

## Carbon-13 Nuclear Magnetic Resonance Study of a Divinylbenzene-*p*-Cresol Oligomer Mixture

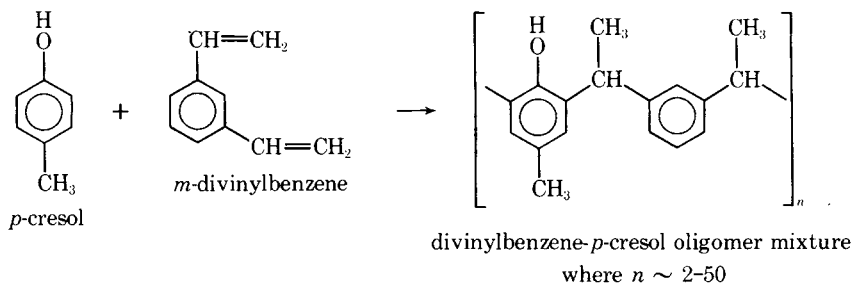
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### Synopsis

$^{13}\text{C}$  NMR has been found to be useful in elucidating the structure of a complex condensation product. Study of a divinylbenzene-*p*-cresol oligomer mixture has shown structural units consisting of approximately 85% 2,6-substituted *p*-cresol, 5-10% 2,5-substituted *p*-cresol, and 5-10% 2-substituted *p*-cresol endgroups.

### INTRODUCTION

Interest in our laboratories in novel oligomeric and polymeric antioxidants<sup>1</sup> prompted us to reinvestigate the synthesis of a divinylbenzene-*p*-cresol oligomer mixture.<sup>2</sup> The basic polymerization reaction is as follows:



In general, the reaction is expected to proceed via condensation of the vinyl groups of divinylbenzene in the ortho position of *p*-cresol. Since the commercially available divinylbenzene used in the reaction contains 22% ethylvinylbenzene (which is a chain terminator), the resulting condensation product would be expected to be an oligomer mixture with a distribution centered about the species containing ten *p*-cresol units. The current study is an attempt to elucidate the structure of the oligomer units resulting from this polycondensation.

### EXPERIMENTAL

The divinylbenzene-*p*-cresol condensation was carried out using 100 mmoles *p*-cresol (Aldrich, 99%) and 120 mmoles Dow 95% pure divinylbenzene of the following composition: 50.5% *m*-divinylbenzene, 23.9% *p*-divinylbenzene, 13.4% *m*-ethylvinylbenzene, and 7.6% *p*-ethylvinylbenzene; 3

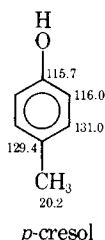
mmoles aluminum (Baker and Adams aluminum turnings) was used as catalyst. The *p*-cresol, the aluminum, and 1 ml xylene were heated at 160°C for 15 min to form the catalyst aluminum cresoxide. Then the divinylbenzene and 24 ml xylene were added. The reaction mixture was heated at reflux (150°C) for 19 hr, diluted with dichloromethane, washed three times with dilute HCl (to remove aluminum), and then precipitated from petroleum ether. The yield was 61% by weight.

The samples for  $^{13}\text{C}$  NMR were prepared by dissolving 1.0 g solid sample in 1.5 ml *p*-dioxane (Matheson Coleman and Bell Spectroquality) and 0.5 ml  $\text{CHCl}_3$  (Merck Sharp and Dohme Silanor\*-C).

Spectra were recorded on a Varian XL-100 spectrometer at 25.2 MHz using pulsed NMR with Fourier transform. The following instrument settings were used: spectral width = 5000 Hz; acquisition time = 0.400 sec; pulse width = 65  $\mu$  sec; sensitivity enhancement = 0.40 sec; true spectral width = 5120; Hz/point = 2.50. The ppm scale was defined by setting the dioxane solvent peak at 67.4 ppm. Spectra were taken of the synthesized oligomer mixture and of the *p*-cresol (Aldrich). The *p*-cresol spectrum was used as an aid in assigning peaks.

