Determination of Cresol Novolak Copolymer Composition and Branch Density Using Carbon-13 NMR Spectroscopy

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ABSTRACT: Carbon-13 NMR spectroscopy is used to determine hitherto unmeasurable novolak copolymer compositions and the *m*-cresol novolak polymer branch density for soluble samples. The estimate of variance in cresol novolak copolymer compositions determined this way is ca. 1% of the value. For copolymers containing phenol, the estimate of variance is ca. 10% of the value. Analysis of the competition for formaldehyde between sites on the same phenolic monomer and between different phenolic monomers yields the relative reactivities of the sites and the monomers. The reactivities of *o*-cresol, *m*-cresol, and *p*-cresol relative to phenol are 2.36 ± 0.05, 6.03 ± 1.78, and 0.47 ± 0.01, respectively.

Novolak resins are the products of the acid-catalyzed condensation of phenols with formaldehyde. Although the first commercial novolak resins appeared in 1910,[1] these materials continue to have significant commercial importance. Novolak resins are commonly characterized by melt or solution viscosity and (less frequently) by gel permeation chromatography. The use of NMR spectroscopy in the analysis of these resins is a technique that has not yet been fully exploited. ^{1}H NMR has been used to determine the M_n of phenol novolak resins by taking the ratio of ring proton resonances to methylene proton resonances.[2] ^{13}C NMR has been used to determine the relative amounts of *o,o'*-, *o,p'*-, and *p,p'*-methylene bridges in phenol novolak homopolymers. Two groups have published ^{13}C NMR chemical shift assignments for the isomeric phenol novolak dimers and trimers.[3] Other workers have reported the ^{13}C NMR spectra of phenol novolak polymers,[4] oligomers, and model compounds[4a,c,5] in solution and in the solid state.[6] One study reported the ^{13}C NMR spectra of Bisphenol A and *p-tert*-butylphenol novolak resins.[7] There are two reports on the use of 2D NMR techniques with phenolic resins.[8]

One high-performance use of novolak resins is as the etch resistant, polymeric component of photoresists for microlithography. The novolak resins most useful for photoresist formulation are based on one or more cresol isomers. There are few reports of the ^{13}C NMR spectra of cresol novolak resins. One group of these drew structural inferences from relative ring carbon peak heights in *m*-cresol novolak homopolymers.[9a–e] Another reported ^{13}C NMR spectra of novolak homopolymers of each of the cresol isomers and used end-group analysis to measure M_n of the *p*-cresol novolak.[9f] One worker reported a method for the determination of the composition of novolak copolymers of *m*- and *p*-cresols with formaldehyde using ^{13}C NMR spectroscopy.[9g] In this paper we report a similar method that is simpler to use and has broader application. This field has been reviewed.[10]

Novolak copolymer compositions are generally reported as the ratio of comonomers charged to the kettle. These can be substantially different from the ratio incorporated into the polymer. Since the existing methods offer no way to determine novolak copolymer composition, we have developed this ^{13}C NMR technique to determine the composition of soluble cresol novolak resins.

Results and Discussion

Peak Assignments. We assigned the peaks in the spectra of the cresol novolak resins by starting with the spectra of cresol novolak dimers. The dimers were prepared by the reaction of formaldehyde with a large excess (≥50 equiv) of phenolic monomer under typical novolak synthesis conditions.

Assignments of the peaks in the NMR spectra of the phenol novolak dimers have been published.[1] We confirmed these by recording the spectra of the pure *o,o'* and *p,p'* isomers (available from Aldrich). Knowing these peak assignments, we were able to compare them with the spectra obtained from the mixtures of isomeric dimers we had prepared. In the case of phenol, we found good agreement with the published assignments. In the case of *o*-cresol, three similar isomers are formed. If, by analogy to the phenol novolaks, we assume that the chemical shifts of the methylene carbons are shifted upfield with ortho substitution of the ring, then the methyl and phenolic carbon resonances can be assigned to the different isomers by comparison of integrated areas in those regions with integrated areas in the methylene region. In the case of *p*-cresol, only one isomer can be formed, so peak assignment is straightforward.

In the case of *m*-cresol, three symmetric and three dissymmetric isomers can be formed (Figure 1), giving six possible resonances for the methylene carbons and nine possible resonances for both the phenolic and the methyl carbons. Unequivocal assignment of these resonances required the preparation of mixtures containing subsets of the set of six possible isomers together with the use of 2D INADEQUATE NMR experiments. The details of these experiments are the subject of another report,[11] but the results are summarized in Figure 1.

