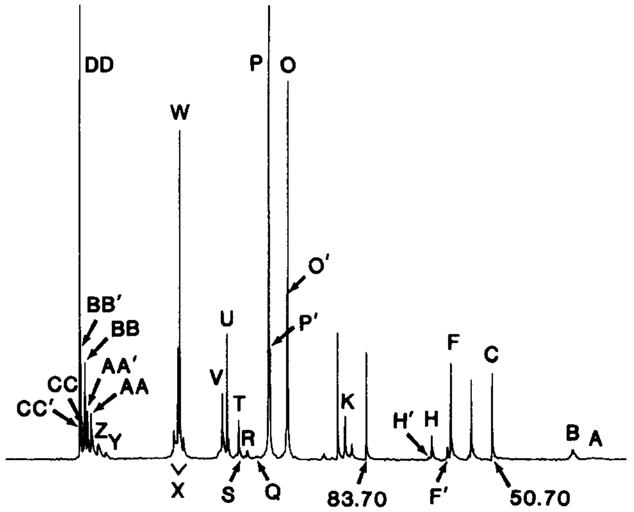


Figure 1 ^{13}C n.m.r. spectrum of a base-catalysed RF (1/1) resin

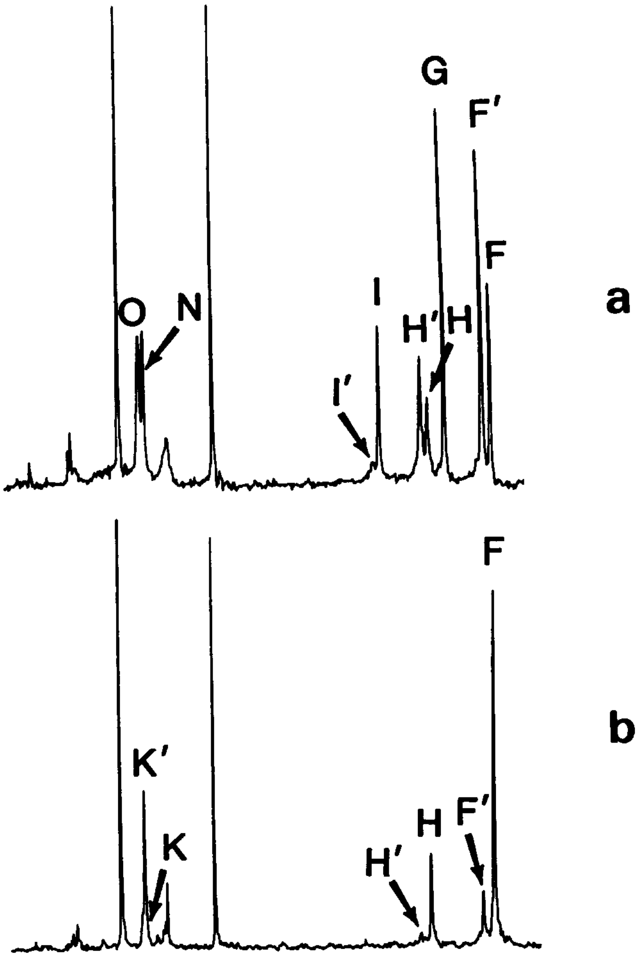
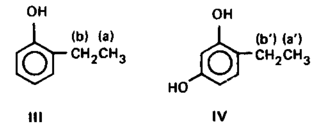


Figure 2 ^{13}C n.m.r. spectrum of (a) PF (1/3) resin and (b) RF (1/1) resin-aliphatic region

For example, *Table 2* compares the chemical shifts of the ethyl carbons in 2-ethyl phenol (**III**) and 4-ethyl resorcinol (**IV**). The chemical shift differences are ±0.7 ppm.



III IV

It is therefore concluded that the para OH effect on the methylol and hemiformal chemical shifts in RF resins is ≤ 0.1 ppm. (This is seen in *Figure 2*.) Peaks G, I, and I' in spectrum (A), *Figure 2*, represent species substituted in the 4 position on the phenolic ring. There are no counterparts for these on the resorcinol ring, and therefore these peaks are absent in spectrum (B).

The hemiformal assignments were supported by the observation that their intensities increased immediately as more formaldehyde was added at RT (which should form more hemiformal)[5]. Excess formaldehyde addition resulted in a new peak at 92.51 ppm (peak N in *Table 1*) which has its counterpart in PF resins also and arises from the structure

$$\phi\text{-}\overset{(H')}{CH_2}O\overset{(N)}{CH_2}O\overset{(J')}{CH_2}OH$$

substituted in the 4 position.

The resonances for H' and J' superimpose on existing resonances, *Table 1*.