## RESULTS AND DISCUSSION

Shifts for monomeric *p*-cresol were found to be as follows:



where shifts are given in ppm downfield from TMS.

The spectra for the divinylbenzene-*p*-cresol condensation product are given in Figures 1 and 2. The basic link resulting from condensation of a divinylbenzene with a benzene ring is  $-\text{CH}(\text{CH}_3)\phi$ . The closest reference structure for which aromatic substituent effects could be found was  $-\text{CH}(\text{CH}_3)_2$ .<sup>3</sup> Substituent effects for adding this group to a benzene ring are as follows: substituted carbon, +20.0 ppm; ortho effect, -2.1 ppm; meta effect, -0.1 ppm; para effect, -2.6 ppm. Using *p*-cresol shift values given above and these substituent effects, predicted shifts were calculated for all possible divinylbenzene-*p*-cresol additions including mono-, di-, tri-, and tetra-substituted *p*-cresol units. Predicted shifts were also calculated for carbons of the divinylbenzene aromatic rings after condensation by applying the same substituent effects to the benzene ring using a value of 128.5 ppm for the benzene carbon. Predicted shifts for ethylvinylbenzene units have been estimated by applying the same substituent effects to the shift values of ethylbenzene which have been published.<sup>4</sup>

Predicted shifts were compared to the shifts observed in the polymer spectrum (Fig. 1). It was found that there were only three possible *p*-cresol units