Our next step was to compare the spectra of higher polymers with those of dimers. Since the spectra of the dimers showed peaks for only end-group rings, the set of experiments allowed us to differentiate end groups from the main chain. In each case, the phenolic carbons at the chain ends are shifted downfield of those inside the chains. (This separation is not perfect when some rings can react with three formaldehyde molecules, as in the case of *m*-cresol or phenol.) For phenolic carbon resonances, free monomer shifts are downfield of polymer shifts. The phenolic carbon region of the spectrum then can be broken down into three regions: free monomer, chain-end, and midchain resonances. The methyl carbon region can also be broken down into monomer and polymer regions. These data are presented in Figure 2.

In comparison of the chemical shifts observed for dimers with those observed for polymers, two additional differences were noticed. First, the chemical shifts of the *o,p'*-

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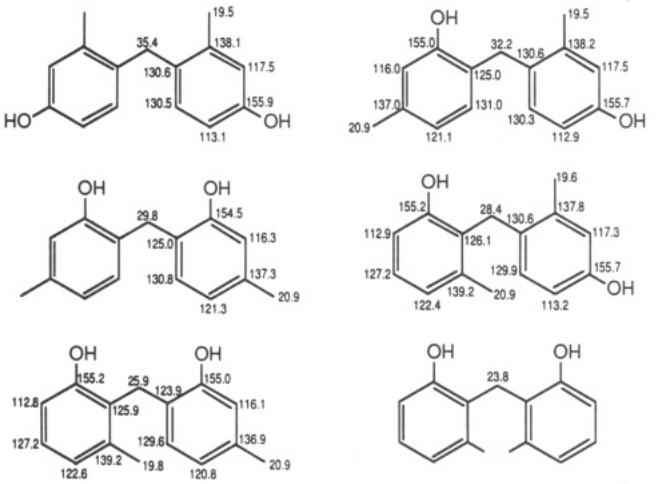

Figure 1. Six possible *m*-cresol novolak dimer isomers and their ^{13}C chemical shifts (dioxane-d_8 solutions, 0.2 g of dimer in 0.4 mL of dioxane).

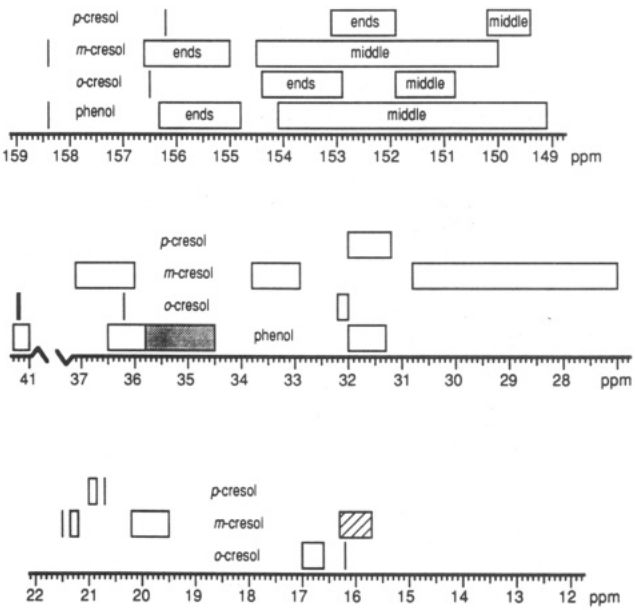

Figure 2. ^{13}C NMR chemical shifts in novolak polymers as solutions in THF-d_8.

methylene carbons in a high-ortho phenol novolak resin (Alnovol resin from Hoechst) fall over a wider range than for any other phenol novolak homopolymer. The anomalous chemical shifts are denoted in Figure 2 by shading. It is possible that these shifts arise from branching of the ortho-linked chain. Second, *m*-cresol novolak polymers, but not dimers, exhibit methyl carbon resonances in the range from 15.7 to 16.3 ppm (the striped area in Figure 2).

