One- and Two-Dimensional NMR Study of Resol Phenol–Formaldehyde Prepolymer Resins

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A one- and two-dimensional NMR study was performed on three commercial resol phenol-formaldehyde (PF) prepolymer resins. ¹H, ¹³C, CSCM and DQF COSY NMR spectral data, in acetone- d_6 , were obtained on each resin and on PF model compounds: phenol, five methylolphenols, four diphenylmethanes, two formals, two dibenzyl ethers and two dibenzylamines. Gated-decoupled ¹³C experiments, using 2,4,6-trimethylphenol as internal standard, were used to quantitate the major components present in each of the three resins. The major chemical differences of the three resins were noted. A DQF COSY method was developed that allowed the qualitative identification of most of the major phenolic components present in each of the PF resins.

KEY WORDS NMR; ¹H NMR; ¹³C NMR; Phenol-formaldehyde resins

INTRODUCTION

Phenol-formaldehyde (PF) resins, the first totally synthetic polymers, have wide commercial applications in products such as molding compounds, coatings, wood binders and high-temperature polymers with ablative properties.^{1,2} Acid-catalyzed (novolac) PF resins generally have different properties from base-catalyzed (resol) resins. It is important to be able to analyze the structure of a resin accurately because resin function is closely related to resin structure.

A large number of analytical techniques have been used through the years to study PF resins, including viscosity,^{3,4} gel permeation chromatography,^{5,6} IR spectrophotometry,^{5,7} HPLC^{8,9} and NMR spectroscopy. The NMR methods started with ¹H studies,^{10–12} progressed to ¹³C because of its increased resolution^{4–6,8,9,13–25} and more recently moved on to cross-polarization magic angle spinning (CP/ MAS),^{5,26–32} ²H NMR³³ and 2-D NMR methods.²⁴ Each method has advantages under certain conditions. Because resin formation is frequently aqueous based, the most common solvent used in the liquid NMR studies has been DMSO-d₆, even though many other solvents have also been reported.

Most NMR studies on PF resins were carried out over a decade ago using a wide variety of solvents and low field strengths. Consequently, chemical shift comparisons among these studies are difficult. Also, very few 2-D NMR methods have been used to analyze PF

CCC 0749-1581/95/090717-07 © 1995 by John Wiley & Sons, Ltd. resins. All of the NMR data reported in this paper were obtained in acetone- d_6 solvent because it provides better ¹H resolution,³⁴ a requirement for the homo- and heteronuclear 2-D studies reported here.

In this paper we report ¹H, ¹³C, DQF COSY and CSCM NMR data on the major components present in resol PF prepolymer resins including methylolphenols 1-6, hydroxydiarylmethanes 7-9 (see Scheme 1), dihydroxydibenzyl ethers, hydroxybenzylamines and formals. Three different commercial resol PF prepolymer resins that have been or are being used in the NASA space program were chosen for this study. Future NMR studies will include chemical analyses on all stages of the PF cure process, including the highly oligomeric prepreg, the final cured resin and composite PF materials made from the resin.



Scheme 1

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EXPERIMENTAL

Materials

Phenol (1), o-methylolphenol (2), p-methylolphenol (3), 4,4'-dihydroxydiphenylmethane (7), 2,2'-dihydroxydiphenylmethane, 2,4,6-trimethylphenol (TMP) and acetone- d_6 were used as purchased from Aldrich Chemical. 2,4'-Dihydroxydiphenylmethane (8) was used as purchased from TCI America.

2,4-Dimethylolphenol (4) was prepared by the lithium aluminum hydride (LAH) reduction of the dimethyl ester of 2-hydroxyisophthalic acid using the procedure of Freeman.³⁵ 2,6-Dimethylolphenol (5) was prepared by the reaction of 4-bromophenol with formaldehyde to give 4-bromo-2,6-dimethylolphenol, which was then treated with Raney nickel and hydrogen using the procedure of Eapen and Yeddanapalli³⁶ to give the desired product 5. 2,4,6-Trimethylolphenol (6) and 3,3',5,5'tetramethylol-4,4'-dihydroxydiphenylmethane (9) were synthesized from the room temperature reaction of phenol and formaldehyde in the presence of NaOH using literature procedures.^{35,37}