2-Substituted methylol and hemiformal

A methylol or hemiformal group substituted in the 2 position has no counterpart in PF resins. Their ^{13}C n.m.r. assignments were made as follows:

$$\delta \text{ benzyl alcohol } \underline{C}H_2 = 64.5 \text{ ppm}$$

$$\delta \text{ } o\text{-hydroxybenzyl alcohol } \underline{C}H_2 = 61.5 \text{ ppm}$$

$$\text{Therefore ortho OH effect} = -3.0 \text{ ppm}$$

$$\begin{aligned}\text{Therefore } \delta\ 2(\text{-}\underline{C}H_2OH) &= \delta \text{ benzyl alcohol } \underline{C}H_2 \\ &\quad + 2 \text{ ortho OH effects} \\ &= 64.5 + 2(-3.0) = 58.5 \text{ ppm}\end{aligned}$$

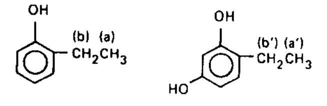
Resonances in the 57.8–58.8 ppm region assigned to methylol carbons substituted in the 2 position have been observed at minor levels in base-catalysed RF (1/1) resins. Differences in the chemical shifts are most likely due to small meta effects due to substitution of a group(s) in the 4 or 4,6 position(s) on the ring.

The resonance for the α carbon of a hemiformal group substituted in the 2 position has been observed at approximately 63.5 ppm. This assignment is based on the 5.0 ppm δ difference between methylol and hemiformal α carbons substituted in the 4 position, *Table 1*.

$$\begin{aligned}\text{Therefore } \delta\ 2(\text{-}CH_2OCH_2OH) &= \delta\ 2(\text{-}CH_2OH) + 5.0 \text{ ppm} \\ &= (57.8\text{–}58.8) + 5.0 \\ &= (62.8\text{–}63.3) \text{ ppm}\end{aligned}$$

The β carbon resonance is presumably superimposed on other β hemiformal resonances in the 89.0–90.0 ppm region.

Table 2 Comparison of the chemical shifts (δ) of the ethyl carbons in 2-ethyl phenol and 4-ethyl resorcinol



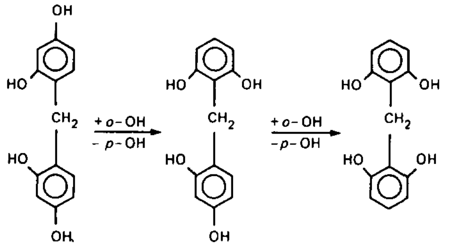
δ (ppm)	δ (ppm)	Diff. (ppm)
(a') 13.9	(a) 14.6	−0.7
(b') 22.9	(b) 22.2	0.7

Methylene bridges (4–4′; 2–4)

A non-catalysed RF (1/1) resin reacted at RT was monitored twice daily for two weeks by ^{13}C n.m.r. In the aliphatic region a peak first appeared at 29.93 ppm followed by a peak at 24.29 ppm. They were assigned as follows.

Since the *o–o′* methylene bridge carbon in a PF resin resonates at 29.21 ppm, the peak at 29.93 ppm in the RF spectrum is assigned to the 4–4′ methylene bridge carbon in agreement with the literature[2]. These bridge carbons are similar in that each is influenced by two ortho OH effects. The 0.72 δ difference presumably results from the fact that the RF 4–4′ methylene bridge carbon (in structure V) is also influenced by para OH effects. The sum of these effects should be modest as shown in *Table 2*.

An *o–p* methylene bridge carbon in a PF resin resonates at 34.91 ppm, 5.70 ppm downfield from the PF *o–o′* methylene bridge resonance[1]. This −5.70 ppm chemical shift difference results from a gain of one ortho OH effect and the loss of one para OH effect in going from the *o–p* to the *o–o′* structure. Consequently, a 2–4 methylene bridge RF carbon (**VI**) would be expected to resonate at $29.93 + (-5.70) = 24.23$ ppm and a 2–2′ methylene bridge carbon (**VII**) at $29.93 + 2(-5.70) = 18.53$ ppm. As a result, the observed resonance at 24.29 ppm is assigned to the 2–4 methylene bridge carbon. A peak at or near 18.5 ppm arising from a 2–2′ bridge carbon was not observed during this study.



4-4′ V   2-4 VI   2-2′ VII

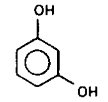
Ring carbons

An enormous amount of information can be obtained from the study of the ring carbon resonances due to the extreme sensitivity of the ring carbons to substitution on the ring. Substitution in any position on the ring influences the chemical shift of each carbon on the ring, with these effects decreasing in the order: $\alpha >$ (ortho or para) $\gg$ meta. The extent of the ortho or para effect depends on the substituent and reaction conditions such as pH. Emphasis in this study was placed on the chemical shifts of the substituted carbon (α effect) and of the C_1 and C_3 carbons which are ortho or para to any substitution on the ring, and therefore yield considerable information about the substitution patterns.

Shift parameters available from the literature for the effects of substitution on a benzene ring[6] are not precise enough for substituted resorcinol rings, so new parameters were established from this study. These parameters, *Table 3*, were developed by monitoring over 40 different reactions as a function of R/F ratio and reaction time.

The methylol and hemiformal parameters were developed from the study of base-catalysed low-conversion resins where monosubstitution predominated. The relative amounts of substituted methylol and hemiformal groups were manipulated as desired by varying the R/F ratio. The ring carbons influenced by these reactions were easily distinguished by monitoring the relative intensities of the newly-formed peaks. Once the parameters were established, the chemical shifts for more complex substitutions were then calculated and matched with observed peaks as the reactions proceeded.