We assign this high-field resonance to a methyl carbon on a *m*-cresol ring that is substituted by methylene bridges at the 2 and 4 positions (at either side of the methyl group). Data that support this assignment are shown in Figure 3 for five (polymethyl)phenol model compounds.[12] We modeled the condensation of *m*-cresol with formaldehyde by assuming that the relative site reactivities of *m*-cresol (vide infra) remain unchanged throughout the reaction.[13] This simple model gave good agreement of the number-average degree of polymerization, DP_n, the total resin yield, and the amount of 2,4-substitution with experiment. As the molecular weight of the resin increases, an increasing fraction of these are branch sites. With use of the data from this model, Figure 4 shows how the fraction of 2,4-

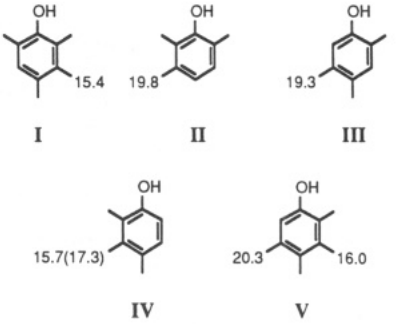

Figure 3. Chemical shifts in ppm of meta methyl carbons in 2,3,6-,[9a] 2,4,5-,[9b] and 2,3,4-trimethylphenols[9a,b] and 2,3,4,6- and 2,3,4,5-tetramethylphenols.[9a] Solutions in $CDCl_3$, referenced to TMS at 0 ppm.

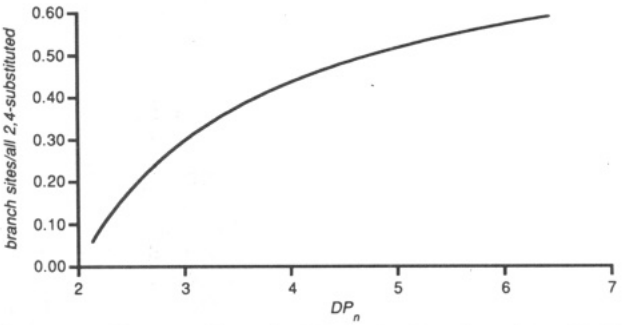

Figure 4. Change with resin DP in the fraction of 2,4-disubstituted rings that are branch sites.

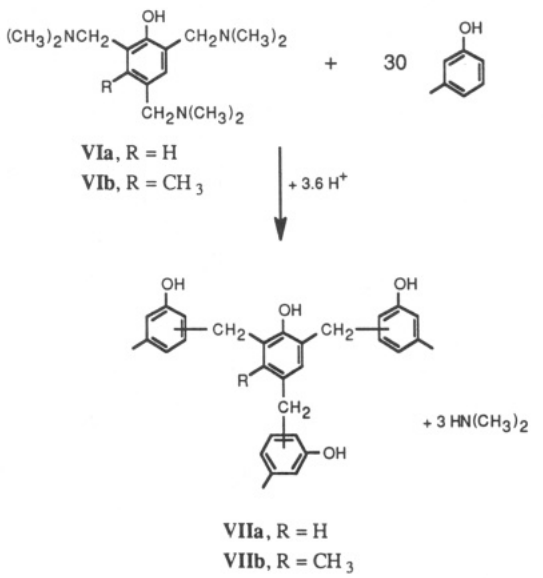

Figure 5. Preparation of branched tetramers VIIa and VIIb from *m*-cresol and tris[(dimethylamino)methyl]phenol (VIa) or tris[(dimethylamino)methyl]-*m*-cresol (VIb).

dialkylated rings that are branch sites increases with the resin DP_n.

We prepared model novolak resins by the reaction of tris[(dimethylamino)methyl]phenol (Rohm and Haas DMP-30; VIa) and tris[(dimethylamino)methyl]-*m*-cresol (VIb) with *m*-cresol, in the presence of oxalic acid, to form the branched tetramers VIIa and VIIb, shown in Figure 5. The methyl carbon portions of the ^{13}C NMR spectra of these materials are shown in Figure 6. When the methyl group is removed from the trisubstituted ring, the high-field resonance disappears.

The chemical shift data are summarized in Figure 2. Spectra of the regions diagrammed in that figure are shown

