

# Determination of Composition of Mixed *meta*- and *para*-Cresol/Formaldehyde Novolaks by $^{13}\text{C}$ -NMR Spectroscopy

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## INTRODUCTION

Cresol/formaldehyde novolaks are important components of photoresists for semiconductor microcircuit fabrication. The relative amount of *m*-cresol and *p*-cresol incorporated into the resin effect important properties such as resist photospeed. The literature includes methods for determination of methylene bridge position of pure *meta*-cresol novolak.<sup>1,2</sup> Pampalone<sup>3</sup> reported that the composition of mixed *meta/para*-cresol novolaks could be determined by  $^{13}\text{C}$ -NMR spectroscopy by integrating the methyl carbons. However, no data were presented to document the accuracy of the method. DeBreet and co-workers<sup>4</sup> reported the utility of  $^{13}\text{C}$ -NMR to determine structure of several phenol and amino formaldehyde resins. This work extends the NMR method to determine copolymer composition quantitatively.

## EXPERIMENTAL

### Spectroscopy

$^{13}\text{C}$ -NMR spectra were obtained using a Bruker WP200 superconducting Fourier transform NMR spectrometer with a carbon frequency of 50.13 MHz. Approximately 1.5 g of resin was dissolved in 5 mL of acetone- $d_6$  and spectra were recorded in 10 mm diameter sample tubes.

Spectra were recorded using a sweep width of 10,000 Hz with a pulse width of 17  $\mu\text{sec}$ . Inverse gated broadband decoupling was used to suppress Nuclear Overhauser effects. A read delay of 5 s was used for recovery of magnetization between pulses. 4000 transients were averaged.

## RESULTS AND DISCUSSION

Table I includes the incremental shifts of substituents on aromatic carbons taken from the literature. These shifts are applied to calculate chemical shifts for the aromatic carbon atoms of *p*-cresol and *m*-cresol oligomers with formaldehyde. All adjacent rings are considered as benzyl groups and all possible isomeric methylene bridged structures were calculated. In the case of *p*-cresol

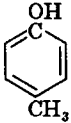
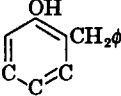
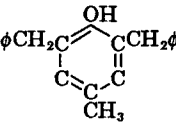
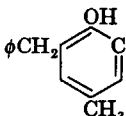
TABLE I  
Incremental Shifts of Aromatic Carbons Relative to Benzene ( $\delta = 128.5$  ppm)

Substituent	Chemical shift of:			
	C1	C2	C3	C4
OH	+28.9	-13.0	+1.0	-9.3
CH <sub>3</sub>	+8.9	+7	-1	-2.9
CH <sub>2</sub> Ø	+12.7	+4	0	-2.6

adducts, only ortho monosubstituted and disubstituted rings were possible. In the case of *m*-cresol, ortho-mono substituted, para-monosubstituted, ortho-ortho disubstituted, and ortho-para disubstituted meta cresol ring carbons were calculated. The assignments of calculated chemical shifts for 100% *p*-cresol novolak and 100% *m*-cresol novolak are included in Tables II and III respectively. The spectrum of *p*-cresol novolak in the aromatic region is represented in Figure 1. The peak clusters found matched those regions which were calculated (Table II). The spectrum of *m*-cresol novolak (Fig. 2) contains many more peaks since more isomers are possible. The peak clusters found are compared to those calculated in Table III and match well.


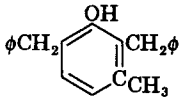
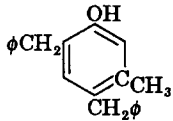
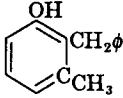
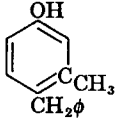
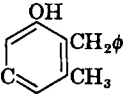
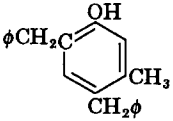
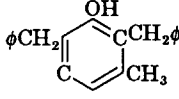
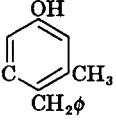
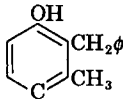
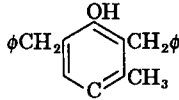
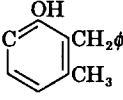
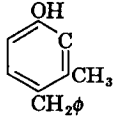
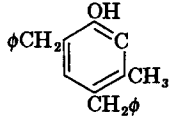
The peaks in the 135 to 138 ppm region are unique to the *m*-cresol rings, representing the methyl substituted meta carbons. The peaks in the 120 to 135

TABLE II  
Chemical Shifts of *p*-cresol-Formaldehyde Resin<sup>a</sup>

Calculated	Found	Assigned
158	150-154	
127,	127-131	
128,		
130		
115	115	

<sup>a</sup> Aromatic carbons assigned are displayed as C in ring.