Table 3 Parameters for calculating chemical shifts of substituted resorcinol rings



Substituent	C_α	Chemical shift effect[a] C_{ortho}[d]	C_{para}[d]	C_{meta}[d]
$-CH_2OH$	10.82[b] 10.68[c]	−0.20	−1.35	±0.1
$-CH_2\phi$	12.11[b] 12.30[c]	−1.93	−2.92	±0.1
$-CH_2OCH_2OH$	7.87[b] 7.98[c]	+0.20	−1.01	±0.1

[a] In ppm, (+) indicates downfield (to the left) shift; (−) indicates upfield shift

[b] Substituted in the 4 position

[c] Substituted in the 2 position

[d] Applies to substitution in the 2, 4 or 6 positions

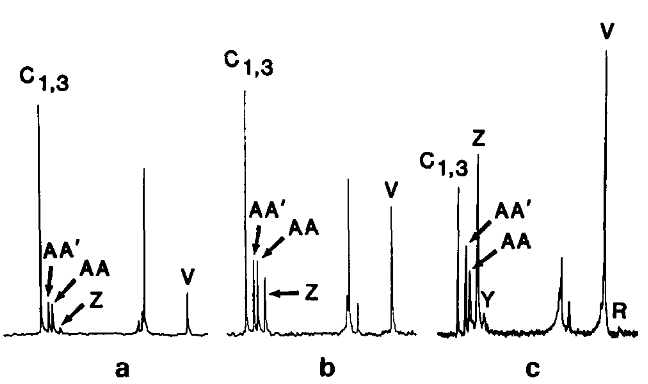


Figure 3 ^{13}C n.m.r. spectrum of the aromatic carbon region of an RF (1/1) resin reacted at room temperature with no catalyst: (a) 12 h, (b) 36 h, and (c) 7 days

The methylene bridge parameters were developed in a similar manner by following non-catalysed R/F reactions at room temperature where a pH$\simeq$4 resulted in methylene bridge substitution only.

Chemical shifts of carbons on rings with more than one type of substituent, e.g. a methylol group and a methylene bridge group, were determined from the latter stages of the base-catalysed RF reactions.

Ring carbons (methylene bridge substitution)

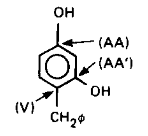
The progression of a typical non-catalysed RF reaction, RF (1/1) resin reacted at RT, is shown in *Figure 3* after 12 h, 36 h, and 7 days reaction. Aliphatic data (not shown) indicate substitution in the 4 position only in *Figure 3a*. The major changes in *Figure 3a* are due to $-CH_2\phi$ monosubstitution, structure **VIII**, resulting in peaks V, AA, and AA′. Peak V arises from the α effect of this substitution based on the broad parameters from the literature[6]. C_1 and C_3 are shifted and split into peaks of equal intensity (AA and AA′) in 4($-CH_2O$) resorcinol for one is ortho and the other para to the substituent. Assignment of the larger shift to the para effect resulted in excellent correlation of observed and calculated values of more complex substitutions. The calculated values are:

$$\alpha\text{-}CH_2\phi \text{ effect} = \delta \text{ peak V} - \delta \text{ resorcinol } C_4 = 121.29 - 109.18 = 12.11 \text{ ppm}$$

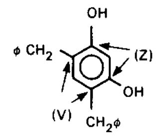
$$o\text{-}CH_2\phi \text{ effect} = \delta \text{ peak AA}' - \delta \text{ resorcinol } (C_1 \text{ and } C_3) = 156.34 - 158.27 = -1.93 \text{ ppm}$$

$$p\text{-}CH_2\phi \text{ effect} = \delta \text{ peak AA} - \delta \text{ resorcinol } (C_1 \text{ and } C_3) = 155.35 - 158.27 = -2.92 \text{ ppm}$$

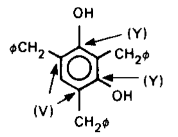
Establishment of these parameters allows the calculation of the more complex ring substitutions shown in structures **IX** and **X**.



VIII



IX



X

The aliphatic data for *Figure 3b* still indicate 4($-CH_2\phi$) substitution only. Peak Z at 153.43 ppm is assigned to the C_1 and C_3 carbons on 4,6($-CH_2\phi$) resorcinol, structure **IX**, as this resonance is in excellent agreement with its calculated value:

$$\delta\,(C_1 \text{ and } C_3) = \delta \text{ resorcinol } (C_1 \text{ and } C_3) + [\text{para } (-CH_2\phi) \text{ effect} + \text{ortho } (-CH_2\phi) \text{ effect}] = 158.27 + (-2.92 - 1.93) = 153.42 \text{ ppm}$$

Further reaction, *Figure 3c*, results in reaction in the 2 position as shown by peaks at 24.29 ppm (2–4 methylene bridge, not shown), 116.55 ppm (S) and 151.52 ppm (Y).