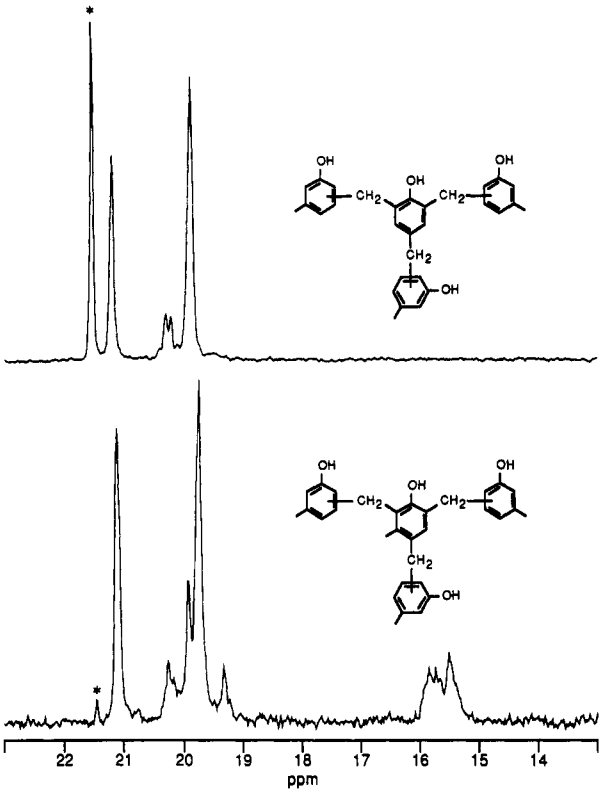

Figure 6. Methyl carbon region of the ^{13}C NMR spectra of branched novolak tetramers VIIa (top) and VIIb (bottom). Solutions in dioxane-d_8, inverse-gated ^1H decoupled, 30° pulse width, 10-s delay. Asterisk indicates free *m*-cresol.

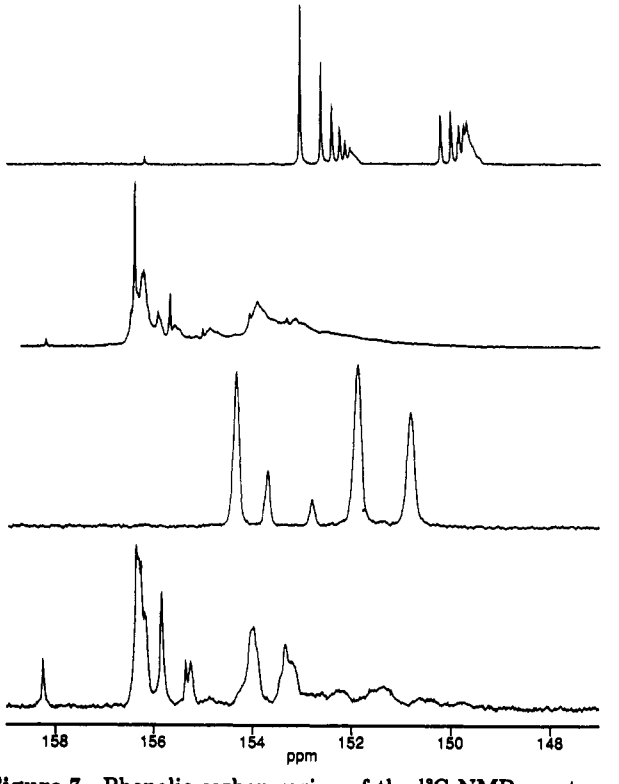

Figure 7. Phenolic carbon region of the ^{13}C NMR spectra of *p*-cresol (second from top), *o*-cresol (second from bottom), and phenol (bottom) novolak homopolymers. Solutions in THF-d_8, inverse-gated ^1H decoupled, 30° pulse width, 4-s delay.

in Figures 7–9.

Calculation of the Branch Density and DP_n. The synthesis of the model compound VIb enabled us to determine the accuracy of the measurement of the degree