Saligenin was self-condensed³⁸ by heating it at 140 °C for 1 h in glycerol to give 2,2'-dihydroxydibenzyl ether; ¹³C NMR (acetone- d_6): $\delta = 69.73$ (CH₂), 116.23 (C-3,3'), 120.23 (C-5,5'), 125.12 (C-1,1'), 129.70 (C-4,4'), 129.90 (C-6,6'), 156.54 ppm (C-2,2'). Similarly, *p*-methylolphenol was self-condensed by heating it at 118 °C for 1 h³⁹ to give 4,4'-dihydroxydibenzyl ether: ¹³C NMR (acetone d_6): $\delta = 72.48$ (CH₂), 115.76 (C-3,3'), 130.09 (C-2,2'), 130.41 (C-1,1'), 157.76 ppm (C-4,4').

Reduction of 2-hydroxybenzonitrile with LAH gave 2-hydroxybenzylamine; ¹³C NMR (acetone- d_6): $\delta = 40.05$ (CH₂), 117.36 (C-3), 120.12 (C-5), 126.11 (C-4), 129.75 (C-6), 131.17 (C-1), 156.68 ppm (C-2). Reduction of 4-hydroxybenzonitrile with LAH gave 4hydroxybenzylamine; ¹³C NMR (acetone- d_6): δ 43.17 (CH₂), 115.94 (C-3), 129.77 (C-1), 131.09 (C-2), 157.42 ppm (C-4).

Phenol, 7.9 g, formaldehyde (37%), 6.7 ml, and ammonia solution, 6 ml, were heated at 60 °C for 6 h and the product mixture was analyzed by ¹³C NMR, giving major peaks at 54.44 (CH₂ of 2,2'-dihydroxydibenzylamine) and 57.77 ppm (CH₂ of 4,4'-dihydroxydibenzylamine) plus minor peaks at 54.69 and 57.32 ppm (CH₂s of 2-hydroxybenzyl-4'-hydroxybenzylamine), respectively.

Equimolar amounts of *o*-methylolphenol and formaldehyde were mixed and the ¹³C NMR spectrum showed two peaks in the aliphatic region: $\delta = 65.49$ (ArCH₂O) and 89.10 (OCH₂OH). The formal of *p*-methylolphenol was formed in a similar reaction with two peaks in the aliphatic region of the ¹³C NMR: $\delta = 69.09$ (ArCH₂O) and 88.75 ppm (OCH₂OH). The ¹³C NMR spectrum of a mixture of *p*-methylolphenol and 2 mol of formaldehyde showed two peaks: $\delta = 69.81$ (ArCH₂O) and 90.84 ppm (both CH₂ s of OCH₂OCH₂OH).

For 2,2'-dihydroxydiphenylmethane, the ¹H NMR spectrum (acetone- d_6) showed peaks at $\delta = 3.95$ (s, 2H), 6.76 (td, 1H, J = 7.4, 1.2 Hz) (H-5), 6.85 (dd, 1H, J = 8.0 and 1.2 Hz) (H-3), 7.03 (td, 1H, J = 7.5 and 1.2 Hz) (H-

4) and 7.14 ppm (dd, 1H, J = 7.7 and 1.7 Hz) (H-6); the ¹³C NMR spectrum (acetone- d_6) showed peaks at $\delta = 30.48$ (CH₂), 116 (C-3), 120.64 (C-5), 128.00 (C-4), 128.17 (C-1), 131.35 (C-6) and 155.39 ppm (C-2).

NMR experiments

All spectra were obtained on a General Electric QE-300 NMR spectrometer at 25 °C, observing ¹H and ¹³C at 300.67 and 75.61 MHz, respectively. NMR samples of compounds 1–9 each contained 40 mg of sample in 0.5 ml of acetone- d_6 , 1% in TMS. The resin samples contained 450 mg of resin, 50 mg of TMP and 600 mg of acetone- d_6 . All samples were run in 5 mm sample tubes.

¹H NMR spectra were collected into 32K data sets over a spectral width of 6 kHz using a 30° pulse. ¹³C spectra NMR were collected into 32K data sets over a spectral width of 20 kHz using a 40° pulse and were processed using exponential multiplication with 1 Hz line broadening. Gated-decoupled ¹³C NMR spectra were collected similarly using the 1PDNA pulse sequence, 1792 transients and a 40 s prepulse delay. All chemical shifts were referenced to internal TMS.

