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Solid-State ^{13}C NMR Study of Resol-Type Phenol–Formaldehyde Resins

Gary E. Maciel* and I-Ssuer Chuang

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Lawrence Gollob[†]

Department of Forest Products, Oregon State University, Corvallis, Oregon 97331.

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ABSTRACT: The ^{13}C NMR experiment with cross polarization (CP) and magic-angle spinning (MAS) provides valuable information on the structure and the curing process of the resol-type phenol–formaldehyde resins. Two major features revealed by this technique regarding the curing process of these resins are the extensive involvements of the hydroxyl group of phenols and condensation of methylene bridges with hydroxyl groups.

Introduction

The technical development of the first fully synthetic resins, the phenol–formaldehyde resins formed from the reaction of phenol with formaldehyde, proceeded very rapidly after the discoveries of Baekeland.[1,2] However, the scientific investigation of the basic chemistry of these resins lagged far behind. The structural pecularities of these resins are due to the polyfunctionality of phenol, i.e., more than one site for aromatic substitution reactions. Under different sets of conditions (e.g., temperature, pH value, catalyst,...), the resins will show differences in their isomeric compositions, chain length, etc. The specific details of the structure of a phenol–formaldehyde resin have a substantial effect on the nature, extent, and rate of hardening.[1-3] Therefore, it is tremendously important to understand the reaction details of different stages in the formation of the phenol–formaldehyde resins under different sets of reaction conditions and their effects on the structures of these resins.

During the 1940s and 1950s there was considerable effort put on the study of reactions between phenols and formaldehyde.[4-10] Due to the very large varieties of compounds occurring in the reaction mixtures, researchers simplified the situation by employing some positionally blocked compounds as model substances to study the kinetics of reaction. Although these partially blocked compounds cannot truly reflect the actual situation occurring in phenol–formaldehyde in the reaction mixtures, these studies did provide valuable information concerning the reaction between phenol and formaldehyde under different sets of conditions. On the basis of these earlier studies, later IR,[6a,11-13] ^{1}H NMR,[14,18c] and ^{13}C NMR[15-21] studies have provided many more details of the reactions between phenols and formaldehyde. During the past several years ^{13}C NMR studies have yielded useful information concerning the positions of linkage between the phenol rings. However, nearly all the ^{13}C NMR studies reported so far[21] have been carried out on the liquid solution state, which has the disadvantage of possible influence of solvent and severe solubility problems for cured resins. Recent papers have dealt with the ^{13}C NMR study of solid phenolic resins.[21]

In recent years there have been major advances in solid-state high-resolution ^{13}C NMR. By combination of cross polarization[22] with high-power ^{1}H decoupling, accompanied by high-speed magic-angle spinning techniques[23] (CP/MAS), one can obtain high-resolution ^{13}C NMR spectra of solid materials. Excellent review articles[24] have recently appeared concerning the applications of this powerful technique in the study of polymers. These techniques are especially promising in the study of phenol–formaldehyde resins, because they provide the opportunity to study the insoluble resins under nondestructive conditions.

Experimental Section

The resin-forming reactions between phenol and formaldehyde were conducted at different molar ratios of formaldehyde to phenol and different initial catalyst (sodium hydroxide) levels. A summary of these conditions and some properties of the resulting resins are given in Table I. Four samples derived from each resin were studied, each representing a different state or extent of polymerization. Each of the four sample types is identified by a suffix after the sample number as follows: a very viscous, tarlike resin (l); a freeze-dried resin from dioxane/water after neutralization with acetic acid (n); a freeze-dried resin from water, nonneutralized (non); a resin cured at 110 °C for more than 24 h (cured). The curing experiments were carried out with thin films of resin on sheets of glass at 110 °C. This is not necessarily a good mimic of curing in a glue line.

The ^{13}C NMR spectra were recorded on a JEOL FX-60QS spectrometer by the CP/MAS technique. The spectra were taken under various contact times (0.03–10 ms) with a 1-s repetition time. Each sample was examined with a MAS spinning rate around 2.2 kHz. The magic-angle setting was checked before and after each ^{13}C CP/MAS experiment by the ^{79}Br–KBr method.[32] In some experiments a pulse sequence described by Opella and co-workers[25] was used in which a delay is inserted (during which there is no decoupling) between the CP contact period and data acquisition; during this interrupt period those carbons having directly attached protons (except those of rapidly rotating methyl groups) are distinguished from those carbons having no directly attached proton(s), because of the grossly different intensities

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[†] Present address: Georgia Pacific Corporation, Decatur, GA 30035.

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Table I
Characteristics of Resol-Type Resins Investigated

sample	mol of formaldehyde/ mol of phenol	initial catalyst level[a]	temperature profile	molecular weight[b]	time to gelation[c]
27	1.9	0.15	rapid climb	42 000	170
29	2.5	0.25	rapid climb	185 000	30
37	2.2	0.25	rapid climb	52 000	210
50	2.2	0.35	low temp hold	191 000	85

[a] The molar ratio of sodium hydroxide to phenol. [b] The weight-average molecular weight of the liquid resin as determined by light scattering. [c] Minutes at 80 °C.

