

^1H - AND ^{13}C -NMR STUDIES ON PHENOL-FORMALDEHYDE
PREPOLYMERS FOR TANNIN-BASED ADHESIVES

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ABSTRACT

The number average structure and the molecular weight distribution of phenol-formaldehyde prepolymers for use in synthesis of tannin-based adhesive resins were determined with ^1H - and ^{13}C -NMR spectroscopy and gel permeation chromatography of acetylated resins. These methods were used to determine differences in phenol-formaldehyde prepolymers prepared under different reaction conditions. Quantitative ^{13}C -NMR techniques provided a detailed analysis of the structure of a phenol-formaldehyde prepolymer.

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INTRODUCTION

Cold-setting phenolic resins used in the manufacture of laminated wood timbers are usually synthesized by the reaction of phenol-formaldehyde prepolymers with resorcinol. More recently, condensed tannin derivatives from wattle or conifer tree bark extracts have been combined with phenol-resorcinol-formaldehyde resins for cold-setting adhesives of use in both face-lamination or end-jointing.¹⁻⁷ Phenol-resorcinol-formaldehyde adhesives have a long history of successful use in the wood industry and resins made with wattle tannins as substitutes for resorcinol are now widely used for end-jointing and timber lamination in South Africa.⁷ Kreibich and Hemingway⁴⁻⁶ have described several cold-setting adhesive formulations containing 50% of condensed tannins from southern pine bark. Further development of tannin-based adhesives could result from additional understanding of the structure of phenol-formaldehyde prepolymers, their reactions with condensed tannins, and the subsequent curing properties of these resins after addition of aldehydes. This paper, one in a series of studies addressing these objectives,^{8,9} concerns the synthesis and definition of the structure of phenol-formaldehyde prepolymers.

Application of NMR techniques to the elucidation of structures of phenol-formaldehyde resins has grown slowly but steadily since the early ¹H-NMR studies of Woodbrey et al.¹⁰ Analyses for the relative proportions of ortho- and para-methylols and ortho-ortho, ortho-para, and para-para methylene bridges have been vastly improved by ¹³C-NMR.¹¹⁻¹⁸ Studies of solvent effects on ¹³C-NMR chemical shifts permitted more direct application of NMR to industrial quality control.¹² Quantitative ¹³C-NMR methods were developed for the characterization of phenol-formaldehyde and resorcinol-formaldehyde polymers.^{14,15} Most recently, solid-state ¹³C-NMR has been used in the elucidation of structure of cured phenol-formaldehyde resols.¹⁶⁻¹⁷

While the above studies established assignments for most of the signals in these spectra, there have been comparatively few recent works that address the chemistry of phenolic resin polymerization or demonstrated the use of NMR techniques to evaluate changes in resin structure associated with different synthesis conditions. Some recent work such as that by Gollub et al.¹⁸ demonstrates continued industrial interest in the chemistry of phenol-formaldehyde polymers. However, Megson's classic book, Phenolic Resin Chemistry,¹⁹ still provides much of our current knowledge of the chemistry of these polymers. Therefore, a series of experiments was made in an attempt to more fully define the influence of reaction conditions on the structures of phenol-formaldehyde resin polymers prepared under different conditions. A further object of this work was to make comparisons of estimates of molecular structure as determined by ¹H-NMR, quantitative ¹³C-NMR, and gel permeation chromatography (GPC).

RESULTS AND DISCUSSION

A. Analyses of some phenol-formaldehyde prepolymers by ¹H-NMR and GPC of acetylated resins.

Phenol formaldehyde prepolymers were prepared under a wide variety of synthesis conditions (Table 1) to obtain further information about the importance of reaction pH, temperature, and aldehyde ratio on number average structure as determined by ¹H-NMR. In addition, the number average molecular weight estimates obtained by NMR were compared with those obtained by GPC of the acetylated resins.