The 116.55 ppm peak, 12.30 ppm downfield from the unreacted 2 resorcinol carbon, reflects the α chemical shift effect on the 2 carbon due to $-CH_2\phi$ substitution, based on the assumption that this type of α effect should be approximately the same as the α effect on a 4 carbon (12.11 ppm). This assignment is consistent with the literature[2,3].

Peak Y, 151.52 ppm, is assigned to the C_1 and C_3 carbons in structure **X**. These carbons are magnetically equivalent and would be predicted to resonate at 151.49 ppm, in excellent agreement with its observed value:

$$\delta\,(C_1 \text{ and } C_3) = \delta \text{ resorcinol } (C_1 \text{ and } C_3) + 2[\text{ortho } (-CH_2\phi) \text{ effects} + \text{para } (-CH_2\phi) \text{ effect}] = 158.27 + 2(-1.93) - 2.92 = 151.49 \text{ ppm}$$

In other RF spectra, *Figures 6, 8*, and *9*, the C_3 carbon in 2,4($-CH_2\phi$) resorcinol has been observed at 154.23 ppm while the C_1 peak superimposes on peak Y at 153.43 ppm. Calculated values are 154.41 ppm (C_3) and 153.42 ppm (C_1).

The resonance for C_1 and C_3 in 2($-CH\phi$) resorcinol, calculated to resonate at 156.34 ppm, superimposes on peak AA' making it more intense than peak AA..This was observed very infrequently in the monitored reactions.

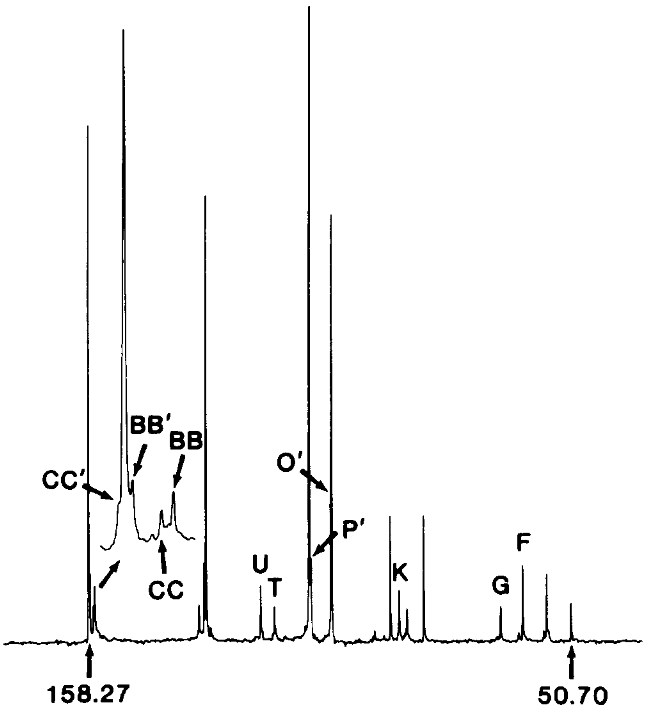
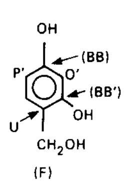


Figure 4 ^{13}C n.m.r. spectrum of a base-catalysed RF (1/1) resin reacted for 1 h at room temperature

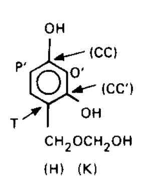
The above data indicate that the entire methylene bridging system in an RF resin can be characterized by ^{13}C n.m.r.

Ring carbons (4-methylol or hemiformal)

Figure 4 shows the ^{13}C n.m.r. spectrum of a base-catalysed RF (1/1) resin reacted for 1 h at room temperature. The aliphatic data indicate largely monosubstitution of methylol and hemiformal groups in the 4 position (structures **XI** and **XII**) with no methylene bridges present.



XI



XII

The intensity of the methylol methylene peak (F) in *Figure 4* is approximately twice that of each of the hemiformal methylene peaks (G and K). The newly-formed aromatic peaks (neglecting the carbon 5 resonances where important information is limited) are O', P', T, U, BB, BB', CC, and CC'. Peaks T and U arise from substitution in the 4 position, based on the broad parameters for substituted benzenes from the literature[6]. Since peak U is approximately twice as intense as peak T, the assignments were made as shown in stuctures **XI** and **XII**. The α parameters are therefore:

$$\alpha\, CH_2OH \text{ effect} = \delta \text{ peak U } (120.00) - \delta \text{ peak P } (109.18) = 10.82 \text{ ppm}$$

$$\alpha\ \mathrm{CH_2O(CH_2)O_xH}\ \text{effect} = \delta\ \text{peak T}\ (117.05) - \delta\ \text{peak P}\ (109.18) = 7.87\ \text{ppm}$$

The resonances for peaks O′ and P′, structures **XI** and **XII**, are slightly shifted (±0.1 ppm) because these unreacted carbons are in the meta position in relation to the reaction site.