One-bond 2D heteronuclear shift correlation (called CSCM, Chemical Shift Correlation Map,40 in standard QE software) spectra were obtained in the TPPI mode⁴¹ with an f_2 spectral width of 12 500 Hz over 2K real data points using 48 transients per t_1 increment, and an f_1 spectral width of 2717 Hz over 128 t_1 increments (zero-filled to 256); exponential multiplication was used in t_2 with 1 Hz line broadening, and Lorentzian-Gaussian multiplication in t_1 with 3 Hz line broadening. Double quantum filtered (DQF) COSY spectra⁴² were obtained using the QE pulse sequence COSY2Q with an f_2 spectral width of 1805 Hz using 1K real t_2 data points and an f_1 spectral width of 1800 Hz over 256 t_1 increments (zero-filled to 1K) with 16 transients per increment; sine-bell multiplication was used in both directions and the spectra were symmetrized.

RESULTS AND DISCUSSION

Model Compounds

¹H NMR. The chemical shifts found in the 300 MHz ¹H spectra of compounds 1–9 in acetone- d_6 solvent are given in Table 1. In the methylolphenols 2–6, aromatic hydrogens ortho and para to the phenolic OH are shielded by resonance donation from the OH group and occur at 6.78 ± 0.02 ppm, while meta-hydrogens occur at 7.13 ± 0.06 ppm. The benzylic ortho-methylol hydrogens occur at 4.70 ± 0.05 ppm and the para-methylol hydrogens at 4.50 ± 0.02 ppm. Ortho coupling constants are 7–8 Hz, meta 1–2 Hz and para are not seen.

In diarylmethanes 7–9, the hydrogens that are ortho and para to the OH occur at comparable chemical shifts to the methylolphenols, but the meta-hydrogens are now deshielded 0.10 ppm owing to the presence of an adjacent CH_2Ar group. The methylene hydrogens between the two aryl rings occur at 3.75 ppm when two para-OHs are present (4,4'), at 3.95 ppm when two

Region	C or H	1	2	3	4	5	6	7	8	8′	9
Aromatic	1	158.24	156.15	157.28	155.18	154.52	153.66	133.71	129.26	132.92	133.42
	2	116.06	128.14	115.75	127.53	127.81	127.51	130.45	155.68	130.62	127.48
		(6.80)	—	(6.78)				(7.01)	_	(7.08)	(6.95)
	3	130.21	128.39	129.16	127.23	127.15	126.23	115.93	115.80	115.80	127.60
		(7.18)	(7.23)	(7.17)	(7.22)	(7.11)	(7.09)	(6.74)	(6.84)	(6.73)	_
	4	120.14	120.11	133.77	134.16	119.84	133.51	156.36	127.82	156.27	152.73
		(6.80)	(6.80)	—		(6.77)		—	(6.99)		
	5	130.21	128.82	129.16	127.30	127.15	126.23	115.93	120.34	115.80	127.73
		(7.18)	(7.08)	(7.17)	(7.05)	(7.11)	(7.09)	(6.74)	(6.74)	(6.73)	—
	6	116.06	115.99	115.75	115.70	127.81	127.51	130.45	131.18	130.62	126.30
		(6.80)	(6.80)	(6.78)	(6.76)		_	(7.01)	(7.06)	(7.08)	(6.95)
Methylene	<i>o</i> -CH₂OH		61.86	_	61.93	61.97	62.15	_	_		62.12
·	-		(4.74)		(4.67)	(4.75)	(4.72)	_		_	(4.69)
	p-CH ₂ OH			64.55	64.66	_	64.67	_			_
		_		(4.52)	(4.48)	_	(4.48)	_	_		_
	o-CH₂Ar	_	_			—	_	—	35.39	_	_
	_		_			—	—	—	(3.87)		_
	p-CH₂Ar	—	_	_		—	—	40.72	_	—	41.09
	-	—	—	—		_	—	(3.76)	—	_	(3.74)
* In acetone-	d ₆ .										