For the first series of resins, phenol and formaldehyde were combined at a mole ratio of 1 to 2 using either 0.13, 0.27, or 0.80 moles of NaOH per mole of phenol as a catalyst and heated at 90 °C. Samples of the reaction products were withdrawn after

TABLE 1

Phenol-formaldehyde prepolymer synthesis conditions

Resin	Phenol 86%*	Formalin 37.8%	NaOH 50%	Temperature of cook	Time at temp	pH final	Viscosity final
	(mL)	(mL)	(mL)	(°C)	(min.)		cPs- Gardner()
1	104.4	158.7	64	90	120		
2	208.8	317.4	21	90	105	10.5	340
3	208.8	317.4	43	90	120	11.7	410
4	208.8	317.4	36	35	840	11.1	(A)
5	208.8	317.4	32	60	1440	11.1	(A)
6	208.8	317.4	64	60	1260	12.2	(A)
7	208.8	317.4	96	60	1440	12.6	(A)
8	104.4	126.9	16	90	150	10.3	(M)
9	104.4	126.9	32	90	150	10.8	(J)
10	104.4	126.9	48	90	150	11.6	(H)
11	104.4	126.9	64	90	150	12.6	(E)
12	104.4	158.7	50	85	180	11.3	310-(J)

*-- as determined by bromination and titration.

15, 60, and either 105 or 120 minutes at temperature and freeze-dried. $^1\text{H-NMR}$ spectra of the phenolic forms of these products were recorded in dimethylsulfoxide- d_6 . Samples were acetylated with acetic anhydride-pyridine (1:1, v/v) overnight at ambient temperature and the acetylated products were examined by $^1\text{H-NMR}$ and GPC. Results of $^1\text{H-NMR}$ analysis of Resin 1 (0.80 moles of NaOH) show good correspondence in estimates of functional groups from analyses of the acetylated and the phenolic resins.

TABLE 2

Functional Group and Molecular Weight Analyses
of Resin 1

<u>Functional Group</u>	<u>Reaction Time (minutes) at 90 °C</u>				
	15	30	60	90	120
Number of Groups per Aromatic Ring					
<u>Acetates</u>					
Ar-O-H (Assumed)	1	1	1	1	1
Ar-H	2.6	2.7	2.6	2.5	2.5
Ar-CH ₂ -O-H	1.8	1.5	1.5	1.4	1.3
Ar-CH ₂ -Ar	0.28	0.40	0.51	0.63	0.70
<u>Phenols</u>					
Ortho-Ar-CH ₂ -OH	1.3	1.4	1.4		1.5
Para-Ar-CH ₂ -OH	0.41	0.39	0.19		0.00
Total Ar-CH ₂ -OH	1.7	1.8	1.6		1.5
Ar-CH ₂ -Ar	0.23	0.32	0.55		0.73
<u>Molecular Weight</u>					
P	1.39	1.67	2.04	2.70	3.33
M ⁿ (¹ H-NMR)	360	400	500	640	830
M ⁿ (GPC)	320	380	440	650	720
M ⁿ (GPC)	440	550	700	1190	1570
M _w ⁿ					
Dispersivity	1.38	1.45	1.59	1.83	2.18

Estimations of the number average molecular weight projected from ¹H-NMR and gel permeation chromatography on microstyrigel columns were also quite consistent (Table 2). Analyses of the Resins 2 and 3 (0.13 and 0.27 moles of NaOH) by ¹H-NMR and GPC of acetylated resins also provided consistent estimates of the number average molecular weights of these polymers (Table 3).

It is known that the methylation of phenol occurs far more rapidly than condensation to dinuclear and higher molecular weight compounds when formaldehyde is added to phenol at alkaline pH.¹⁹