TABLE III  
Chemical Shifts of *m*-cresol-Formaldehyde Resins

Calculated	Found	Assigned	
153,	152-156		
156			
137,	135-138		
138,			
139			
125,	124-133		
127,			
128,			
129, 130			
122	120-123		
123			
113			
116	112-118		
117			

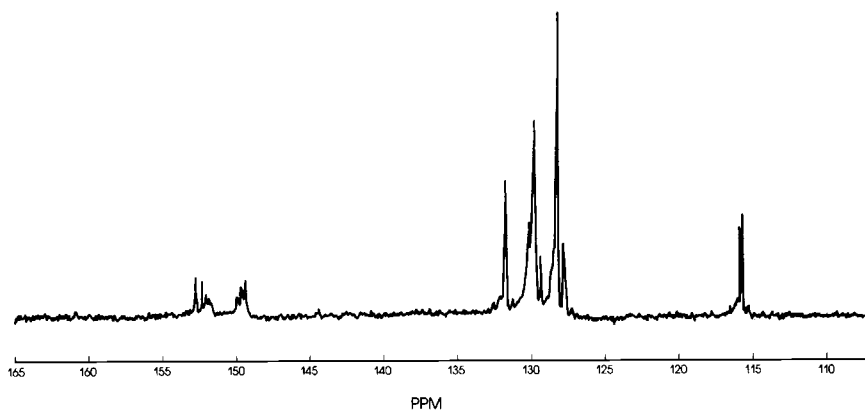


Fig. 1.  $^{13}\text{C}$ -NMR spectrum of *p*-cresol novolak in aromatic region.

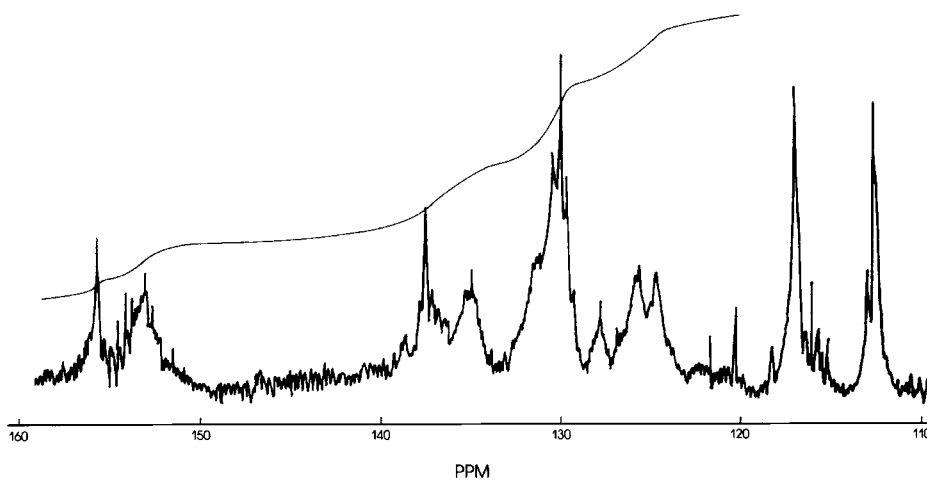


Fig. 2.  $^{13}\text{C}$ -NMR spectrum of *m*-cresol novolak in aromatic region.