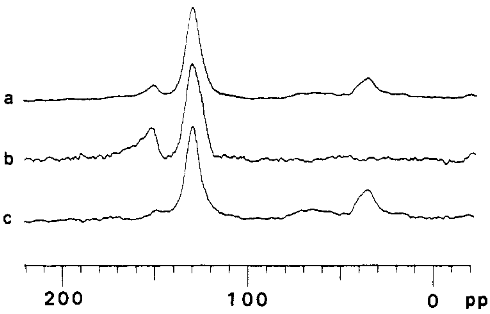


Figure 1. ^{13}C CP/MAS spectrum (15 MHz) of a cured phenol–formaldehyde resin, sample 29 (contact time, 1 ms; repetition time, 1 s): (a) usual CP/MAS spectrum; (b) 100-μs interrupted-decoupling spectrum; (c) result of subtracting 0.38 times spectrum b from spectrum a. This subtraction eliminates completely the peak around 160 ppm, which survives the interrupted decoupling best, and most carbons without directly attached hydrogen(s).

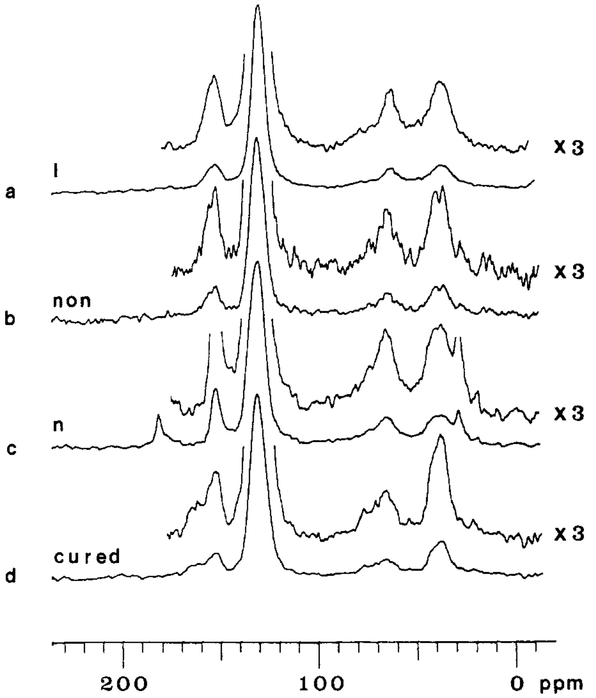


Figure 2. ^{13}C CP/MAS spectra (15 MHz) of the four resins, samples 37 (contact time, 1 ms; repetition time, 1 s): (a) "l" resin; (b) "non" resin; (c) "n" resin; (d) cured resin.

of ^{13}C–^{1}H dipolar interaction and corresponding rates of dephasing of the ^{13}C magnetization.

Results and Discussion

^{13}C CP/MAS experiments were carried out on the 16 resol phenolic resins samples described above and one cured novolak resin for comparison. A considerable variation of spectral characteristics was recorded, with the detailed nature of the spectrum of a particular sample depending on its history. Representative examples are seen in Figures 1–3. Figure 1b shows an example of the interrupted-decoupling experiment; this type of experiment was carried out on all of the resin samples in order to help distinguish carbons having directly bonded protons from those carbons that do not.

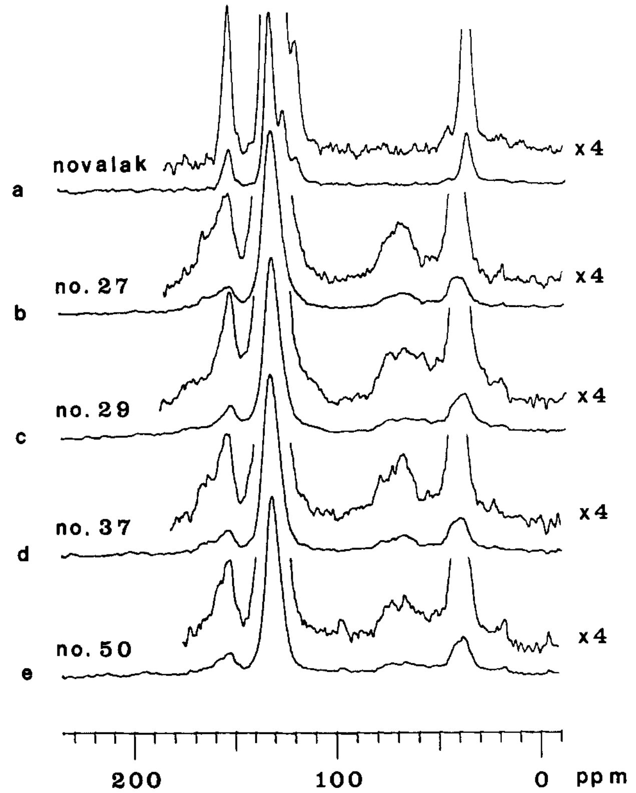


Figure 3. ^{13}C CP/MAS spectra (15 MHz) of five cured samples (contact time, 1 ms; repetition time, 1 s): (a) high-ortho novolak; (b) sample 27; (c) sample 29; (d) sample 37; (e) sample 50.