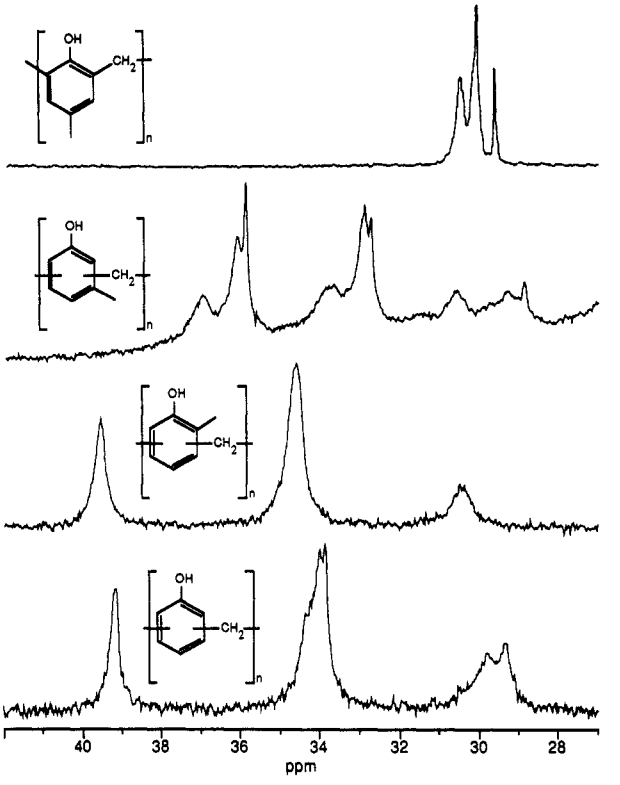

Figure 8. Methylene carbon region of the ^{13}C NMR spectra of *p*-cresol (top), *m*-cresol (second from top), *o*-cresol (second from bottom), and phenol (bottom) novolak homopolymers. Solutions in THF-d_8, inverse-gated ^1H decoupled, 30° pulse width, 4-s delay.

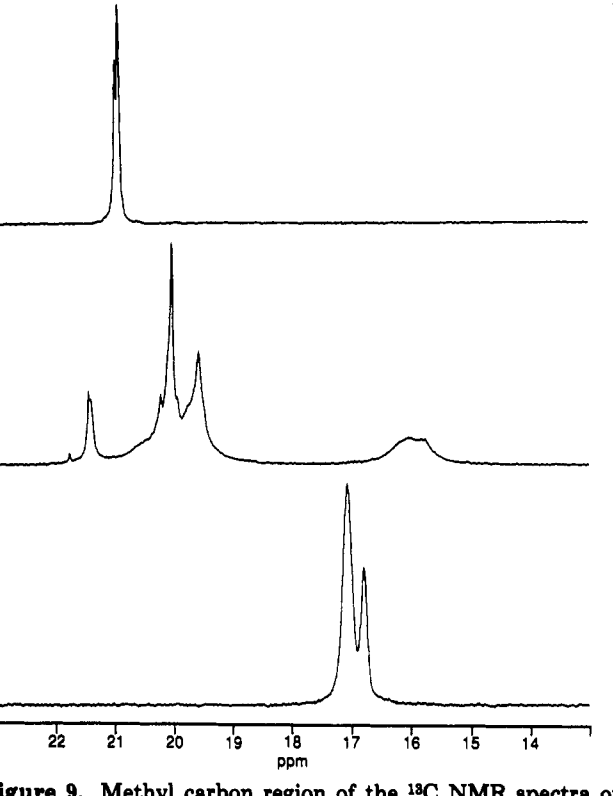

Figure 9. Methyl carbon region of the ^{13}C NMR spectra of *p*-cresol (top), *m*-cresol (second from top), and *o*-cresol (bottom) novolak homopolymers. Solutions in THF-d_8, inverse-gated ^1H decoupled, 30° pulse width, 4-s delay.

of branching. The area under the high-field peak in the compound VIb is 21.3% (estimate of variance 0.7%) of the total area under the methyl carbon peaks. It is likely that this number is low because this carbon has a long relaxation time (T_1). Changing the pulse delay from 4 to

Table I
M_n Determination by NMR, GPC, and Vapor-Phase Osmometry for Novolak Resins

sample	NMR	GPC	osmometry
LEB527A[a]			283
LEB530A[b]			257
HFS1479-39	1179	880	888
GAH2381	1346	1660	1339
GAH2382	1406	1750	947
GAH2386	2115	1490	1514
GAH2467	1442	1030	1062

[a] Sample LEB527A is a mixture of *m*-cresol novolak dimers, FW 228.29. [b] Sample LEB530A is 4,4'-bis(hydroxyphenyl)methane, FW 200.24.

10 s did not change this ratio, so it appears that this method has better precision than accuracy for the measurement of branching. In other words, it is better used to compare relative amounts of branching in different *m*-cresol novolak resins than to determine the absolute amount of branching in any given resin. Homopolymer novolaks of the *m*-cresol having $M_w > 4000$ have a branch density of ca. 15%. This was predicted for phenol novolak homopolymers by computer simulations.[14]

As stated in the section on peak assignments, free monomer, chain-end, and midchain ring phenolic carbon resonances are resolved in the spectra of homopolymers. Determination of free monomer becomes trivial. For homopolymers of *o*- or *p*-cresol, one can determine DP_n simply by dividing the area of the chain-end resonances by twice the area of all the phenolic carbon resonances. The situation is complicated somewhat for phenol or *m*-cresol, since chain branching will put more than two chain ends on a polymer molecule. Since the number of chain branches can be measured for *m*-cresol novolaks, this may be accounted for in the calculation of the DP_n of those resins. The determination of chain branching has a great effect on the calculated DP_n, so the accuracy and precision already described for this measurement dictate that the best use of these DP_n measurements is for the comparison rather than the determination of the absolute degree of polymerization. A comparison of M_n determination by NMR, GPC, and vapor-phase osmometry is given in Table I to aid in the assessment of the accuracy of this method. The significant level of error in each measurement makes correlations difficult to draw. We conclude that the determination of novolak resin branching by NMR is more useful than the determination of novolak resin DP_n by NMR.