TABLE 3

Functional Group and Molecular Weight Analyses of Resins 2 and 3

Functional Group	Resin 2			Resin 3		
	Reaction Time (minutes) at 90 °C					
	15	60	105	15	60	120
Number of Functional Groups per Aromatic Ring						
<u>Acetates</u>						
Ar-OH (Assumed)	1	1	1	1	1	1
Ar-H	2.94	2.63	2.63	2.94	2.64	2.48
Total Ar-CH ₂ -OR	1.82	1.49	1.21	1.84	1.51	1.29
Ortho-	1.32	1.17	1.09	1.44	1.30	1.29
Para-	0.50	0.32	0.12	0.45	0.21	0.00
Ar-CH ₂ -Ar	0.14	0.50	0.62	0.17	0.45	0.68
<u>Molecular Weight</u>						
P	1.16	2.00	2.63	1.20	1.82	3.13
M ⁿ (1H-NMR)	313	485	606	355	455	742
M ⁿ (GPC)	321	474	748	322	437	730
M ⁿ (GPC)	448	724	1482	455	709	1571
Dispersivity	1.40	1.53	1.98	1.38	1.62	2.15
Viscosity (cps)			340			410
Final pH			10.7			11.7

It has also been established that the para position is more reactive toward formaldehyde and the resulting para-methylols are more reactive than ortho-methylols in condensation reactions. This higher reactivity is often desirable in polymethylolphenol prepolymers. It might be possible to make a resol with a large amount of para-methylol by reacting formaldehyde and phenol at a low mole ratio, cooling the reaction to about 30 °C and adding more formaldehyde. To test this approach, Resin 4 was prepared by reacting phenol and formaldehyde at a mole ratio of 1 to 2 with 0.23 moles

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TABLE 4

Functional Group Analyses of Resin 4

Functional Group	Reaction Time (Hours.) at 35 °C		
	1	6	14
Ar-OH	1	1	1
Ar-H	3.20	3.12	2.85
Total Ar-CH ₂ OH	1.89	1.94	1.94
Ar-CH ₂ -Ar	0.0	0.0	0.02

of NaOH at 35 °C. ¹H-NMR showed that the methylation of the phenol was nearly complete after only 1 hour and that there was little condensation of methylolphenols after 14 hours of reaction (Table 4). Because Freeman and Lewis¹⁹ carefully described the kinetics of very similar methylation reactions previously, the structure of these products was not explored further. It does seem possible that useful phenol-formaldehyde prepolymers with appropriate methylol functionality could be made in this way.

The strong influence of reaction temperature on the rate of condensation of methylolphenols was examined further by reacting phenol and formaldehyde at a mole ratio of 1 to 2 with 0.2, 0.4, or 0.6 moles of sodium hydroxide (Resins 5, 6 and 7) at 60 °C (Table 5). Nearly 24 hours of reaction at 60 °C were required to achieve a degree of condensation equivalent to that obtained after 1 hour at 90 °C (compare Tables 2 and 5). A strong systematic relationship between the rate of condensation and sodium hydroxide content was not evident in the results of analysis of the series of Resins 1 to 3 or 5 to 7. To further explore the influence of sodium hydroxide content on the condensation rate, a series of

Table 5

Functional Group Analyses of Resins 5, 6, and 7

Resin	pH	Functional Group	Reaction Time (Hours) at 60 °C		
			2	6-7	21-24
			Groups per Aromatic Ring		
5	11.1	Ar-OH	1	1	1
		Ar-H	2.93	2.65	2.72
		Ar-CH ₂ -OH	1.96	1.83	1.32
		Ar-CH ₂ -Ar	0.06	0.25	0.48
6	12.2	Ar-OH	1	1	1
		Ar-H	2.77	2.70	2.35
		Ar-CH ₂ -OH	1.97	1.85	1.41
		Ar-CH ₂ -Ar	0.14	0.22	0.62
7	12.6	Ar-OH	1	1	1
		Ar-H	2.83	2.66	2.16
		Ar-CH ₂ -OH	1.92	1.85	1.68
		Ar-CH ₂ -Ar	0.13	0.24	0.40

resins was made by reacting phenol with formaldehyde at a mole ratio of 1 to 1.6 with either 0.2, 0.4, 0.6, or 0.8 moles of sodium hydroxide at 90 °C (Resins 8, 9, 10, and 11). Analysis of these resins (Table 6) also suggests that the amount of sodium hydroxide used in these reactions has little influence on the rate of condensation although reactions at pH 10.8 consistently gave the highest degree of condensation. However, the viscosity of the