^{13}C CP/MAS spectra of each resin sample were obtained at no less than eight different CP contact times, ranging from 30 μs to 10 ms. From the variation of ^{13}C intensity as a function of contact time one can extract the CP relaxation time, T_{CH}, of each individual carbon and the proton rotating-frame spin–lattice relaxation time, $T_{1\rho\mathrm{H}}$.[33] On the basis of these results, the following experimental parameters were chosen for generating the spectra shown in Figures 2 and 3 to ensure quantitative significance for relative peak intensities: 1-ms contact time; 1-s repetition delay. Examples of the variable-contact-time spectra obtained on one sample are given in Figure 4.

Due to rapid ^{1}H spin diffusion in these resins, which have high proton densities, $T_{1\rho\mathrm{H}}$ is essentially the same for each proton in a given sample. $T_{1\rho\mathrm{H}}$ values of these 16 resin samples were found to be in the range from 3 to 10 ms. For each sample, the peak around 152 ppm was found to have the longest T_{CH} value, ranging from 60 to 350 μs. In each spectrum the peak around 130 ppm is composed of a large variety of components; nevertheless, we can still

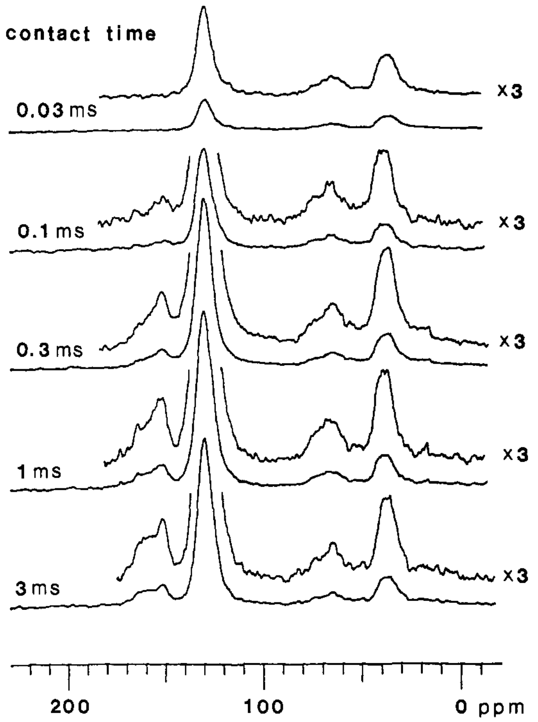


Figure 4. ^{13}C CP/MAS variable-contact-time spectra (15 MHz) of cured sample 27 (repetition time, 1 s; contact times as shown).

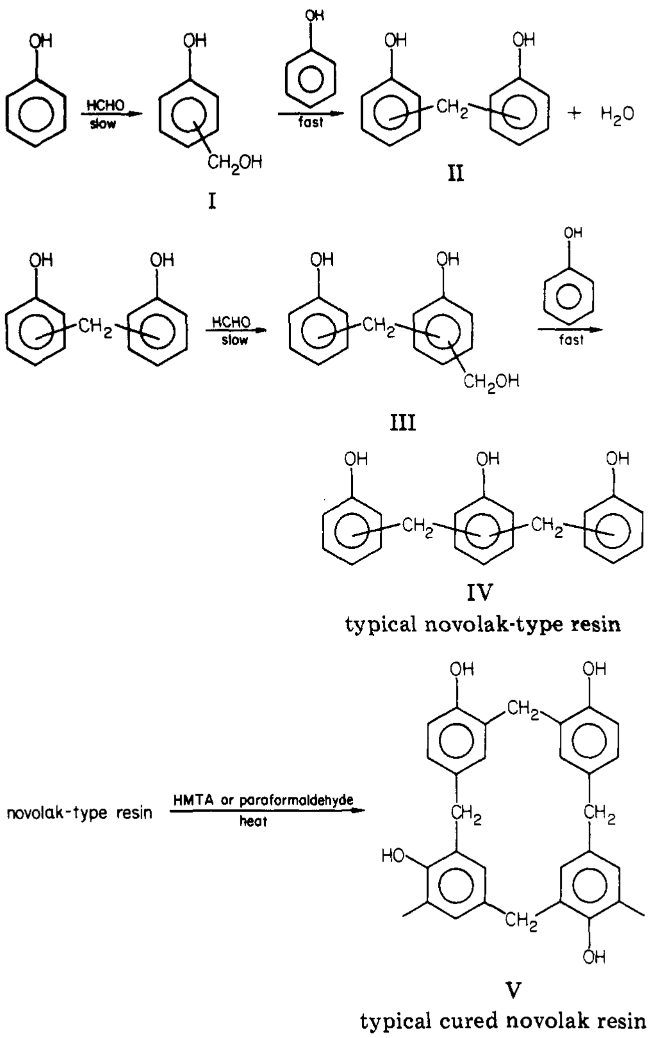
obtain qualitatively useful, averaged T_{CH} values for these samples. The T_{CH} value of this peak is the second largest for each given sample and ranges from 60 to 300 μs for the 16 samples. For a given sample the T_{CH} values for those peaks in the 58–73-ppm region (Ar–CH_2OH, Ar–O–CH_2–Ar, –CH_2–O–CH_2 carbons) and 30–40-ppm region (–CH_2–) are about the same, ranging from less than 40 μs to 150 μs, and in most cases they are much smaller than the T_{CH} values for the 152-ppm peak and the 130-ppm peak. Although essentially the same $T_{1\rho H}$ value is obtained for each proton in a given sample, useful information can be obtained from measured variations in T_{CH} values. The stronger the dipolar interaction(s) between ^{13}C and nearby proton(s), the smaller will be the T_{CH} value (neglecting rapid motion, such as that in CH_3 groups, which can effectively attenuate the ^{13}C–^{1}H dipolar interaction(s) by averaging). These considerations are useful in making structural assignments in the complex spectra obtained.