Determination of Copolymer M_n and Copolymer Composition. For homopolymers, it is possible to deduce the amount of free monomer in and the M_n of the resin from the phenolic carbon and methyl carbon regions of the spectrum. For copolymers, the fact that some regions overlap prevents the measurement of a copolymer M_n by integration of phenolic carbon resonances. Copolymer *composition* can, however, be determined without the complication of overlapping resonances by integration of the cresol methyl resonances. The amount of phenol in a copolymer is then best determined by the difference, using the phenolic and methyl carbon regions together. These observations are displayed graphically in Figure 2.

We measured the accuracy of such determinations by performing them on known mixtures of novolak homopolymers. The results are presented in Table II. For mixtures of *m*- and *p*-cresols or *m*- and *o*-cresols, the accuracy of the determination is very good, within 2% of the value. For mixtures of cresols with phenols, the measurements are reported as area of $^{13}CH_3$/area of ^{13}COH − 1.1(area of $^{13}CH_3$/area of ^{13}COH) because our work with homopolymers has shown the ratio area of ^{13}COH/area of $^{13}CH_3$ to fall in the range 1.00–1.10 under the conditions of these experiments. For mixtures of phenol novolaks with *o*- or *m*-cresol novolaks, the actual value is within this range. For mixtures of phenol novolak with *p*-cresol novolak, however, this determination underestimates the amount of *p*-cresol by 9% at the middle of the measured range. In general, then, this method has good accuracy, particularly for systems not containing phenol novolak.

Table II
Determination by ^{13}C NMR of the Compositions of Standard Mixtures of Novolak Homopolymers[a]

actual composition	measd composition
39.5 *p*-cresol/60.5 *m*-cresol	39.6 (0.5) *p*-cresol
53.4 *o*-cresol/46.6 *m*-cresol	53.1 (0.4) *o*-cresol
50.9 *o*-cresol/49.1 *p*-cresol	53.8 (0.0) *o*-cresol
31.6 *o*-cresol/31.5 *m*-cresol/36.9 *p*-cresol	32.0 (0.2) *o*-cresol/32.1 (0.2) *m*-cresol/35.9 (0.1) *p*-cresol
44.5 *m*-cresol/55.5 phenol	42.0–46.1 *m*-cresol
45.4 *o*-cresol/54.6 phenol	44.4–48.9 *o*-cresol
49.9 *p*-cresol/50.1 phenol	43.7–48.1 *p*-cresol

[a] Solutions in dioxane-d_8, inverse-gated ^1H-decoupled, 30° pulse width, 4-s delay. The data were phased and integrated three times, and the estimate of variance (1σ) is reported in parentheses.

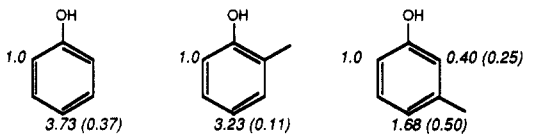

Figure 10. Relative reactivities of ortho and para ring sites on the same monomer toward formaldehyde. [phenolic monomer] = 7.4 M, [formaldehyde] = 0.15 M, [oxalic acid] = 0.042 M, temp = 100 °C.

Reactivity Ratios. Different phenolic monomers, as well as the ortho and para sites on the same monomer, are known to have different rates of reaction with formaldehyde. These rates have been determined for the base-catalyzed reactions but not for the acid-catalyzed reactions, in which we are more interested. The combination of a method for the preparation of novolak dimers, together with a method for quantifying the isomeric components of the mixture, allows us to measure these reactivity ratios.

For the phenol and the *o*-cresol dimers, integration of the phenolic carbon resonances allowed us to calculate the relative reactivities of the ortho and para sites. For the *m*-cresol dimers, this information was obtained by integration of the methylene carbon resonances in a spectrum obtained with an inverse-gated pulse sequence and a 300-s delay.[11] Our results are presented in Figure 10.