Table 6

Effect of Sodium Hydroxide Concentration on Structure and
Molecular Weight Distribution of Phenol-Formaldehyde
Resins 8 through 11

Resin	pH	Functional Group	Reaction Time (Hours.) at 90 °C		
			0.5	1.0	2.5
<u>8</u>	10.3	Ar-OH	1	1	1
		Ar-H	3.06	2.87	2.93
		Ar-CH ₂ -OH	1.39	1.25	1.09
		AR-CH ₂ -Ar	0.28	0.44	0.59
		M _n (¹ H-NMR)	329	409	564
		M _n ⁿ (GPC)	246	436	564
		M _w ⁿ (GPC)	436	633	1703
<u>9</u>	10.8	Ar-OH	1	1	1
		AR-H	2.92	2.95	2.64
		AR-CH ₂ -OH	1.40	1.14	0.93
		AR-CH ₂ -Ar	0.34	0.45	0.71
		M _n (¹ H-NMR)	363	401	712
		M _n ⁿ (GPC)	280	355	560
		M _w ⁿ (GPC)	473	686	1170
<u>10</u>	11.6	Ar-OH	1	1	1
		AR-H	3.00	2.96	2.74
		AR-CH ₂ -OH	1.40	1.28	1.06
		AR-CH ₂ -Ar	0.30	0.38	0.59
		M _n (¹ H-NMR)	340	370	525
		M _n ⁿ (GPC)	260	---	491
		M _w ⁿ (GPC)	413	---	1064
<u>11</u>	12.6	Ar-OH	1	1	1
		AR-H	3.04	3.04	2.92
		AR-CH ₂ -OH	1.57	1.30	1.12
		AR-CH ₂ -Ar	0.20	0.33	0.48
		M _n (¹ H-NMR)	313	344	420
		M _n ⁿ (GPC)	242	292	369
		M _w ⁿ (GPC)	461	595	786

resins decreased from a Gardner M at a final resin pH of 10.3 for Resin 8 to a Gardner E at a final resin pH of 12.6 for Resin 11.

B. Quantitative ^{13}C -NMR of phenol-formaldehyde prepolymers.

Analysis of phenol-formaldehyde resins by ^{13}C -NMR provides much more detailed information than is obtained from ^1H -NMR, particularly with regard to the ratio of ortho and para methylols as well as the ratio of ortho-ortho, ortho-para and para-para methylenes. Results obtained from analyses of Resin 12 are illustrative of the wealth of information that can be obtained and some of the problems that are encountered in using ^{13}C -NMR to characterize these resins. Resin 12 was made by reacting phenol and formaldehyde at a mole ratio of 1 to 2 at pH 11.0 for 3 hours at 85 °C. The final resin was at pH 11.3 and, at ambient temperature, the viscosity was 310 cps as measured with a Brookfield viscometer or a Gardner J. Spectra were obtained for the sodium salt in methanol- d_4 and for acetylated resins in chloroform- d . When analyzed as the sodium salt, the methylols appear as a complex series of signals that are not readily interpretable in terms of the proportion of ortho and para methylols (Figure 1). A similar problem is encountered in the interpretation of the methylenes. Although the para-para methylene is nicely resolved, the ortho-para and ortho-ortho methylenes appear together as a cluster of signals due to a strong down-field shift of the ortho-ortho methylenes. It is possible to estimate the total methylol and total methylene carbons per phenolic ring but further detail is difficult to extract from these spectra.¹²

^{13}C -NMR spectra of the acetates were much more readily interpreted than those of the free phenols. The spectra (e.g., Figure 1) were normalized by setting the total integral for the aromatic carbons (120-155 ppm) equal to six carbons. The substitution of the ring can then be accounted for as summarized in Table 7. The number of phenolic OH groups can be measured from the