The spectral variations represented in the ^{13}C NMR spectra obtained in this study manifest the great structural diversity attributed to phenolic resins prepared in various ways. In making peak assignments extensive use was made of ^{13}C chemical shift data in the literature on soluble phenolic resins and model compounds.[15-20]

Certain conditions, mainly pH and temperature, under which reactions of phenols with formaldehyde are carried out have a profound effect on the character of the products obtained. These reactions have three distinct stages: (1) the initial addition of formaldehyde to phenol to form methylolphenols, (2) chain growth by alternative condensation and addition at temperature below 100 °C, and finally (3) the cross-linking or hardening of the resins at temperature above 100 °C. Differences in details of these three stages lead to phenol–formaldehyde resins of two general types, namely the novolak type and resol type. The main emphasis in this paper is on resol resins, with a novolak resin examined only for comparison.

Novolaks are obtained by the reaction of phenols and aldehydes under acidic conditions with molar excess of phenols. Due to the slowness of the addition of formaldehyde to phenols, novolaks contain no reactive methylol groups and therefore cannot readily condense by themselves on heating. When mixed and heated with compounds capable of providing methylene bridges, e.g., hexamethylenetetramine (HMTA) or paraformaldehyde, and provided that they contain enough reactive positions on the phenol rings (unsubstituted positions ortho or para to the hydroxy group), they become cross-linked and harden to insoluble and infusible, cured resins. The three stages of the formation of novolak resins can be summarized by Scheme I.

Scheme I

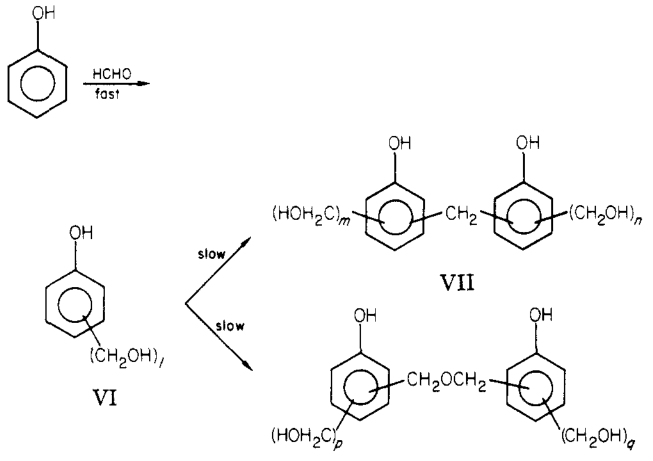


Due to the orientation effect of hydroxy groups in phenols, the methylol groups and methylene bridges are ortho or para to the hydroxy group. Figure 3a shows the ^{13}C CP/MAS spectrum of a cured high-ortho novolak.

Resols are obtained by the reaction of formaldehyde and phenols under basic conditions and usually by employing an excess of formaldehyde. The initial substitution reaction of formaldehyde with phenol is faster than the subsequent condensation reaction between substituted phenol rings; consequently, methylolphenols (e.g., I) are initially the predominant intermediate compounds. These methylolphenols condense either with other methylol groups to form ether linkages or, more generally, with the available reactive, unsubstituted positions in the phenol ring (ortho or para to the hydroxy group) to form methylene bridges as in novolaks. Due to the orientation effect of hydroxyl groups in substitution reactions on phenols, as in novolaks, the methylol (–CH_2OH) groups, methylene bridges (–CH_2–), and/or dimethylene ether bridges

[$-CH_2OCH_2-$) are ortho or para to the hydroxyl group.