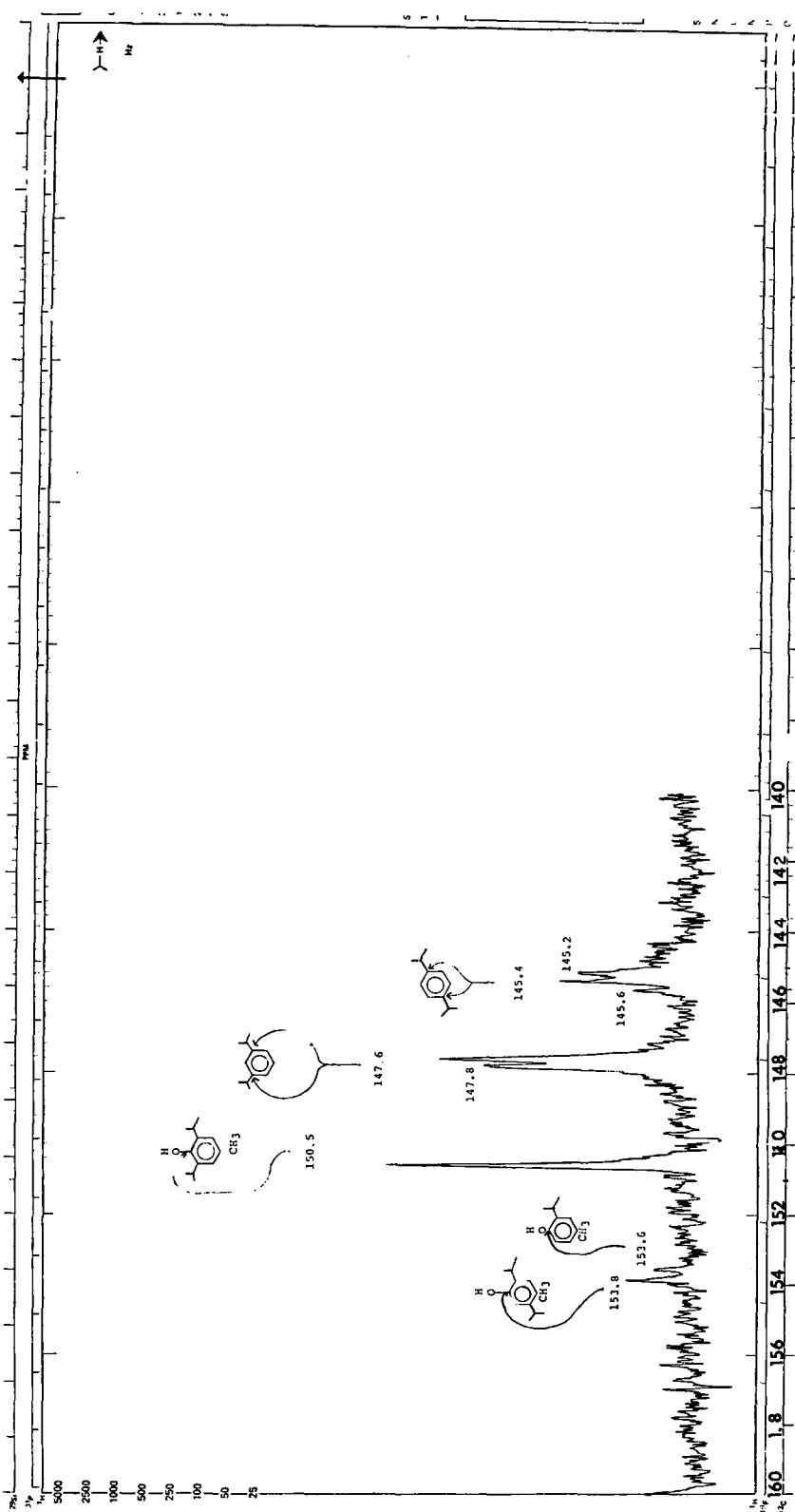


Fig. 2. Expanded low field region of the  $^{13}\text{C}$  NMR proton decoupled spectrum of poly (DVB/*p*-cresol) in dioxane and  $\text{CDCl}_3$  as given in Fig. 1. Peak assignments for the carbons of the various mer units are shown in the given structures. Scale is downfield from tetramethylsilane (TMS).

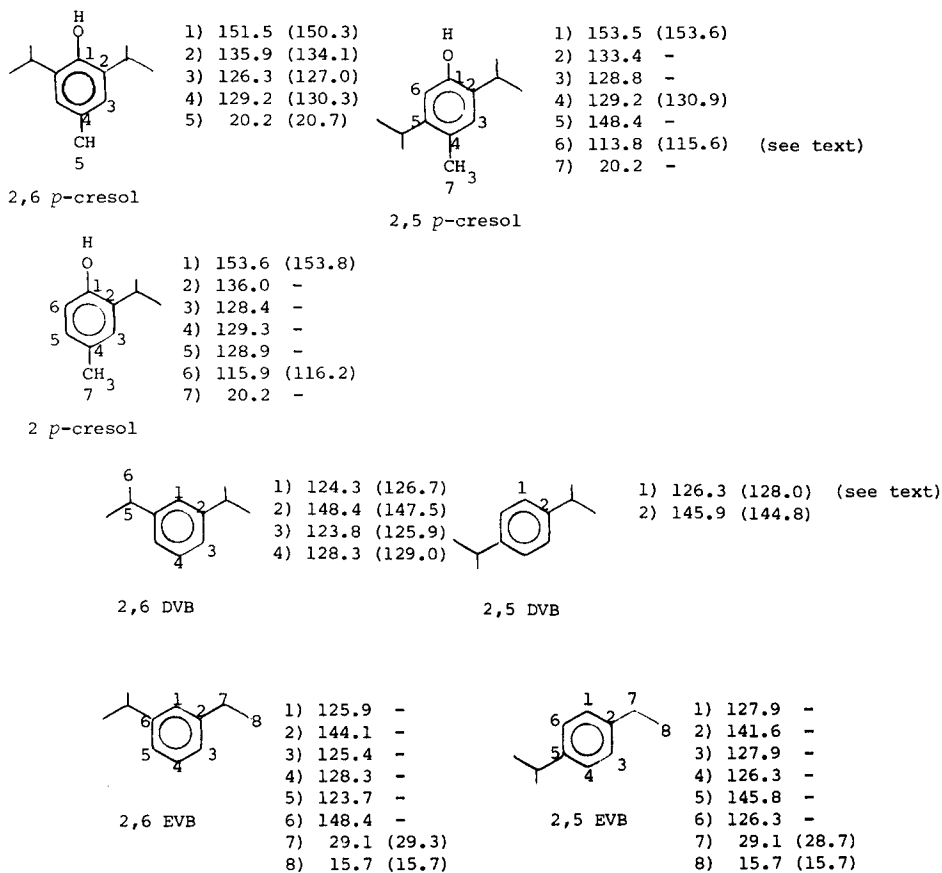
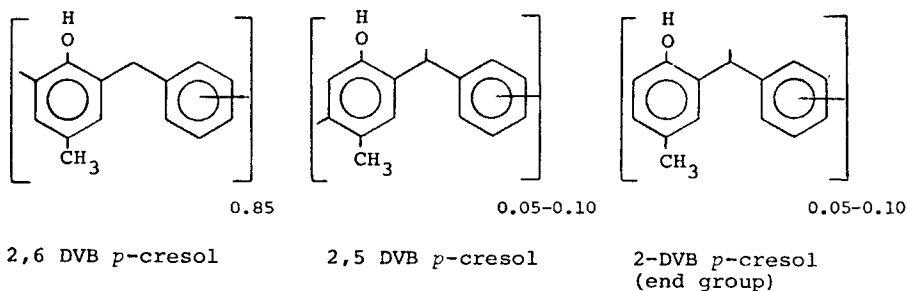