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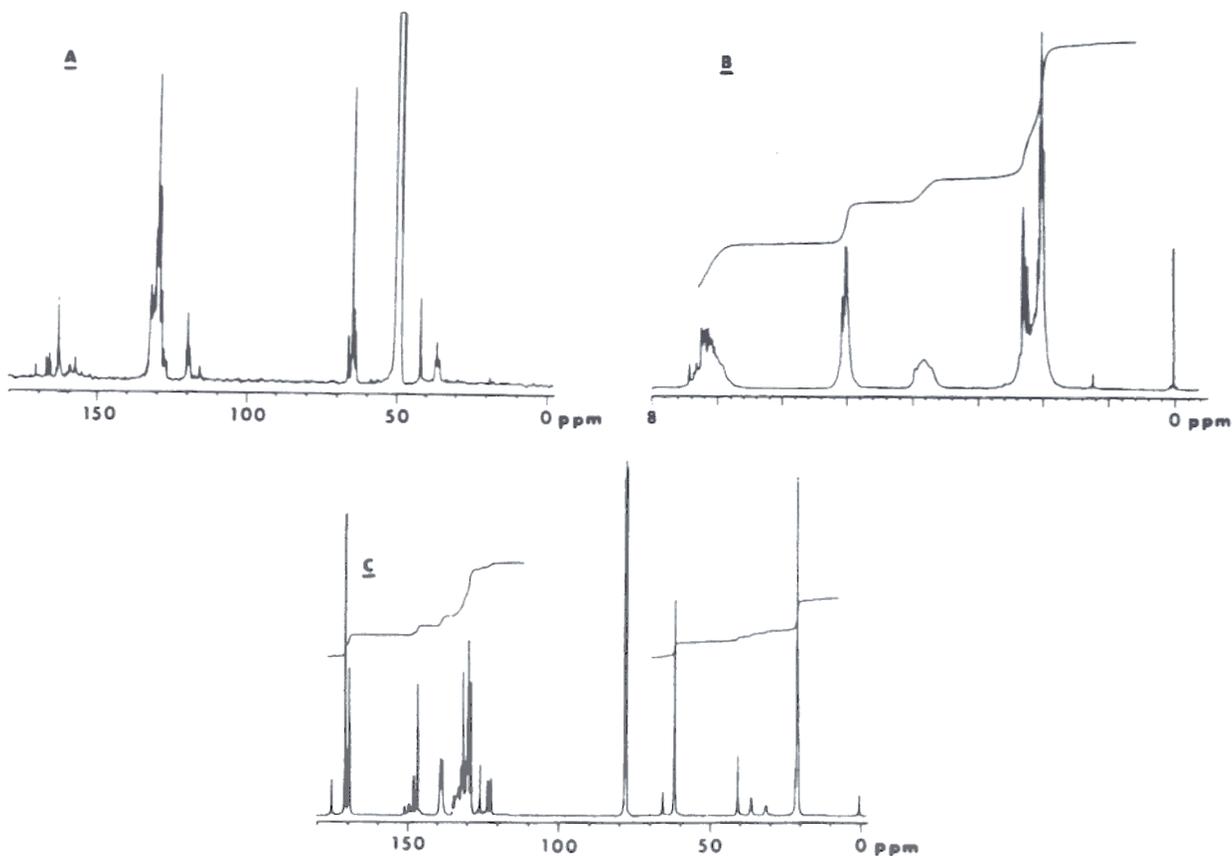


Figure 1. NMR Spectra of Phenol-Formaldehyde Prepolymers; A) Quantitative ^{13}C -NMR spectrum of resin 12 as the sodium salt, B) ^1H -NMR spectrum of the acetylated resin 12, C) Quantitative ^{13}C -NMR spectrum of the acetylated resin 12.

resonance of the phenolic acetyl $\text{C}=\text{O}$ at 169 to 170 which integrates as 1.00 carbon per ring. The C-3 and C-5 (assumed to be unsubstituted as equal to two carbons/ring) and the substituted C-2, C-4 and C-6 carbons appear as a complex group of resonances between 128 and 139 ppm. The latter substituted carbons can then be calculated from the integral of this region and in the Resin 12 amount to 2.63 carbons per ring. Integration of the signals at 121.1 and 122.3 due to the unsubstituted carbons ortho or para to C-1 respectively gave an estimate of a total of 0.37 unsubstituted C-2 + C-6 and C-4 carbons for this resin.