The molecules of resol resins differ from the molecules of novolak resins in that the resols contain reactive methylol groups and possibly also in having occasional dimethylene ether linkages in place of simple methylene bridges between the phenol rings. Heating or acidification of resol resins causes cross-linking to take place through uncondensed methylol groups and possibly also through the reaction of formaldehyde liberated by the breakdown of the ether linkages.[4] The stages of the formation of resol-type resins can be summarized as follows:

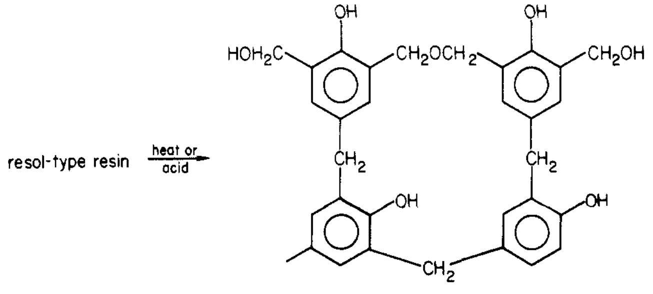


VI

VII

VIII

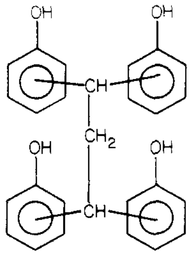
resol-type resin



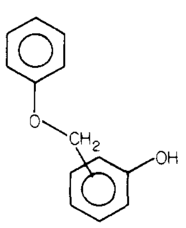
IX

l = 1, 2, or 3; m, n, p, q = 0, 1, or 2

Since the 1940s there have been many controversies concerning the nature of the curing process of resol-type resins,[1] especially the chain-growing process and what happens after the breakdown of the dimethylene ether linkages above 160 °C. Different conditions have been employed by different research groups; and it seems most probable that several different reactions occur simultaneously in these processes. The Zinke group concludes that formaldehyde is liberated when the dimethylene ether linkage is broken to form a methylene bridge.[4] The formaldehyde thereby liberated reacts at unsubstituted positions that may remain on the phenol ring or with the methylene bridges or even with phenolic hydroxyl groups, to yield compounds of types X and XI.



X

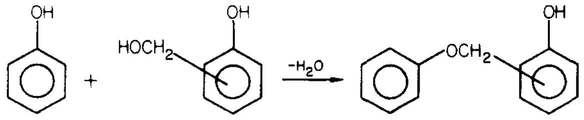


XI

Evidence supporting the possibility of the phenolic hydroxyl groups taking part in the cross-linking reaction is provided by the work of Hultzsch, Ziegler, and von Euler (see ref 1).

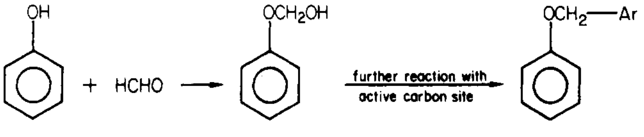
Figure 1a shows the ordinary CP/MAS spectrum of cured resin sample 29; this spectrum includes all the ^{13}C peaks that can be cross polarized. Figure 1b shows the corresponding spectrum with 100-μs interrupted decoupling. The surviving peaks in Figure 1b are due to those carbons having no directly bonded hydrogens, as the magnetization of those carbons with directly bonded protons is rapidly destroyed due to the large proton–carbon dipolar interactions. When one subtracts spectrum 1b from spectrum 1a (with a suitable amplitude-scaling constant) the resulting spectrum 1c corresponds to those carbons with directly bonded protons. Figure 2 shows the spectra of resin 37 at four different stages of polymerization. From the variations among these spectra, one can monitor the chemical changes corresponding to these stages as discussed below. The types of spectra shown in Figures 1 and 2 are representative of the types of experiments carried out on all of the resol samples of this study. Figure 3 shows the spectra of the four cured resin samples and one "high ortho" novolak sample.

There are several features of these spectra that can be identified directly with structural features pertinent to the questions raised above. The peak around 152 ppm that survives in the interrupted decoupling experiment is assigned to the phenol-ring carbon bearing a hydroxyl group; all samples show a strong peak around this region. For all four cured resins there is a shoulder around 160 ppm which grows in its intensity more slowly during cross polarization than does the peak around 152 ppm, as revealed by variable-contact-time experiments (see Figure 4); this shoulder survives the interrupted decoupling period better than does the peak around 152 ppm. In rigid-lattice solid states, the strength of an internuclear dipolar interaction is inversely proportional to the cube of the relevant internuclear distance.[26] The main mechanism for cross polarization is the internuclear dipolar interaction between the nuclei involved,[22] in our case ^{13}C and nearby proton(s). A larger internuclear distance usually corresponds to a larger T_{CH} value. On the other hand, the signal of the peak in the interrupted-decoupling experiment is modulated by this same internuclear dipolar interaction.[25] The stronger the dipolar interaction, the weaker the surviving peak. Therefore, if a ^{13}C peak corresponds to a large T_{CH} value and survives a long interrupted-decoupling period, it is reasonable to assume that the internuclear distance between the carbon atom and the nearest hydrogen is larger than for carbons not able to survive the interrupted-decoupling period and with shorter T_{CH} values. From the position of this peak, its larger T_{CH} value and its prolonged interrupted-decoupling behavior, the shoulder around 160 ppm is assigned to the phenolic ring carbon attached to oxygen in the ether structure, Ar–O–CH_2–Ar (where Ar stands for an aromatic ring). The formation of this species could occur by some combination of the following processes:



XII

or



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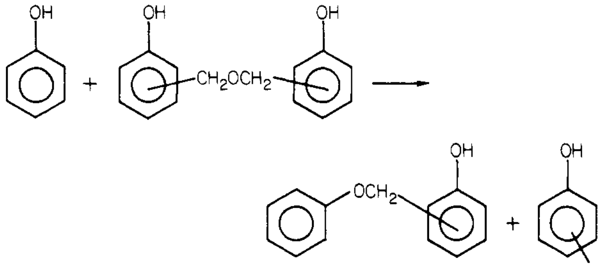


XII

The ^{13}C spectra show that cured resin 27 exhibits the largest propensity for this kind of species and cured resin 37 has the second largest tendency, whereas cured sample 29 shows the least tendency among these cured samples to form this kind of species. All the uncured resin samples show very little evidence, if any, of this type of species. Therefore, the formation of this type of structure is accompanied by the curing of these resins. It is interesting that there seems to be an inverse relationship between the formaldehyde/phenol mole ratio and the relative intensity of this shoulder at 160 ppm. This is explainable in terms of the relative concentrations of methylol groups and phenolic OH groups and their expected relationship to the formation of products of types VII and VIII relative to type XII.

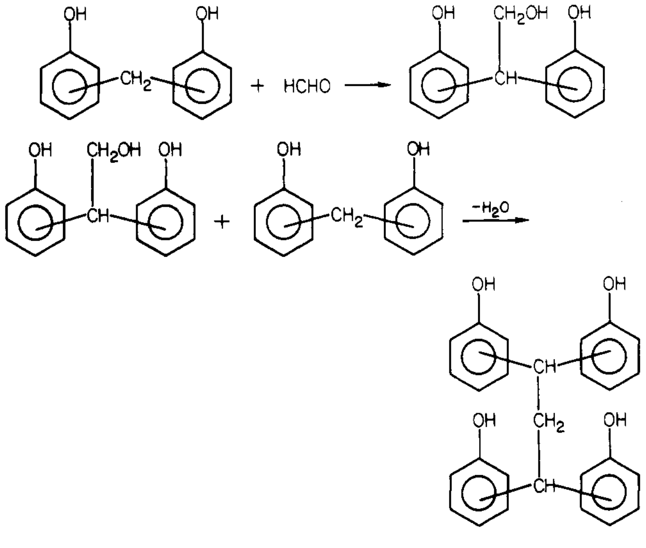
The peak around 130 ppm can be assigned to the remaining phenol-ring carbons. That portion of this peak surviving the interrupted-decoupling period is assigned to the substituted ring carbons, which can bear the methylol group, formyl group, methylene linkage, or dimethylene ether linkage. For the cured resol samples of this investigation we can conclude on the basis of arguments presented below that all of the phenol-ring substitutions are in the ortho or para positions relative to the hydroxyl group.

For each resin sample the subtracted spectrum[28] analogous to Figure 1c has intensity in the 110–130-ppm region, which can be assigned to unsubstituted phenol-ring carbons. Most of this intensity is near 129 ppm, which can be assigned to the unsubstituted meta carbons. Resonance intensity around 115 ppm is assigned to unsubstituted ortho carbons, whereas intensity in the 120-ppm region is assigned to unsubstituted para carbons. For all 16 resol resins investigated the intensity corresponding to unsubstituted ortho and para positions relative to the hydroxyl group is relatively small, sometimes even invisible in the subtracted spectra, in comparison to the intensity associated with substituted ring carbons. This is consistent with the highly substituted character of resol-type resins. For each of the four sets of resin samples the spectra show that the extent of substitution increases in going from uncured resin sample to the cured resin samples; there are almost no unsubstituted phenol rings in any of the samples.

Those peaks in the 68–73-ppm region can be assigned either to the carbon of the dimethylene ether linkages or to the methylene carbon structures, Ar–O–CH_2–Ar. For the uncured resin samples the intensities in the 70–75-ppm region are weak; because of the absence of a shoulder around 160 ppm for the uncured samples, these weak 73-ppm resonances are assigned to the dimethylene ether carbons. For cured samples, one finds stronger intensity in the 73-ppm region, especially on the low-shielding side. In combination with the appearance of the shoulder around 160 ppm for the cured samples, it is reasonable to assume most of the increased intensity in the 73-ppm region for the uncured samples is due to the formation of the species of the type C_6H_5–O–CH_2–Ar.

