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Investigation of the Mechanism of the Thermal Decomposition of Cured Phenolic Resins by High-Resolution ^{13}C CP/MAS Solid-State NMR Spectroscopy

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ABSTRACT: The structural changes occurring in cured phenol-formaldehyde resins when exposed to high temperatures have been investigated by high-resolution ^{13}C solid-state NMR. The initial step in the degradation involves the loss of methylol groupings. Continued degradation results in the appearance of oxidized functionalities, with a simultaneous loss in methylene groupings. The oxidized functionalities have been identified as aldehydes, ketones, carboxylic acids, and anhydrides. At higher temperatures the structure becomes mainly aromatics with a few methylene linking groups. When the same resins are heated under vacuum, there is a complete loss of methylols and a reduction in the amount of methylenes along with the appearance of methyl groupings but no oxidation, and the structural and chemical integrity of the sample is largely preserved.

Introduction

Phenolic resins were the first completely synthetic polymeric materials synthesized and they have found wide application in a variety of different areas.[1] Because of their excellent ablative properties and structural integrity, they can be used as high-temperature polymers.[2]

The purpose of the present work is to investigate by high-resolution solid-state ^{13}C NMR spectroscopy the chemical and structural changes that occur in these materials at elevated temperatures, to elucidate the mechanism of the degradation process. In this technique, as first shown by Schaefer and Stejskal,[3] a combination of cross-polarization[4] and "magic-angle" spinning[5] with high-power dipolar decoupling yields ^{13}C NMR spectra of moderate to good resolution from completely solid materials.[6] An important feature of the spectra is that they yield the isotropic average values of the chemical shifts (for the solid state) just as high-resolution NMR spectra in solution, and therefore chemical shift correlations from solution NMR may be used for structure elucidation. One of the most important areas of application of these techniques is the investigation of the structures of amorphous materials where X-ray diffraction techniques are not applicable: Polymeric resins are one such important class of materials[7,8] and we have previously reported the application of high-resolution solid-state ^{13}C NMR techniques to the determination of the structures of phenolic resins and the nature of the curing process.[8] In the present work we present results from their application in an investigation of the mechanism of their high-temperature degradation and the nature of the solid products formed.

Previous investigations of these processes have been reported,[9-15] the most extensive of which are a series of reports by Conley and co-workers[11-15] on the application of IR spectroscopy to this problem. The results of these investigations will be referred to subsequently and compared to those from the present work.

Experimental Section

^{13}C MAS and CP/MAS spectra were obtained at 22.6 MHz with a Bruker CXP100 spectrometer equipped with a homemade probe with an Andrew-Beams type of spinning apparatus. The sample spinners were constructed of Kel-F, poly(chlorotrifluoroethylene), were of ~460-μL capacity, and were spun at ~3 kHz, using air as driving gas. The samples were run as finely divided powders under experimental conditions discussed in detail in the text.

Two separate resin samples were prepared: The first was made by condensing phenol and formaldehyde (phenol/formaldehyde/NaOH = 1/2/0.01) under basic conditions followed by vacuum distillation at 80 °C and an absolute pressure of 15 mmHg. The second was prepared under identical conditions except that formaldehyde enriched to approximately 5% in ^{13}C was used. Both samples were cured under pressure (15-psi nitrogen) in thin films to minimize heterogeneity in curing from temperature gradients. Curing was carried out at 180 °C for 160 min, which is known to give the limiting cure (as reflected by the methylene to methylol ratio) for this temperature.[8b] The cured samples were then ground to fine powders and held at elevated temperatures either in air or under vacuum for fixed time intervals. After each treatment, the sample was cooled and weighed and its solid-state NMR spectrum recorded as described in the text.

Results and Discussion

CP/MAS spectra in all cases were recorded with a 1-ms contact time and a 1-s delay between sequences, as these conditions were known from previous work to yield quantitatively reliable spectra for these types of phenolic resins.[8b] In addition, a spectrum was recorded for each sample using a simple 90° pulse sequence and a 60-s delay with MAS only to check the quantitative reliability. The results for the air and vacuum decompositions were quite different and are presented separately.