We have used similar experiments to determine the relative reactivities of the different phenolic monomers. In competition experiments similar to the ones described for the determination of site reactivity ratios, mixtures of equimolar amounts of phenol and a cresol isomer were reacted with 0.02 equiv of formaldehyde. Unreacted monomers were removed by distillation, and the residue was examined by NMR. The results of these experiments are shown in Table III. Our calculation of the same reactivity ratios from analyses of the product mixtures obtained by using different pairs of monomers in competition and using unequal mole ratios of the different monomers shows that the compositions of the product mixtures are under kinetic rather than thermodynamic control.

The greater reactivity of *o*-cresol compared to phenol contrasts with our observation that formaldehyde is

Table III
Relative Reactivities of Phenol and Cresols toward Formaldehyde[a]

phenolic monomer	relative reactive	phenolic monomer	relative reactivity
p-cresol	0.47 ± 0.01	*o*-cresol	2.36 ± 0.05
phenol	1.00 (ref)	*m*-cresol	6.03 ± 1.78

[a] [phenolic monomer] = 6.8–7.1 M, [formaldehyde] = 0.14 M, [oxalic acid] = 0.042 M, temp = 100 °C.

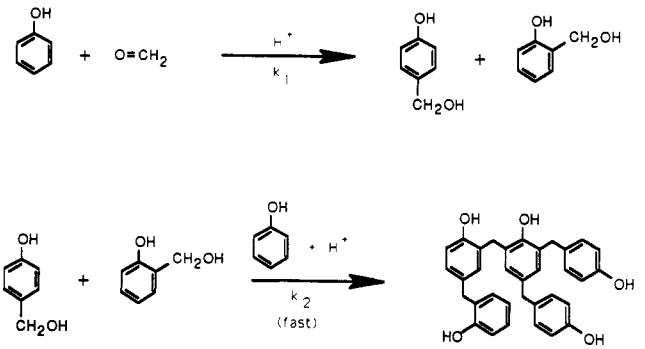

Figure 11. Two-step reaction mechanism of phenol–formaldehyde condensation.

consumed faster by phenol than by *o*-cresol. This anomaly is a direct consequence of the two-step mechanism of the reaction of formaldehyde with phenolic monomers, illustrated in Figure 11. The addition of a methylol derivative to another ring is approximately 10 times as fast as the formation of that methylol from formaldehyde and monomer[15] ($k_2 \approx 10k_1$ in Figure 11). The rate of conversion of monomers to polymer carries information only about k_1, the rate constant for the rate-limiting step. However, when one carries out competition experiments to determine relative reactivities, one gathers information about both steps, so the relative reactivities reflect both k_1 and k_2. This explains why the relative reactivity of *o*-cresol is greater than that of phenol even though k_1 is higher for phenol than for formaldehyde. It also explains why the relative reactivity of *m*-cresol is 6 times that of phenol, even though it reacts only about twice as fast with formaldehyde as phenol does.

Conclusions

We have described a method for the determination of novolak copolymer composition and *m*-cresol novolak polymer branch density. Using this method to analyze the products of competition experiments, we have measured relative site reactivities for phenol and the three cresols with formaldehyde under acid catalysis.

Experimental Section

Monomers and solvents were obtained from commercial sources. Formaldehyde solutions were titrated before use, and formaldehyde was charged on the basis of this titer. Vapor-phase osmometry was done by the ArRo Laboratory, Inc., P.O. Box 686, Caton Farm Road, Joliet, IL 60434.

Typical Dimer Synthesis. In a 500-mL flask, *m*-cresol (74.7 g, 0.69 mol), water (34.6 g), and oxalic acid dihydrate (0.5 g) were combined under N_2 and heated to reflux. To this mixture was added 37% CH_2O(aq) (1.1 mL, 1.0 g, 0.012 mol) in one portion. The mixture was held at reflux for 90 min, and then the unreacted materials were removed by distillation under a N_2 sweep at a maximum temperature of 205 °C.

Typical Polymer Synthesis. A monomer solution was prepared by mixing *m*-cresol (238.7 g, 2.21 mol), 36.5% CH_2O(aq) (136.2 g, 1.55 mol), and diglyme (20 g). A catalyst solution was prepared by mixing oxalic acid dihydrate (12.4 g, 0.098 mol) and diglyme (194.7 g). A 1-L flask equipped with a C-stirrer, a reflux condenser, a thermometer, and two addition funnels was charged with diglyme (60 g) and catalyst solution (4.9 g) and heated to 100 °C under N_2 with stirring. The monomer solution and the remaining catalyst solution were fed to the kettle over 3 h, and the reaction mixture was maintained at 100 °C for 1 h after the addition was completed. Volatiles were distilled from the reaction mixture, at first under a N_2 sweep, and then under vacuum, reaching ≤40 mmHg at 230 °C. At this point the system was filled with N_2 and cooled in dry ice for 1 h. The flask was broken to yield ca. 200 g of solid novolak resin.