^{13}C resonance intensity in the 58–65-ppm region can be assigned to the methylol carbon that is directly attached to the ortho or para position of the phenol ring. The intensity in this region was found to decrease somewhat during the curing process; this can be due to the detachment of the methylol group from the phenol ring, condensation with other methylol groups, or condensation with active carbon sites.

As a result of the curing process one might expect ^{13}C NMR intensity to develop in the 42–57-ppm region, corresponding to sp^3 $\gg$C–H moieties. These kinds of structural units could result from the attack of methylene bridges by formaldehyde liberated in the cleavage of the dimethylene linkages or by condensation with methylol groups. These kind of reactions have been suggested by Zinke.[4] A similar mechanism suggested by Conley and Metil[29] for the curing of furfuryl alcohol have been verified by ^{13}C CP/MAS studies.[30] The possible reactions are as follows:



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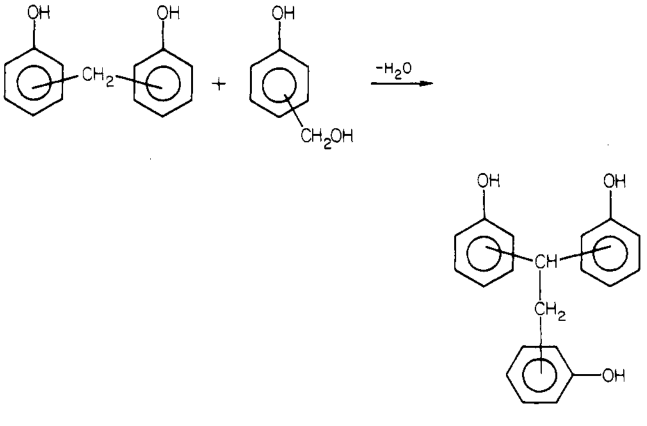
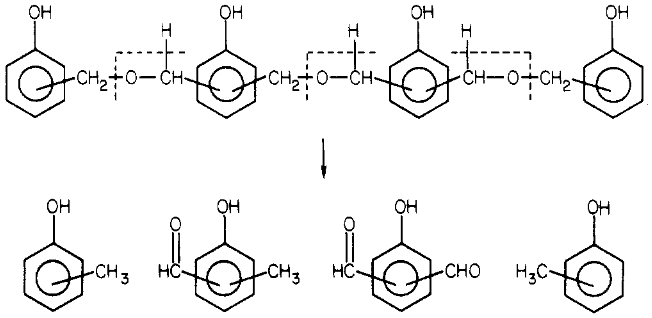


Although some intensity increase is found in this region for some cured resins of this study, this does not appear to be true for the resin-37 case shown in Figure 2.

Those resonance peaks found around 40 ppm can be assigned to 4,4′-methylene linking carbons, those around

35 ppm to the 2,4′-methylene linking carbons, and those around 30 ppm to the 2,2′-methylene linking carbons, as suggested by the recent solution-state ^{13}C NMR studies.[15-18] The relative intensities of these three resonances indicate the relative populations of these three kinds of methylene links in the resins. Due to the severe overlap of these three peaks, it is unreasonable to make a quantitative statement concerning their distribution at the present level of these studies. Perhaps improved resolution-enhancement methods will make such an analysis possible. Nevertheless, one point that can be developed unequivocally from the spectra is that the methylene bridge increases in population during the curing process. In most cases, we can conclude from the ^{13}C spectra that the 2,4′-linkage is the predominant one (with resonance at about 35 ppm), whereas the 2,2′-linkage (resonance about 30 ppm) is the least important and sometimes even hard to detect in the spectra. The preferred mode of methylene linkage is somewhat different for different resins, as can be seen from examining the 30–40-ppm regions in the spectra of Figure 3.

For all four cured resin samples (Figure 3) there is a pronounced intensity around 18 ppm and a weak intensity at about 194 ppm, which can be assigned to methyl carbons directly attached to the phenol ring at the ortho position (relative to the hydroxyl group) and to –CHO carbons directly attached to the phenol ring, respectively. These two types of structures can be formed by the following routes suggested by Zinke:[4]



The formation of these species through quinone methides is ruled out for temperatures below 180 °C,[31] which is well above our curing temperature, 110 °C.

Meta substitution (relative to the OH group) should show a peak near 140 ppm. There is weak, ill-defined resonance intensity in this region for some "l" or "non" resin samples; this is totally absent for all the cured samples. Therefore, we can conclude that the occurrence of meta substitution is very minor at most, especially in cured resins.

For the n-resin samples, for which neutralization with acetic acid was employed, the ^{13}C CP/MAS spectra show sharp peaks around 26 and 180 ppm, which can be assigned to acetic acid. Because of the mobility of acetic acid, these peaks are strongly attenuated in spectra obtained with short CP contact times. These two peaks are completely absent for the cured samples. In general the line widths of peaks in the spectra of these phenolic resins are much larger than those of the entrapped acetic acid in the n-resins. These larger line widths are strongly suggestive of the existence of considerable structural heterogeneity, including conformation variation, in these resins.