Degradation in Air. Spectra A and B of Figure 1 are the ^{13}C CP/MAS spectra of the starting resin cured at 180 °C for 160 min, known to give the limiting cure for this temperature ($CH_2/CH_2OH = 2.89$).[8b] Figure 1B shows clearly the effect of ^{13}C enrichment of the formaldehyde and confirms the origin of the aliphatic groupings as being the formaldehyde component of the resin. As previously, these may be assigned to CH_2, CH_2OH, and OCH_2O groupings as indicated in the figure, the latter arising from a small amount of unreacted paraformaldehyde in the resin. In the aromatic region, Ar_1 is due to the hydroxyl-bearing phenol carbons and Ar_2 to the unsubstituted meta carbons and the substituted ortho and para carbons; there are very few unreacted ortho and para sites present contributing to the small absorption at 115 ppm indicated by the star. The nonprotonated carbon selection experiment (see later) may be used to discriminate between the two different contributions to Ar_2.

Spectra C and D of Figure 1 are the ^{13}C CP/MAS spectra of the same two samples after heating in air for 95 min at 300 °C, the comparison between the enriched

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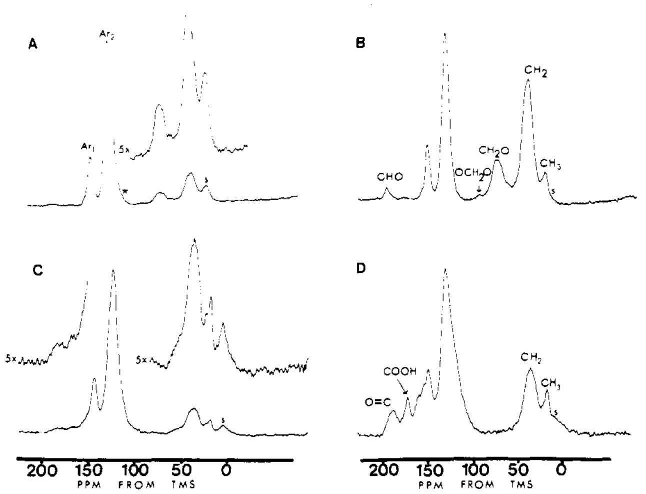


Figure 1. ^{13}C CP/MAS spectra of various resoles P/F/NaOH = 1/2/0.01 cured at 180 °C for 160 min under 15-psi nitrogen. (A) Spectrum of cured resole, 5200 scans; (B) spectrum of cured resole prepared with 5% ^{13}C-enriched formaldehyde, 2200 scans; (C) spectrum of cured resole heated in air at 300 °C for 95 min, 5100 scans; (D) spectrum of cured resole prepared with 5% enriched formaldehyde heated in air at 300 °C for 95 min, 2200 scans. All spectra obtained with 1-ms contact and 1-s recycle delay. Small peaks marked "s" denote spinning sidebands.

and nonenriched samples again making it possible to clearly distinguish the contribution of the formaldehyde-derived groupings to the total spectrum. The overall process is obviously one of oxidation as evidenced by the appearance of the series of peaks in the region 150–195 ppm, characteristic of carbonyl functions. There is the simultaneous disappearance of the CH_2OH absorption and a reduction in the intensity of the CH_2 absorption. Comparison of the spectra of the enriched and nonenriched samples of confirms that the main source of the carbonyl functionalities is the formaldehyde-derived aliphatic groupings in the original resin. Care must be taken in this conclusion, however, as Figure 1D discriminates in favor of the enriched carbons and against carbonyl resonances such as quinone groupings which might be derived from the phenol moiety. However, from the spectra of reference compounds such as 2-methyl- and 2,6-dimethylbenzoquinone, these would be expected to absorb in the region 186–188 ppm, and the absence of large absorptions in this region in Figure 1C and the corresponding spectrum of a sample cured at 300 °C for 300 min indicate that this cannot be a *major* oxidation product. The spectra do not, however, rule out the formation of small to moderate amounts of such species.

Figure 2 shows representative spectra from a more detailed examination of the oxidation process at various temperatures using enriched resin. Two spectra are presented for each set of conditions: The spectrum on the left is a ^{13}C CP/MAS spectrum recorded under conditions known to be quantitatively reliable and checked by a simple 90° pulse experiment with a very long delay time. The right spectrum in each case was recorded with a CP sequence in which a short delay in which the proton decoupling field is switched off is inserted between the cross-polarization step and the acquisition of the free induction decay.[16] The net effect of this sequence is that only those carbons with no attached protons will be observed (methyl carbon resonances still appear although with substantially reduced intensity due to their particular nuclear relaxation properties). Comparison of the two spectra in each set makes it possible to make further assignments of the resonances, and subtraction of the two spectra yields the spectrum due to only those carbons with directly bonded protons (not shown).