Table 1. ¹³ C and (¹ H) chemical shifts (ppm) ^a of PF model compound	s 1	i–	-9
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ortho-OH's are present (2,2') and at 3.87 when one of each is present (2,4'). The chemical shift data for 2,2'dihydroxydiphenylmethane are given in the Experimental section instead of in Table 1 because this compound was not found in any of the three commercial resins studied here. It was included in the model compound study because it has been found in some PF prepolymer resins.

¹³C NMR. ¹³C NMR is currently the most common NMR method used to study PF resins and their model compounds. The large chemical shift dispersion range of carbon (>200 ppm) allows the identification of many different components—especially the methylolphenols and diphenylmethanes—that make up the complex mixture called PF prepolymer resin.

The complete chemical shift assignment of all of the carbons in compounds 1-9 are given in Table 1. The most useful ¹³C phenolic range for compound identification is the ipso region from 160-150 ppm, where aromatic carbons directly bonded to an OH group are found. Each phenolic ring in a resin component has one and only one such ipso C-OH carbon. In compounds 1-9, the C-OH of phenol, 1, is the most deshielded ipso carbon (158.24 ppm), and the C-OH carbons of 9 are the most shielded ipso carbons (152.73 ppm). The addition of an ortho-methylol group to phenol causes the C-OH carbon to be shifted upfield by about 2.0 ppm, while the addition of a para-methylol group gives an upfield shift of about 1.0 ppm. The four ortho-methylol groups on 9 make its C-OH carbon the most shielded ipso carbon commonly found in PF prepolymer resins. Another benefit of looking at the ipso region is that since the C-OH carbons are not bonded to any hydrogens, they experience little if any NOEs, with the result that phenolics can be reasonably quantitated by integration of the ipso region. A gated-decoupling experiment must be performed for a quantitative analysis of all of the carbons, which include unsubstituted aromatic carbons, methylol carbons and diarylmethane methylenes carbons.

Other regions of the ¹³C NMR spectrum also give useful information. The aromatic region from 122–135 ppm contains unsubstituted *meta*-carbons and *ortho*- or *para*-carbons bonded to a methylene. Unsubstituted ortho-carbons occur at 115.9 ± 0.2 ppm and unsubstituted *para*-carbons at 120.2 ± 0.3 ppm. These two regions can be used to follow the progress of resin cure where more and more ortho and *para* positions become progressively substituted with formaldehyde residues.

The major methylene regions of importance are the methylol and diarylmethane regions. In methylolphenols 2-6, ortho-CH₂OHs occur at 61.98 ± 0.12 ppm and para-CH₂OHs at 64.61 ± 0.06 ppm. The diarylmethane methylene regions are, likewise, well resolved with o,o-CH₂s at 30.5 ppm, o,p-CH₂s at 35.4 ppm and p,p-CH₂s at 40.8 ppm. The ca. 5 ppm separation of the diarylmethane methylene carbons in the 30-40 ppm region makes it easy to determine whether the cross-linking methylene carbons are o,o-, o,p- or p,p-.

Solvent effects. Proton NMR spectra of phenolic resins, or their model compounds, have been reported in a variety of solvents, including DMSO- d_6 , ^{5,6,8,9,15,23,25} CD₃OD, ^{21,22} D₂O, ^{20,22} acetone- d_6 , ^{12,16,18,19} CDCl₃, ^{4,12,24} THF- d_8 ¹⁴ and dioxane- d_8 , ⁴³ Aromatic protons are sharper and better resolved in acetone- d_6 than in any other of the common NMR solvents, ^{34,44} an important consideration for CSCM and DQF-COSY experiments. Both ¹H and ¹³C chemical shifts are strongly affected by magnetically anisotropic solvents (acetone- d_6) in which mutual orientations between solvent and solute molecules (phenolics) are possible. This is the reverse effect of the more common use of

benzene- d_6 to cause solvent-induced shifts in the aliphatic hydrogens of keto steroids.⁴⁵

Solvent effects play an important role in ¹³C NMR, as can be seen in Table 2. The general shielding/ deshielding trends for *ipso* carbons parallel each other in acetone- d_6 and DMSO- d_6 , but the chemical shift values can differ by as much as 3.0 ppm depending on the solvent used. The relative positions of two ¹³C peaks that differ by only a few tenths of a ppm can easily be reversed in acetone- d_6 compared with their relative order in DMSO- d_6 . It is important to use only one solvent when comparing compounds of a similar chemical nature.