The C-1 carbon appears as a series of four major groups of signals from about 145 to 151 ppm due to substitution ortho and para to this carbon. Comparisons of the C-1 chemical shifts of phenyl acetate with acetate derivatives of ortho- and para-hydroxybenzyl alcohols and 2,2- or 4,4-di(hydroxyphenyl) methanes indicate that there are only small differences in the substitution effects (-1.0 to -1.3 ppm) of methylol or benzyl functions and that their location (ie. ortho or para to C-1) also has little effect (+0.2 ppm for para-para in comparison to the ortho-ortho isomers) on the chemical shift. The upfield shifts are due to substitution of the ring, and integration of these signals permits assignment of the proportions of unsubstituted (150.2 ppm, 3%), mono-substituted (148.5-148.8 ppm, 10%), disubstituted (147.2 ppm, 18%), and trisubstituted (145.8 ppm, 55%) phenol in the reaction product (Table 7). Therefore, we accounted for 2.11 moles of formaldehyde $[0.10+2(0.18)+3(0.55)=2.11]$ using this procedure to estimate the degree of substitution. It is possible to account for all the remaining aromatic carbons through interpretation of the signals in the 121-139 ppm region. The signals at 121.1 and 122.3 ppm, due to the unsubstituted C-2 + C-6 and C-4 carbons respectively integrate to 0.15 and 0.22 carbons per ring. The signals from 128-139 ppm, due to C-3 and C-5 together with the substituted C-2, C-4 and C-6 carbons integrate to 4.63 carbons per ring for a total of 5.00.

The C-4 carbons substituted with a benzyl group are shifted down field to about 137.3-138.2 ppm [e.g., C-4 carbon in the acetate of 4,4-bis(hydroxyphenyl)methane occurs at 138.1 ppm] while those carrying a methylol function would be expected to occur at about 133 ppm (e.g., C-4 in the acetate of p-hydroxybenzyl alcohol occurs at 133.7 ppm). Therefore, it is possible to measure the number of C-4 carbons substituted with a methylene bridge by integration of the signal at 137.3-138.2 ppm which, in this resin, amounts to 0.80 carbons per ring. Integration of the methylene signal at 40.0 ppm gave 0.27 para-para methylenes. The ortho-para methylene resonance at 35.3 integrates as 0.23 methylenes. Inte-

TABLE 7
 Analysis of Resin 12 by Quantitative ^{13}C -NMR
 of the Acetylated Resin

Functional Group	Chemical Shift (ppm)	Carbon atoms per ring
Acetyl Methyls	20-22	
<u>o</u> , <u>o</u> biphenyl methylenes	30-32	0.15
<u>o</u> , <u>p</u> biphenyl methylenes	36-37	0.23
<u>p</u> , <u>p</u> biphenyl methylenes	40-41	<u>0.27</u>
Total Methylene ^{13}C NMR		0.65
Total Methylene ^1H NMR		0.70
<u>o</u> -methylol methylenes	61-63	0.98
<u>p</u> -methylol methylenes	65-66	<u>0.12</u>
Total Methylol ^{13}C NMR		1.10
Total Methylol ^1H NMR		1.22
Unsubs. C-2, and C-6	121.1	0.15
Unsubs. C-4	122.3	0.22
Substituted C-2, C-4, & C-6 and unsubs. C-3 & C-5	128-139	Total 4.63 Unsubs. (-) <u>2.00</u> Subs. 2.63
C-4-benzyl	137-139	0.80
C-1	145-151	
Phenolic acetyl carbonyls	169-170	
<u>o</u> -methylol acetyl carbonyls	170-171	1.15
<u>p</u> -methylol acetyl carbonyls	174.4	<u>0.14</u>

gration of the para methylol signal at either 65-66 or the acetyl C=O at 174.4 accounted for 0.12-0.14 C-4 positions.