Peaks CC, CC′, BB, and BB′ are C_1 and C_3 resonances resulting from methylol or hemiformal substitution in the 4 position. Reaction in this position is ortho to C_1 or C_3 and para to the other. These effects are different, resulting in a peak for each carbon. Since the intensity of $\mathrm{CC} \cong \mathrm{CC'}$, $\mathrm{BB} \cong \mathrm{BB'}$, $(\mathrm{BB}+\mathrm{BB'})/(\mathrm{CC}+\mathrm{CC'}) \cong 2$, and methylol/hemiformal $\cong 2$, the assignments were made as per structures **VIII** and **IX**. The para effect is larger then the ortho effect based on data from the literature[6] for the pH of this reaction (pH = 8–9). The ortho and para effects are therefore:

$$o\text{–}\mathrm{CH_2OH}\ \text{effect} = \delta\ \text{peak BB'}\ (158.07) - \delta\ \text{peak DD}\ (158.27) = -0.20\ \text{ppm}$$

$$p\text{–}\mathrm{CH_2OH}\ \text{effect} = \delta\ \text{peak BB}\ (156.92) - \delta\ \text{peak DD}\ (158.27) = -1.35\ \text{ppm}$$

$$o\text{–}\mathrm{CH_2O(CH_2O)_xH}\ \text{effect} = \delta\ \text{peak CC'}\ (158.47) - \delta\ \text{peak DD}\ (158.27) = 0.20\ \text{ppm}$$

$$p\text{–}\mathrm{CH_2O(CH_2O)_xH}\ \text{effect} = \delta\ \text{peak CC}\ (157.26) - \delta\ \text{peak DD}\ (158.27) = -1.01\ \text{ppm}$$

Ring carbons (2-substituted methylol or hemiformal)

Resorcinol C_2 carbons substituted with methylol or hemiformal groups are assigned to peaks Q and R respectively, *Figure 5* and *Table 1*, again based on the broad parameters from the literature[6]. The α chemical shift effects for 2 substitution and 4 substitution are only slightly different, i.e. 10.68 cf. 10.82 (methylol) and 7.98 cf. 7.87 (hemiformal), *Table 3*. Excellent correlation was observed between calculated and observed data for complex substitution patterns (involving 2 substitution) using the *o*, *m*, and *p* effects developed for 4 substitution. Thus, it is concluded that these effects are essentially the same for 2 substitution and 4 substitution, *Table 3*.

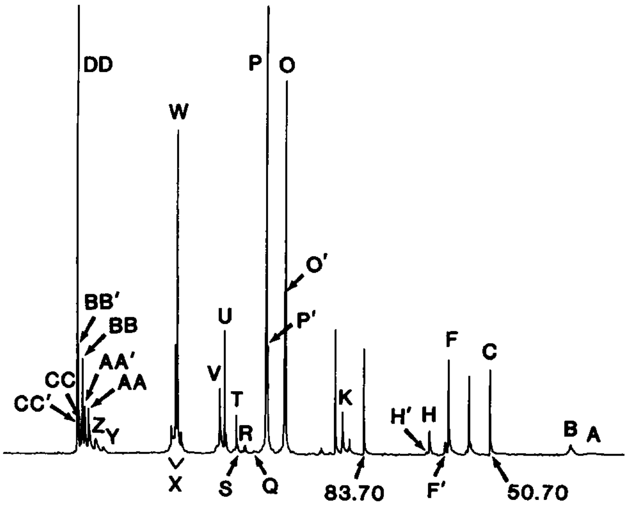


Figure 5 ^{13}C n.m.r. spectrum of a base-catalysed RF (1/1) resin reacted for 5 h at room temperature

Ring carbons (assignments for complex structures)

Further reaction resulted in many complex structures being formed resulting in numerous new C_1 and C_3 peaks (due to ortho and/or para effects) while the C_4 and C_2 peaks varied only slightly (±0.2 ppm due to the meta effects). The new C_1 and C_3 peaks were assigned using the hemiformal, methylol, and $-\mathrm{CH_2}\phi$ substitution parameters determined above (*Table 3*), correlated with

Table 4 Calculated and observed ^{13}C n.m.r. C_1 and C_3 chemical shifts for substituted resorcinol rings