Table	2.	Solvent	effects	on	the	chemical	shifts
		(ppm) o	f the C	-OI	I ph	enolic car	bons

Compound	Acetone-d ₆ *	DMSO-d ₆ ⁵	Difference
1	158.24	157.4	0.84
3	157.28	156.2	1.08
7	156.36	155.3	1.06
8' (C-4')	156.27	155.2	1.07
2	156.15	154.0	2.15
8 (C-2)	155.68	154.8	0.88
4	155.18	152.9	2.28
5	154.52	151.8	2.72
6	153.66	150.5	3.0
9	152.73	149.9	2.83

^a This work at 75.6 MHz with internal TMS. ^b Ref. 8 at 22.6 MHz with DMSO-*d*₆ set at 39.44 ppm.

Resol PF prepolymer resins

1-D NMR. Three different commercial resol PF resins were chosen for study, including the Borden resin called SC 1008. This study was initiated to see if NMR methods are capable of detecting significant differences in PF prepolymer resins. Each resin contained the solvent isopropyl alcohol (IPA). The ¹H NMR spectra of these resins were of limited use in identifying individual components, even in acetone- d_6 . The two IPA peaks—a doublet (6H) at 1.15 ppm and a multiplet (1H) at 3.97 ppm—are very prominent in the proton spectra. The aromatic region contains complex sets of multiplets from 6.6-7.4 ppm (see Fig. 2 for the aromatic region of SC 1008). The amount of methylol (4.9-4.4 ppm) and diarylmethane (4.1-3.5 ppm) methylenes present can be determined from the integrals of these two regions after subtracting the IPA hydrogen from the latter range.

All nine of the model compounds 1–9 were identified in the C-OH regions of the ¹³C spectra of each resin [see Fig. 1(a) and Table 3]. A ¹³C NMR spectrum of SC 1008 was run in CDCl₃ to verify the absence of 2,2'dihydroxydiphenylmethane, because its methylene peak near 30 ppm is very near the chemical shift of the CD₃ peaks of the NMR solvent acetone- d_6 . To verify the assignments of these model compounds, compounds 1, 2, 3, 7 and 8 were added to SC 1008 and the spectra of the spiked resins were measured. Also, a mixture of these five compounds and IPA was studied to provide further assignment of all of the carbons of this sixcomponent mixture. Compounds 4, 5, 6 and 9 were synthesized and their spectra measured, but not enough of



Figure 1. 1-D Gated-decoupled ¹³C NMR spectrum of SC 1008 containing 2,4,6-trimethylphenol standard, showing (a) phenolic *ipso* region (160–150 ppm) and (b) entire ¹³C region including phenolic and methylene regions.

Table 3.	Compositions	(mol.%)	of	three	commercial	resol
	PF resins					

Component	SC 1008*	Resin A ^b	Resin B ^b			
Phenolics						
1	27.0 ± 1.6	21.2 ± 2.6	30.2 ± 2.0			
2	13.4 ± 0.9	9.8 ± 2.3	9.7 ± 0.7			
3	7.3 ± 0.7	10.9 ± 0.5	8.2 ± 1.8			
4	7.7 ± 0.4	9.3 ± 2.0	1.7 ± 3.0			
5	9.8 ± 0.7	7.4 ± 0.5	8.9 ± 0.8			
6	6.2 ± 0.7	5.0 ± 1.4	5.9 ± 1.0			
7	2.0 ± 0.4	1.6 ± 0.2	2.3 ± 2.1			
8	5.6 ± 0.5	6.1 ± 2.3	8.1 ± 1.0			
9	2.1 ± 0.9	1.8 ± 0.5	3.4 ± 2.1			
Total phenolics: ^c	81.1	73.1	78.4			
м	ethylenes (from for	maldehyde)				
Formals	5.4 ± 4.3	0.7 ± 0.6	11.7 ± 2.7			
ArCH ₂ O	64.9 ± 5.8	58.5 ± 4.8	49.7 ± 1.4			
ArCH ₂ Ar	16.2 ± 3.3	8.2 ± 2.1	14.3 ± 3.4			
ArCH ₂ N	9.2 ± 3.7	32.6 ± 3.8	6.4 ± 3.6			
Bn₂O	4.4 ± 4.2	0.0 ± 0.0	17.8 ± 2.4			
	Solvent (wt.	%)				
IPA	24.7 ± 1.8	13.4 ± 0.5	6.2 ± 1.2			
^a Values for SC 1008 are based on samples from five different lots						

^b Values for resins A and B are based on three determinations from one lot.