While not perfect, these measurements provide a wealth of information about the number average structure of this polymer. The example shown here does not contain any benzyl ether linkages but these too could be measured as their chemical shifts are well resolved from other signals. Comparison of results obtained from $^1\text{H-NMR}$ spectra of resin 12 with the conclusions reached from these analyses of the carbon spectrum show that the conclusions reached on the total methylol and methylene functionality are very similar, giving $P_n=3.33$ with $M_n=776$ and $P_n=2.86$ and $M_n=640$, respectively. Amos²⁰ suggests that $^{13}\text{C-NMR}$ spectra often project lower proportions of methylenes even when comparatively long pulse delays are used because of restricted rotation. He recommends determining the total methylene/aromatic ring by subtraction of the number of methylols from the total of substituted aromatic carbons or $2.63 - 1.10 = 1.53/2 = 0.765$ as compared with 0.70 methylenes/ring as measured by $^1\text{H-NMR}$ (Table 7). Overall, the results highlight the large amount of additional information that can be derived from a quantitative $^{13}\text{C-NMR}$ spectrum.

EXPERIMENTAL SECTION

A. Analyses of some phenol-formaldehyde prepolymers by $^1\text{H-NMR}$ and GPC of acetylated derivatives.

Reaction conditions used in the synthesis of the Resins 1 through 12 are summarized in Table 1. The phenol content of the "90%" solution was determined by bromination and titration. Analytical 37.8% formalin solutions were used in all the resins described here. The resins were prepared in a glass reaction kettle heated with a steam coil and cooled with a cold-water coil,

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both of which were fitted to temperature controlled valves. The reaction kettle was fitted with a condenser, a stirrer, and a tube to permit sampling of the product after different reaction times. Resin samples were freeze-dried and acetylated as described previously⁸ with the exception that the dichloromethane-soluble material was washed several times with dilute acetic acid rather than using repeated evaporation of toluene to remove pyridine.

Proton spectra of the phenolic samples were recorded in dimethylsulfoxide-d₆ and spectra of the acetylated resins were recorded in chloroform-d at 60 MHz using a Perkin Elmer-Hitachi^b spectrometer. GPC of acetylated resins was done using a Waters Associates instrument fitted with a series of Microstyrigel columns (10⁴A⁰ x 1'; 10³A⁰ x 1', 500A⁰ x 2', and 100A⁰ x 2') and eluted with chloroform. Standard polystyrene and polypropylenes were used for calibration.

The degree of polymerization (P_n) was determined by $P_n = 1/(1-M_b)$, where M_b is the number of methylene bridge units per ring as determined by ¹H NMR. The number average molecular weight (M_n) was calculated by multiplying the P_n times the mass of the functional group times the number of groups per ring and then combining the values for each group. For example, number average molecular weight for Resin 2 (Table 3) after heating for 105 minutes would be $M_n = \text{ArOAc} (2.63 \times 131 \times 1) + \text{ArH} (2.63 \times 1 \times 2.62) + \text{ArCH}_2\text{OAc} (2.63 \times 73 \times 1.21) + \text{ArCH}_2\text{Ar} (2.63 \times 14 \times 0.62) = 606$.

B. Quantitative ¹³C-NMR of phenol-formaldehyde prepolymers.

A phenol formaldehyde prepolymer (Resin 12) was made as shown in Table 1. The sample was freeze-dried. A portion was dissolved

^b--Use of trade names does not constitute endorsement by the United States Department of Agriculture.

in methanol-d₄ and the ¹H- and ¹³C-NMR spectra were recorded at 250 MHz for protons and 62.9 MHz for carbons on a Bruker WM-250 spectrometer controlled by an Aspect 2000A minicomputer. Another portion was acetylated using excess pyridine-acetic anhydride at ambient temperature for 48 hours. The sample was worked up by extraction into dichloromethene from water followed by repeated (4-5 times) evaporation of toluene to remove residual acetic acid and pyridine. When the odor of pyridine was no longer detectable, the sample was placed under high vacuum for 1 hour at ambient temperature and dissolved in chloroform-d (500 mg in 2.0 mL) for NMR analysis. The quantitative ¹³C-NMR spectra were acquired with a Bruker WM-250 spectrometer as previously described²¹ with the exception that the relaxation delay was lengthed to 14 seconds (45° tip angle).

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