Conclusions

Although resol-type resins are much more complicated than the novolak-type resins, one can nevertheless obtain some very useful information concerning the resin curing process of resols by the ^{13}C CP/MAS technique. For the curing process of the resins we investigated, the direct involvements of the hydroxyl group of the phenol ring and methylene bridges are unambiguously exhibited for the first time. It is reasonable to assume that cross-linking through the hydroxyl group and by methylene bridges and/or $>$CH moieties are not of minor importance. The presence of $-CH_3$ and –CHO groups directly attached to the phenol rings is also revealed by this ^{13}C CP/MAS study. More detailed studies of these and other resins systems are under way.

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Registry No. (Phenol)·(formaldehyde) (copolymer), 9003-35-4.

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^{13}C NMR Study of Curing in Furfuryl Alcohol Resins

I-Ssuer Chuang and Gary E. Maciel*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

George E. Myers

Forest Products Laboratory, U.S. Department of Agriculture, Madison, Wisconsin 53705.

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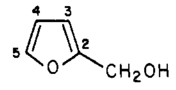
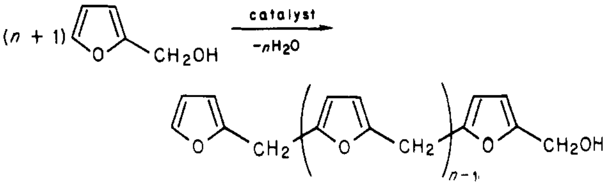
ABSTRACT: A ^{13}C CP/MAS NMR study of furfuryl alcohol resins is reported. A conformational rigidity is found for uncured or less cured resins. The contents of methylol groups and dimethylene ether linkages are found to be very small. It is postulated that cross-linking involves the breaking of methylene bridges in the curing process. Further confirmation is given that the major cross-linking processes that occur during curing involve linkages with bridging CH_2 groups, rather than substitution at the 3- and 4-positions of furan rings in the resins.

Introduction

General features of the initial process of formation of furfuryl alcohol resins from furfuryl alcohol (I) are well understood. It is accepted[1-3] that the methylol group of one furan ring condenses with the 5-position of another furan ring with dehydration to form a methylene linkage (II) or with the methylol group of another furan ring to form a dimethylene ether linkage (III):



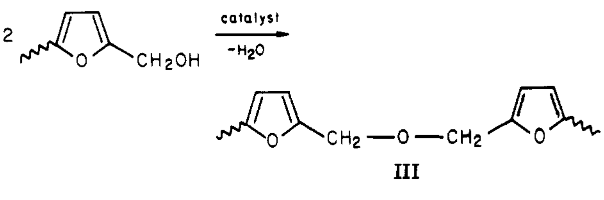
I



(1)

II

or

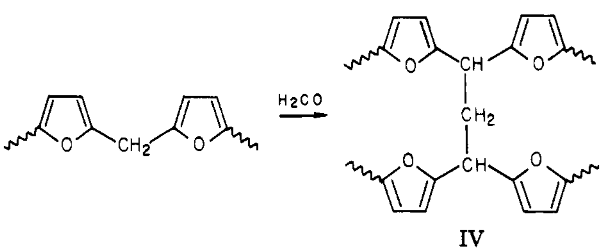


(2)

III

However, the curing process(es) of these resins initiated by heating, with or without a catalyst, is much less understood. The main reason for the difficulty in understanding the curing process(es) of furfuryl alcohol resins is the high molecular weights and low solubilities typical of the cured resins and the resulting difficulty of investigating them by ordinary analytic methods designed for liquid samples.

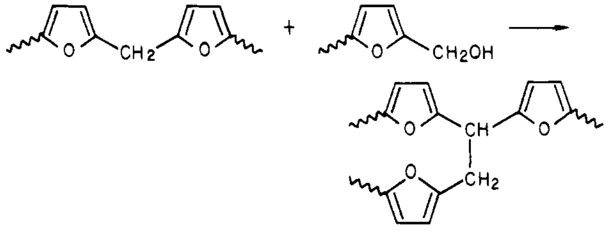
During the past decade, advances in high-resolution solid-state nuclear magnetic resonance (NMR) have been impressive. The combination of cross-polarization (CP)[4] and high-power proton decoupling with magic-angle spinning (MAS)[5] makes it possible to obtain high-resolution ^{13}C NMR spectra of complex molecules in a nondestructive way. This technique has recently been employed in the study of furfuryl alcohol resins,[6] a study which found evidence that some side reactions which appear to be unimportant in the early stages of resin formation occur during the curing process. This conclusion is perhaps not surprising in view of the more severe conditions employed for the curing of furfuryl alcohol resins in comparison to the early stages of formation of these resins. The main feature revealed by the previous study[6] is that the main curing process is the formation of cross-linking branches through the methylene linkage, as follows:[6,7]



(3)

IV

or



(4)

V

0024-9297/84/2217-1087$01.50/0