 $^\circ$ Cumulative totals of 1–9 identified in the phenolic 150–160 ppm region.

these compounds was made to use in the spiking experiment.

Gated-decoupled ¹³C NMR spectra were then measured to determine the amounts of the individual components in each resin. To aid in the quantification, 2,4,6trimethylphenol (TMP) was used as an internal standard. TMP is an excellent standard because its C-OH carbon occurs at 151.77 ppm, which is outside the range of all of the other *ipso* carbons of the phenolics present in the resins. Also, the presence of two different kinds of methyls in TMP—two *ortho*-methyls at 16.51 and one *para*-methyl at 20.47 ppm—allows for easy quantification of IPA and all methylene carbons of the methylolphenols and diarylmethanes. Figure 1(b) shows a typical gated-decoupled ¹³C NMR spectrum of SC 1008 with important regions assigned.

The *ipso* chemical shift values for compounds 1-4, 7 and 8 are all sharp and probably represent only the compounds assigned. The peaks in the range 154.5-152.5 ppm are broader and undoubtedly represent several oligomeric compounds with similar structures to the assigned compounds: 5 (with 2,4-dimethylol groups), 6 (with 2,4,6-trimethylol groups) and 9 (with multiple methylol groups on diarylmethanes). This problem will be addressed in our NMR studies of PF prepreg resins. Identical regions of the ¹³C NMR spectra of each resin were integrated to insure the validity of all comparisons.

Integrations of the methylene regions of the gateddecoupled ¹³C NMR spectra of PF resins are not as accurate as those of the C-OH region since the former covers a 65 ppm range (95–32 ppm) and the latter a 10 ppm range (160–150 ppm). The following methylene regions were used in the assignments of Table 3: formals 96-85 ppm, benzyl ethers 85-68 ppm, methylols 68-60 ppm, benzylamines 60-45 ppm, diarylmethanes 45-32 ppm and IPA 27-24 ppm. In support of these assignments, the following additional compounds were synthesized and their ¹³C NMR spectra obtained. The benzyl methylene carbon of 2,2'-dihydroxydibenzyl ether occurs at 69.73 ppm and the methylene carbon of 4,4'-dihydroxydibenzyl ether at 72.48 ppm. The formals formed independently from 1 mol of 2 and 3 with formaldehyde (ArCH₂OCH₂OH) occur at 89.10 and 88.75 ppm, respectively, while their benzyl methylenes (ArCH₂OCH₂OH) carbons occur at 65.49 and 69.09, respectively. The benzylic carbons of 2,2'-dihydroxydibenzylamine and 4,4'-dihydroxydibenzylamine occur at 54.44 and 57.77 ppm, respectively.

A comparison of the compositions of these three commercial PF resins can be made by looking at the horizontal columns in Table 3. The most significant differences between these three resins are as follows: (a) resin A has a larger amount of hydroxybenzylamines (32.6%) than the other two resins (6.4% and 9.2%); (b) resin B has more benzyl ether (17.8%) and unreacted formaldehyde (11.7%) than the other two; the latter may or may not be significant since the freshness of the samples may not have been identical; and (c) the amount of isopropyl alcohol solvent varied widely in the three resins.

2-D NMR. Duff *et al.*²⁴ reported a 2-D NMR study of some phenolic resins. Most of their data were for resins prepared from cresol and naphthol with formaldehyde or benzaldehyde. A heteronuclear correlation spectrum of a PF novolac was also reported, but since the complicated ¹H spectrum was not included on the 2-D spectrum, assignments of the individual Hs were not clear.