Fig. 3. Predicted shifts from substituent effects of +20.0, -2.1, -1.1, -2.6, applied to *p*-cresol shifts, benzene value of 128.5 ppm and ethylbenzene spectrum.<sup>4</sup> Assigned values are given in parentheses. Where a small peak would be contained in larger peak, no entry has been made under assigned value. Note: The methyl and methine carbons of the —CH(CH<sub>3</sub>)—linking group are easily assigned by comparison with the spectrum of cumene.<sup>4</sup> The assignments are as follows: methine, meta isomer, 38.6 ppm; methine, para isomer, 38.0 ppm; and methyl, 21.2 ppm.

that had shifts consistent with the observed ones. The expected meta and para divinyl- and ethylvinylbenzene units were also observed. The three *p*-cresol units and the vinylbenzene units consistent with the spectrum are given along with predicted and assigned shifts in Figure 3. At this point, some interesting observations on the relationship between predicted and experimental shift values for each of the units might be made as follows.

The predicted values for the 2,6-substituted *p*-cresol unit in Figure 3 are in agreement within 2 ppm with a set of uniformly large peaks in the spectrum given in Figure 1. There seems to be little doubt that these peaks represent the 2,6-substituted *p*-cresol unit.

The predicted set of values for the 2,5-substituted *p*-cresol unit are tabulated in Figure 3. Comparison with observed peaks in the spectrum in Figure 1 shows small but clear signals in agreement ( $\pm 2$  ppm) with predicted values for carbons 1 and 3. Predicted values of 133.4 and 148.4 for carbons 2 and 5 may not be as reliable as other predicted values since they involve the large



Where the structure may be a DVB link to another *p*-cresol unit or may be a terminal EVB.

Fig. 4. Estimate of composition of poly(DVB/*p*-cresol).