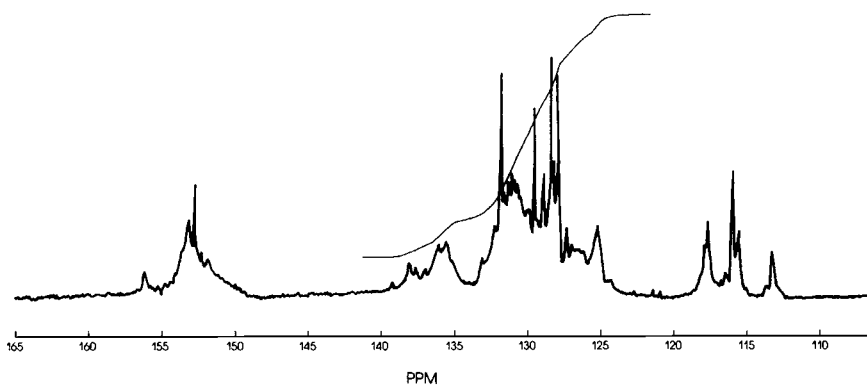


Fig. 3.  $^{13}\text{C}$ -NMR spectrum of 62% *m*-cresol/38% *p*-cresol novolak in aromatic region.

TABLE IV  
Integrated NMR Ratio vs. Stoichiometric Composition

Wt % <i>m</i> -cresol <sup>a</sup>	Area 135–138 ppm Area 120–135 ppm	Value calculated from least-squares plot
58	0.15	53
62	0.16	57
69	0.20	72
80	0.22	78
100	0.30	105

<sup>a</sup> Percent of total cresol content.

ppm region contain aromatic carbons from both cresols. The ratio of the integrated area of the 135 to 138 ppm region to that of the 120 to 135 ppm region should be proportional to % cresol.

The NMR spectra of several cresol novolaks in the range from 58% *m*-cresol to 80% *m*-cresol were recorded under identical conditions. Figure 3 is a spectrum of a 62% *m*-cresol/38% *p*-cresol novolak which is typical. The percentage of each isomer in the mixed cresol novolak was calculated from the charge of each cresol and the amount remaining after polymerization determined by gas chromatography. Table IV includes the integrated ratios vs. composition and Figure 4 is the linear least squares plot of the data. The correlation coefficient was .9979 and the average value of each sample calculated from the least squares

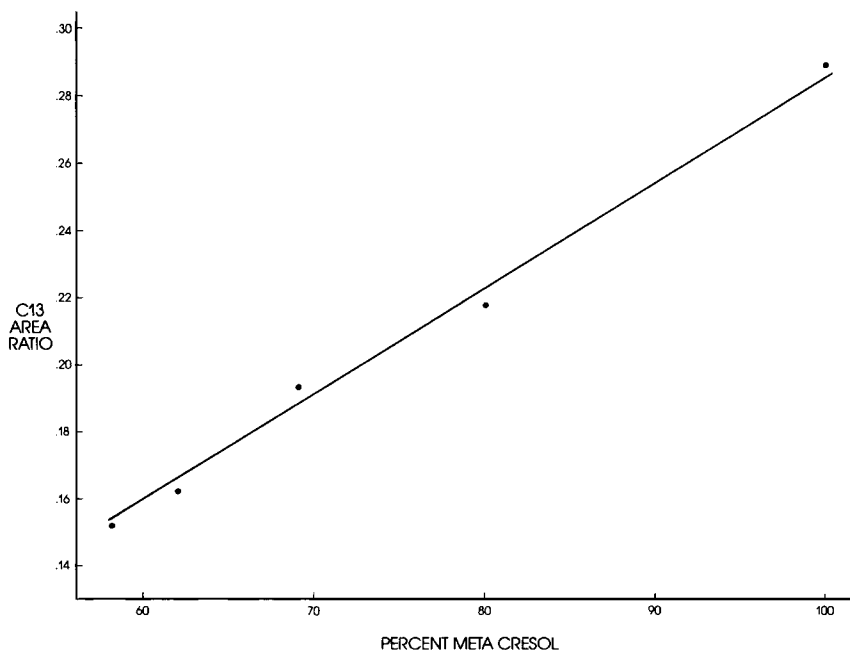


Fig. 4. Linear least-squares plot of NMR ratio vs. percent composition.

plot was within 5 wt % of the stoichiometric value. The experimental data fit the line defined by  $y = .002824x + .00026$ , where  $y$  = area ratio and  $x$  = wt % *m*-cresol. The linearity was not investigated below 58% *m*-cresol.

The NMR method is a relatively fast, nondestructive technique which is accurate within 5 wt % in the region of 58 to 100% *m*-cresol content.

### References

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