Tris[(dimethylamino)methyl]-*m*-cresol (VIb). Tris[(dimethylamino)methyl]-*m*-cresol (VIb) was prepared as described in the literature.[16] The reported procedure gives a significant amount (ca. 20%) of bis[(dimethylamino)methyl]-*m*-cresol, which was converted to VIb by reaction with excess amine and formaldehyde in diglyme solution, followed by removal of volatiles in vacuo with heating. The identity and purity of the purified product were checked by NMR in dioxane-d_8. ^{13}C NMR: 156.5, 137.4, 130.8, 128.0, 123.2, 120.2, 63.4, 60.8, 56.2, 45.5, 45.0, 44.9, 14.9 ppm. ^1H NMR: 10.8, 6.8, 3.5, 3.4, 3.2, 2.3, 2.2, 2.1 ppm (all singlets). Tris(pyrrolidinomethyl)-*m*-cresol was prepared by an analogous method. The identity and purity of the purified product were checked by NMR in dioxane-d_8. ^{13}C NMR: 156.1, 136.1, 129.7, 128.3, 123.1, 120.8, 59.6, 56.8, 54.6, 54.1, 54.0, 52.5, 24.2, 24.1, 14.7 ppm. ^1H NMR: 6.9 (s), 3.7 (s), 3.6 (s), 3.4 (s), 2.5 (d), 2.4 (s), 2.3 (s) 1.7 (t) ppm.

Branched Novolak Tetramers VIIa and VIIb. Rohm and Haas DMP-30 (80 g, 0.30 mol), VIa, *m*-cresol (1040 g, 9.62 mol, 10.7 equiv), and oxalic acid dihydrate (120 g, 0.95 mol, 2.1 eq) were combined under nitrogen and stirred for 2 h at 100 °C. The remaining volatiles were distilled by heating to a maximum of 210 °C, first under a nitrogen sweep and then under reduced pressure for 15 min. The residue was cooled under nitrogen to yield the branched tetramer VIIa, characterized by ^{13}C NMR. A similar procedure was used to prepare tetramer VIIb from tris-[(dimethylamino)methyl]-*m*-cresol (VIb).

NMR. NMR spectra were recorded at 62.896 or 250.134 MHz on a Bruker AM-250 or at 100.6 MHz on a Varian XL-400 NMR spectrometer. Samples were dissolved in dioxane-d_8 (0.2 g of polymer/0.4 mL of THF) or THF-d_8 (same concentration), and spectra were referenced to TMS at 0 ppm. An inverse-gated ^1H decoupling pulse sequence was used with a 30° pulse width and a 4-s delay. Integrated peak areas did not change when the delay was varied from 4 to 64 s. The total area of the phenolic carbon resonances ranged from 1.00 to 1.10 times the total area of the methyl carbon resonances in either solvent. Although other solvents, notably acetone-d_6 and methanol-d_4, dissolve the resins more quickly and give solutions having a lower viscosity, they are not as useful for these experiments because the samples require a longer delay for quantitative results. In methanol, for example, the ratio of the total area of phenolic carbon resonances to methyl carbon resonances is 1.57 with an 8-s delay and 1.10 with a 30-s delay. DP_n was determined for *m*-cresol novolak resins using the formula $DP_n = 2$(total phenolic carbon)/[end phenolic carbon − (branched fraction)(total phenolic carbon)]. Data were processed, and DP_n was calculated three times for each sample to provide an estimate of variance in the measurement. This was an average 2.4% of the measurement for the degree of branching and 4.6% of the measurement for DP_n.

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Registry No. VIa, 90-72-2; VIb, 54567-07-6; VIIa, 134628-80-1; VIIb, 134628-81-2; (MeC_6H_4-*p*-OH)(CH_2O) (copolymer), 25053-88-7; (MeC_6H_4-*o*-OH)(CH_2O) (copolymer), 25086-36-6; (MeC_6H_4-*m*-OH)(CH_2O) (copolymer), 25053-96-7; (PhOH)-(CH_2O), 9003-35-4; (MeC_6H_4-*p*-OH)$_2$, 134628-82-3; (MeC_6H_4-*o*-OH)$_2$, 52519-44-5; (MeC_6H_4-*m*-OH)$_2$, 134628-83-4.