+20.0 ppm direct substitution effect. The predicted values fall near large peaks at 147.5 and 134.1 ppm and are probably contained in these larger envelopes. Carbon 7 is not expected to be differentiated from carbon 7 of the other *p*-cresol units. Carbon 6, however, is predicted to have a shift of 113.8 ppm. This prediction would be expected to be very reliable since the basis of the prediction is a  $-0.1$  ppm meta effect and a  $-2.1$  ppm ortho effect applied to the observed shift of carbon 6 of *p*-cresol. This predicted value of 113.8 ppm is then in real disagreement with the observed shift at 115.6 ppm. It should be noted, however, at this point that the predicted substituent effects of the  $-\text{CH}(\text{CH}_3)_2$  group of +20.0 ppm for the substituted carbon ortho  $-2.1$  ppm, meta  $-0.1$  ppm, and para  $-2.6$  ppm are derived from cases of *monosubstitution*. Clearly, in the case of the 2,5-substituted *p*-cresol unit, there are *two* substituents and these are para to each other. It might be expected that such symmetrical disubstitution might reduce substituent effects. There is in the spectrum given in Figure 1 a simple example of a structural unit which would imply that such is the case. The *para*-divinylbenzene structural unit is the only such unit with four equivalent carbons. This peak is unmistakable at 128.0 ppm. The given substituent effect values would predict a shift at 126.3. This prediction would be expected to be very reliable since the basis of the prediction is a  $-0.1$  ppm meta effect and a  $-2.1$  ppm ortho effect applied to the observed shift of 128.5 ppm for benzene carbons. If one assumed a similar diminished substituent effect for symmetrical disubstitution for the 2,5-substituted *p*-cresol unit, this would change the predicted shift for carbon 6 given in Figure 3 to 115.5 ppm. This is in close agreement with an observed signal at 115.6 ppm.

A set of predicted values for shifts of the 2-substituted *p*-cresol unit (*p*-cresol endgroup) is shown in Figure 3. Small but clear peaks correspond to predictions for carbons 1 and 6. Other signals would be expected to be obscured by larger peaks.

With the exception of the 1, 3, 4, and 6 carbons of the 2,5-divinylbenzene unit as discussed above, predicted and observed shifts for the divinylbenzene and ethylvinylbenzene units agree well and peak areas qualitatively correspond to stoichiometry.

The primary conclusion of this study is that the *p*-cresol units of the oligomeric antioxidant have been incorporated into the divinylbenzene-*p*-cresol structure as approximately 85% 2,6-substitution, 5–10% 2,5-disubstituted, and 5–10% 2-monosubstituted *p*-cresol units. An overall structure is given in Figure 4.

A secondary observation made in the course of this study relates to the apparent nonadditivity of substituent effects for para disubstitution of a benzene ring as in the case of the 2,5-*p*-cresol and 2,5-DVB units of Figure 3.

Considering the overall structural findings summarized in Figure 4, the only unexpected result is that there are two types of *p*-cresol units other than the principal 2,6-substituted *p*-cresol. A previous study of alkylation of 4-substituted phenols with aluminum phenoxide-type catalysts has shown that a mixture of 2- and 2,6-substituted products would be expected.<sup>5</sup> With the stoichiometry used in the synthesis of the compound studied herein, the 2,6-substituted *p*-cresol unit would be expected to be the exclusive product. The 2-substituted unit would of course be an endgroup *p*-cresol unit. The other *p*-cresol unit, the presence of which is clearly indicated in Figures 1 and 2, has been assigned the 2,5-*p*-cresol structure. The presence of such units might be caused by steric blocking of the 6-position resulting from polymer chain conformation for some additions of divinylbenzene to the polymer chain.

### References

1. T. Furia and N. Bellanca, Paper presented at the 66th Annual Meeting of the A.O.C.S, Dallas, Texas, April 1975.
2. O. L. Hunt, (to E. I. du Pont de Nemours, Inc.), U.S. Pat. 3,546,173 (Dec. 8, 1970).
3. G. Levy, unpublished data.
4. L. Johnson and W. Jankowski, *Carbon-13 NMR Spectra*, Wiley-Interscience, New York, 1972.
5. A. Kolka, J. Napolitano, A. Filbey, and G. Ecke, *J. Org. Chem.*, **22**, 642 (1957).

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