Once all of the carbons of the major components of a resin mixture have been identified, the chemical shifts of the hydrogens directly bonded to each of these carbons can be identified by the CSCM experiment. The most intense peaks in the aromatic region of both the ¹H and ¹³C NMR spectra of SC 1008 come from phenol (1). In the CSCM spectrum of SC 1008, the unsubstituted ortho-carbons near 116 ppm and the unsubstituted para-carbons near 120 ppm both correlate with hydrogens on the right one-third of the aryl hydrogen region (see the top of Fig. 2 for a 1-D ¹H spectrum of this complicated aromatic region). The meta-carbons between 126 and 131 ppm correlate with the hydrogens on the left two-thirds of the aromatic hydrogen region. In a like fashion, the ortho-methylol hydrogens can be identified at 4.7-4.8 ppm and the para-methylol hydrogens at 4.5 ppm. The two proton peaks to the immediate right of the IPA multiplet are assigned to o,pmethylene hydrogens (3.87 ppm) and p,p-methylene hydrogens (3.74 ppm). The CSCM spectra of resins A and B were also very useful because in addition to the peaks just mentioned, identification of the methylene hydrogens of the benzyl ethers and benzylamines was also possible.

The double quantum filtered COSY spectrum of resin SC 1008 is both interesting and useful because it can be used to identify qualitatively most of the phenolic components of this PF prepolymer resin (see Fig. 2). The



containing 2,4,6-trimethylphenol standard. Arrows point to cross peaks which allow identification of components **1**, **2**, **3**, **5**, **7** and **8**.

DQF COSY spectra of compounds 1-9 were each run and plotted in the aromatic region from 7.5-6.5 ppm. Phenol (1) has only one cross peak cluster caused by coupling between the meta-hydrogens at 7.18 ppm and the ortho, para-hydrogens at 6.8 ppm. o-Methylolphenol (2) has two cross peaks with the one between H-3 and H-4,6 being in a distinctive region where no other cross peaks are found. p-Methylolphenol (3) has only the square four-peak cross peak from the equivalent pairs of ortho- and meta-hydrogens. 2,4-Dimethylolphenol (4) as a square four-peak cross peak between H-5 (7.05 ppm) and H-6 (6.76 ppm). 2,6-Dimethylolphenol (5) has a rectangular cross peak between the doublet at 7.11 and the triplet at 6.77 ppm. 2,4,6-Trimethylolphenol (6) 3,3',5,5'-tetramethylol-4,4'-dihydroxydiphenylmeand thane (9) do not have any aromatic cross peaks. 4,4'-Dihydroxydiphenylmethane (7) has only the square fourpeak cross peak, but it is at a very different position from the similar shaped cross peak of 3. 2,4'-Dihydroxydiphenylmethane (8) has the most complicated COSY spectrum, because it has both an *ortho-* and a *para*substituted phenol in it. The distinctive cross peak for identification of 8 is the rectangular one between H-3 (6.84 ppm) and H-4 (6.99 ppm), which is located very close to the diagonal.

At the digital resolution of 1.3 Hz per point used in the DQF COSY experiments, a small cross peak was seen between the *meta*-hydrogens and both the *ortho*and *para*-methylol methylene hydrogens in 6. In our synthesis of 6, a fair amount of 9 was also present and the DQF COSY spectrum allowed complete assignments of both because the *meta*-hydrogens in 9 have a cross peak with the *ortho*-methylol and diarylmethane methylene hydrogens and the latter peaks are absent in 6.

Coupling constants are less sensitive to solvent influences than are chemical shifts in these compounds. The result of this different behavior of J and δ is that most cross peaks tend to occur at slightly different chemical shift locations in the resin mixture than in the pure compound, but the shape of each cross peak is virtually the same in both. A helpful procedure in the assignments of the COSY peaks in PF resins was to make a transparency of each of the pure compounds 1-8 and then to overlay each individually on the DOF COSY spectrum of the resin. From this procedure, compounds 1, 2, 3, 5, 7 and 8 could all clearly be identified in the resin spectrum and 4 has a probable identification since it is close to one of the cross peaks of 8. These assignments are shown in Fig. 2 with the arrow pointing from the compound number to the center of the assigned cross peak.

A DQF COSY spectrum of the mixture of equal amounts of 1, 2, 3, 7 and 8 was also useful in making the assignments shown in Fig. 2. The DQF COSY spectra of resins A and B confirm the usefulness of this qualitative evaluation technique.

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