Substituent	Carbon[a]	Chemical shifts[b] Observed	Calculated[c]
(1) 4-$\mathrm{CH_2OH}$	C_1	156.92	156.92
	C_3	158.07	158.07
(2) 4,6-$\mathrm{CH_2OH}$	C_1	156.73	156.67
	C_3	156.73	156.67
(3) 2-$\mathrm{CH_2OH}$	C_1	158.07	158.07
	C_3	158.07	158.07
(4) 2,4-$\mathrm{CH_2OH}$	C_1	157.83	157.87
	C_3	156.73	156.72
(5) 2,4,6-$\mathrm{CH_2OH}$	C_1	156.57	156.52
	C_3	156.57	156.52
(6) 4-$\mathrm{CH_2}\phi$	C_1	155.35	155.35
	C_3	156.34	156.34
(7) 2-$\mathrm{CH_2}\phi$	C_1	156.34	156.34
	C_3	156.34	156.34
(8) 2,4-$\mathrm{CH_2}\phi$	C_1	–	153.42
	C_3	154.23	154.41
(9) 4,6-$\mathrm{CH_2}\phi$	C_1	153.43	153.42
	C_3	153.43	153.42
(10) 2,4,6-$\mathrm{CH_2}\phi$	C_1	151.52	151.49
	C_3	151.52	151.49
(11) 4-$\mathrm{CH_2OCH_2OH}$	C_1	157.26	157.26
	C_3	158.47	158.47
(12) 2-$\mathrm{CH_2OCH_2OH}$	C_1	158.47	158.47
	C_3	158.47	158.47
(13) 4,6-$\mathrm{CH_2OCH_2OH}$	C_1	157.23	157.46
	C_3	157.23	157.46
(14) 4-$\mathrm{CH_2}\phi$, 6-$\mathrm{CH_2OH}$	C_1	155.09	154.99
	C_3	155.09	155.15
(15) 4-$\mathrm{CH_2}\phi$, 6-$\mathrm{CH_2OCH_2OH}$	C_1	–	155.34
	C_3	155.72	155.54
(16) 4-$\mathrm{CH_2OH}$,6-$\mathrm{CH_2OCH_2OH}$			
	C_1	157.07	157.06
	C_3	157.07	157.12
(17) 2(–$\mathrm{CH_2OH}$), 4(–$\mathrm{CH_2}\phi$)	C_1	–	155.15
or 2(–$\mathrm{CH_2}\phi$), 4(–$\mathrm{CH_2OH}$)		156.08	156.14

[a] Carbons 1 and 3 on an unsubstituted or 2-substituted resorcinol ring are magnetically equivalent. On 4 monosubstituted rings, C_3 is the carbon ortho to the substituent, C_1 is the carbon para to the substituent. On disubstituted rings with different substituents, C_1 = carbon ortho to the first substituent listed, C_3 = carbon ortho to the second substituent listed

[b] In ppm downfield relative to $[\mathrm{(CH_3)_3SiCD_2CD_2CO_2Na}]$, an internal standard

[c] Calculated chemical shifts using the parameters in *Tables 1* and *4*

aliphatic carbon spectral data. Comparison of calculated and observed data (monitored base-catalysed RF reactions) resulted in the assignments in *Table 4*. The agreement of the data is excellent. Examples are shown in *Figures 5–9*.

Examples of complex RF resin structures

The base-catalysed RF (1/1) resin reacted for 1 h (see *Figure 4*) was allowed to react at RT for 5 h (see *Figures 5* and *6*). The following structures are obviously present in the more complex spectrum in *Figure 5*: unreacted resorcinol rings (O, P, W, and DD); 4(–CH$_2$OH) resorcinol (F, F′, U, BB, and BB′); 4(–CH$_2$OCH$_2$OH) resorcinol (H, H′, T, CC, and CC′); and resorcinol rings mono-, di-, and trisubstituted with methylene bridges (AA′ and AA, Z, and Y, respectively, correlated with peaks A and B). Expansion of the C$_1$ and C$_3$ resonance area (see *Figure 6*), allows one to observe several other structures as well.

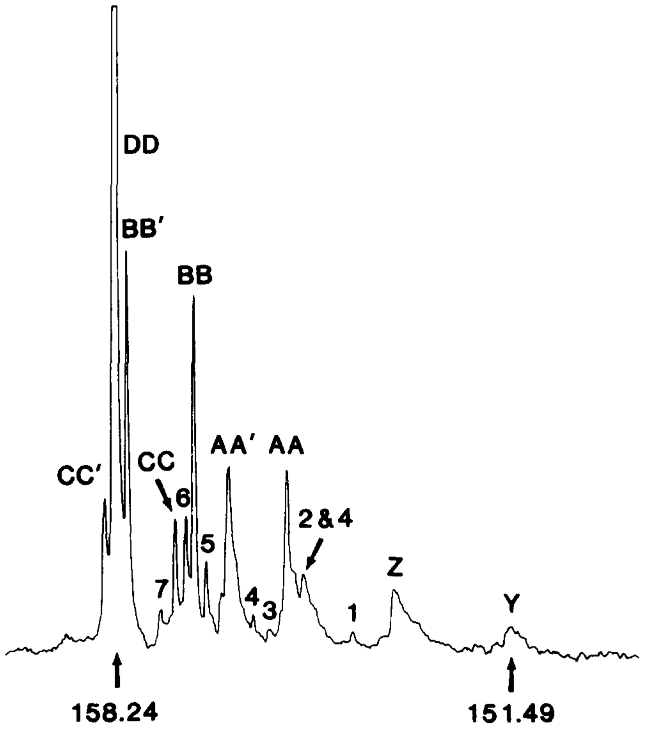


Figure 6 Expansion of the C$_1$ and C$_3$ region in *Figure 5*

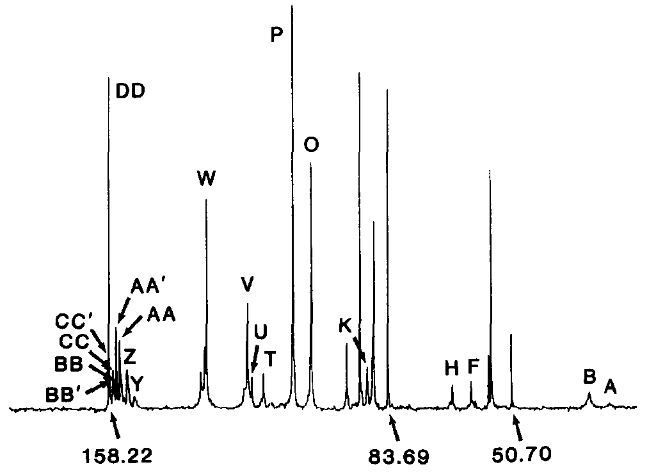


Figure 7 ^{13}C n.m.r. spectrum of a base-catalysed RF (1/2) resin reacted for 5 h at room temperature

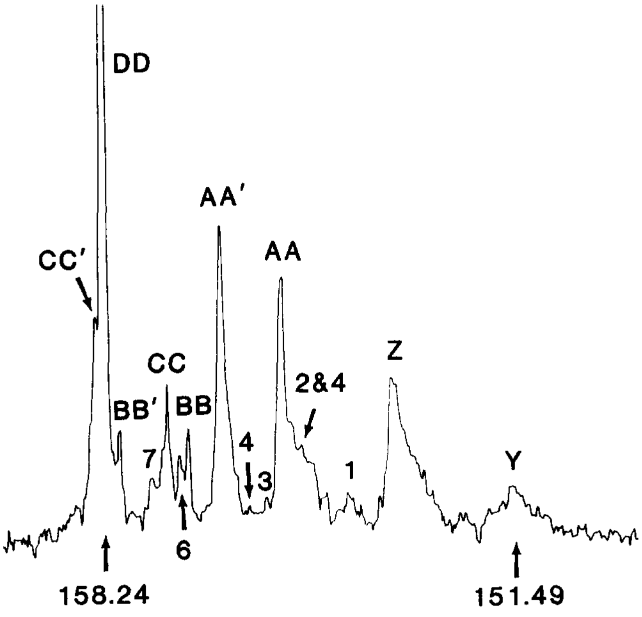


Figure 8 Expansion of the C$_1$ and C$_3$ region in *Figure 7*

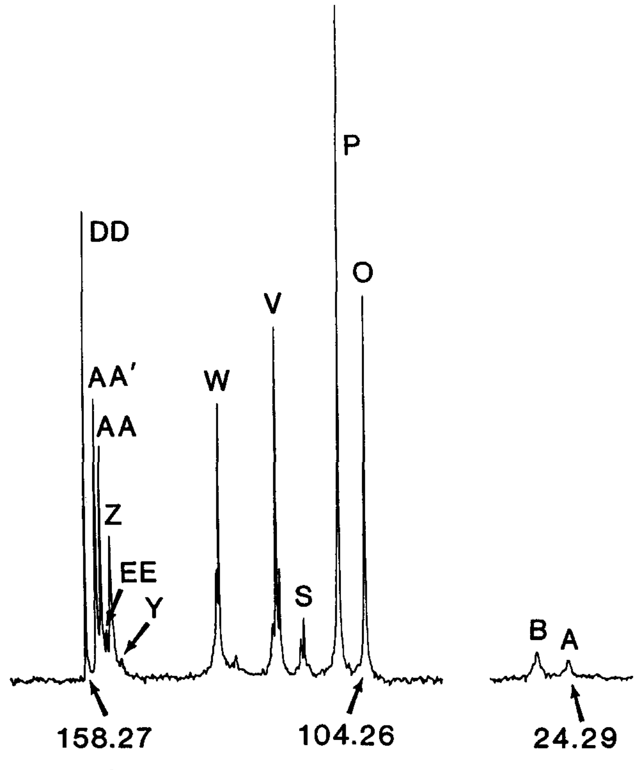


Figure 9 ^{13}C n.m.r. spectrum of R2170 Penacolite resin

A base-catalysed RF (1/2) resin reacted for 5 h at RT is shown in *Figures 7* and *8*. The dominance of the $-CH_2\phi$ substituted structures is evident in these Figures, i.e. peaks Y, Z, AA and AA′ > peaks BB, BB′, CC and CC′ in the C$_1$, C$_3$ region and peak V > peaks U and T in the reacted C$_4$ resonance region.

NOE factors

The NOE factors determined from this study are listed in *Table 5*. These factors were established to quantify the data.

Applications

The data in *Table 6* demonstrate the types of quantitative information which are readily available from

Table 5 NOE factors for resorcinol–formaldehyde resin carbons

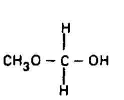
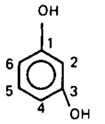
Structure		NOE
	Formaldehyde (oxymethylene oligomer C's)	2.4
 $CH_3O-\underset{H}{\overset{H}{C}}-OH$	C_1	2.7
	C_2	2.7
$\underline{C}H_3OH$		2.1
$4\text{-}\underline{C}H_2OH$		2.6
$2\text{-}\underline{C}H_2OH$		2.4
$4\text{-}\underline{C}H_2O\underline{C}H_2OH$	C_1	2.6
$\overset{\uparrow}{(1)}\quad\overset{\uparrow}{(2)}$	C_2	2.8
$\phi\text{-}CH_2\text{–}\phi$	4–4′	2.3
	2–4	2.4
	$C_{1,3}$	2.2
	$C_{2,4,5,6}$	2.4

Table 6 ^{13}C n.m.r. data on base-catalysed RF resins

	Mole%	
	RF (1/1) resin	RF (1/2) resin
Unreacted resorcinol	35.2	19.0
Total positions		
Unreacted	77.6	46.1
Reacted	22.4	53.9
Methylol	8.2	7.3
Hemiformal	2.3	7.8
Methylene bridge	11.9[a]	38.8[b]
4-Positions		
Unreacted	70.5	30.1
Reacted	29.5	69.9
Methylol	10.2	9.0
Hemiformal	3.0	9.6
Methylene bridge	16.3	51.3
2-Positions		
Unreacted	91.8	78.0
Reacted	8.2	22.0
Methylol	4.3	4.0
Hemiformal	1.0	4.3
Methylene bridge	2.9	13.7
Ratio of reacted positions 4/2	3.60	3.18

[a] Mono-, di- and trisubstitution = 7.4/3.7/0.8

[b] Mono-, di- and trisubstitution = 19.5/16.2/3.1

^{13}C n.m.r. analysis of RF resins. These data compare the RF (1/1) resin in *Figure 5* with the RF (1/2) resin in *Figure 7*, quantitatively. The only difference in reaction conditions is the ratio of the starting materials.

The data indicate that the RF (1/2) resin has obviously been further reacted and condensed than the RF (1/1) resin. 53.9% of the reactive sites in resorcinol have been reacted in the RF (1/2) resin compared with only 22.4% for the RF (1/1) resin. Condensation (methylene bridges) in the RF (1/2) resin exceeds that in the RF (1/1) resin by more than 3/1. Condensation branching in the RF (1/2) resin is also more advanced, i.e. di- and trimethylene bridge substitution is more significant relative to monosubstitution. The 4 position is obviously favoured for reaction in each resin. As the resorcinol reacts further, relatively more reaction takes place in the 2 position.

The data in *Table 6* were normalized to 1.00 and 2.00 total formaldehyde-type carbons per phenol carbon for RF (1/1) and RF (1/2) resins, respectively, before the % values were calculated. The observed values were 1.05 and 1.92 respectively, in good agreement with the expected values.

Figure 9 is the ^{13}C n.m.r. spectrum of Koppers R2170, one of many commercially available RF resins whose structures are relatively unknown. Since the data indicate that there is no methylol or hemiformal structure present, this is most likely an acid-catalysed resin. There are both 2-4 and 4-4′ but not 2-2′ methylene bridges present.

Quantitatively, 42.5% of the available 4 positions and 25.7% of the available 2 positions have been reacted. Thus, the 4 positions are favoured for reaction over the 2 position by a factor of 1.73 on a per site basis. Mono-, di- and trisubstituted rings are present in the ratio: 17.5/7.4/1.0. Of the disubstituted rings, 81% are 4-6 and 19% are 2-4 substituted. 17.6% free resorcinol is present in this resin.

SUMMARY AND CONCLUSIONS

This study has filled many of the voids in the literature for ^{13}C n.m.r. assignments of RF resins. Particular emphasis has been placed on assignments in base-catalysed RF resins and for the aromatic carbons in acid-catalysed RF resins.

The applicability of these data to experimental and commercial RF resins has been demonstrated. Quantitative data using NOE parameters determined by this study appear to be very good. It is now possible to almost totally characterize the structures of RF resins, quantitatively. This allows one to make more accurate, detailed studies of the nature of various RF reactions. This also provides an extensive data base for future solid-state n.m.r. studies.

ACKNOWLEDGEMENTS

The author is grateful to GenCorp for permission to publish this work. The information and materials supplied by S. C. Sharma are gratefully acknowledged. The assistance by M. E. Wacker, C. R. Kennedy and A. J. Kirschner in sample preparation is appreciated.

REFERENCES

1 Werstler, D. D. *Polymer* 1986, **27**, 750

2 Dankleman, W. and de Wit, J. *Angew. Chem.* 1977, **62**, 101

3 de Breet, A. J. J., Dankleman, W., Huysmans, W. G. B. and de Wit, J. *Angew. Makromol. Chem.* 1977, **62**, 7

4 Sebenik, A., Osredkar, U. and Vizovisek, *Polymer* 1981, **22**, 804

5 Woodbrey, J. C., Higginbottom, H. P. and Albertson, A. *J. Polym. Sci., Part A*, 1965, **3**, 1079

6 Mukoyama, Y. and Tanno, T. *J. Polym. Sci., Polym. Chem. Edn.* 1973, **11**, 3193