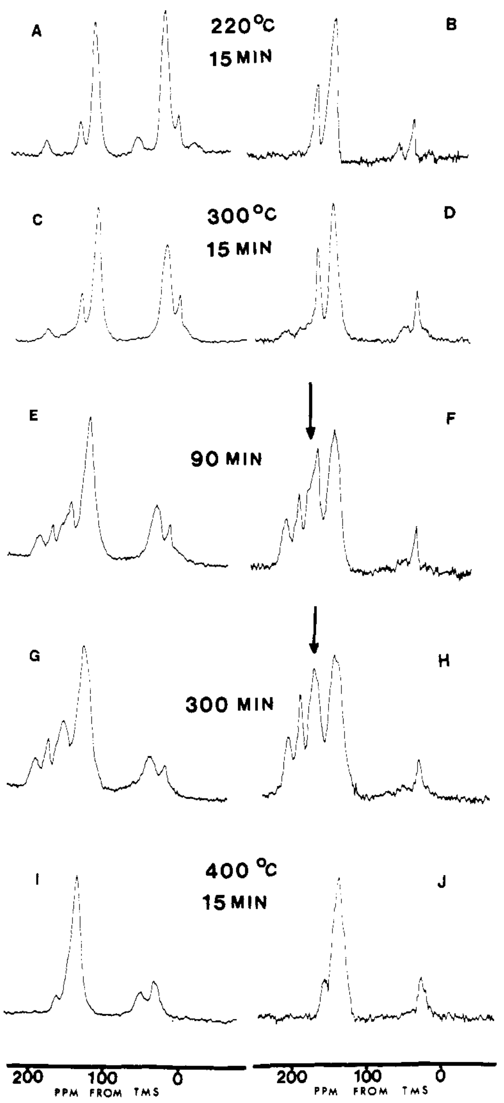
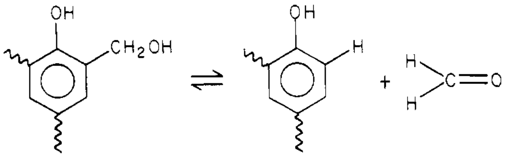


Figure 2. ^{13}C CP/MAS spectra of various heat-treated resoles. Resins were prepared with 5% ^{13}C enriched formaldehyde P/F/NaOH = 1/2/0.01 and cured at 180 °C for 160 min under 15-psi nitrogen. CP spectra obtained with 1-ms contact and 1-s recycle delay. Nonprotonated spectra obtained with 1-ms contact, 1-sec recycle delay, and decoupler gated off for 50 μs before acquisition.[8b] (A) Spectrum of cured resole heated in air to 220 °C for 15 min, 3600 scans; (B) same sample as (A), only nonprotonated carbon selection, 3600 scans; (C) spectrum of cured resole heated in air to 300 °C for 15 min, 3600 scans; (D) same sample as (C), only nonprotonated carbon selection, 3600 scans; (E) spectrum of cured resole heated in air to 300 °C for 90 min, 5200 scans; (F) same sample as (E), only nonprotonated carbon selection, 5200 scans; (G) spectrum of cured resole heated in air to 300 °C for 300 min, 2200 scans; (H) same sample as (G), only nonprotonated carbon selection, 2200 scans; (I) spectrum of cured resole heated in air to 400 °C for 15 min, 3600 scans; (J) same sample as (I), only nonprotonated carbon selection, 3600 scans.

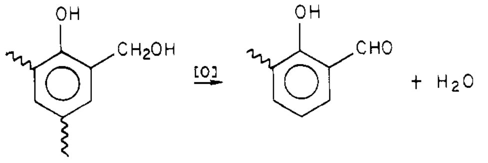
The effect of curing the enriched sample at 220 °C is shown in Figure 2A,B. The main change in the spectrum of Figure 1B is the marked decrease in the relative intensity of the peak at 70 ppm due to methylol groupings and the increase in the methylene absorption. Although there may be some direct loss of methylol groups by the reverse of the addition equilibrium, eq 1, it would appear from the peak intensities that, in this resin at least, most are converted to methylene groupings by the normal curing mechanism, utilizing the few remaining free ortho and para sites. Consistent with these conclusions, the weight loss



(1)

at this stage is less than 3%.

There is also a small amount of oxidation at this stage, indicated by the small absorption at $\delta = 190$. Comparison of spectra A and B of Figure 2 reveals that this is due to a protonated carbon and it is assigned to aldehyde groupings formed presumably by the direct oxidation of methylol groupings as in eq 2.

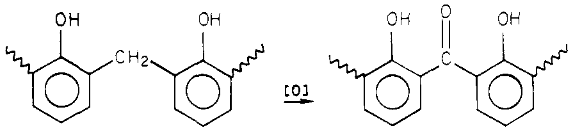


(2)

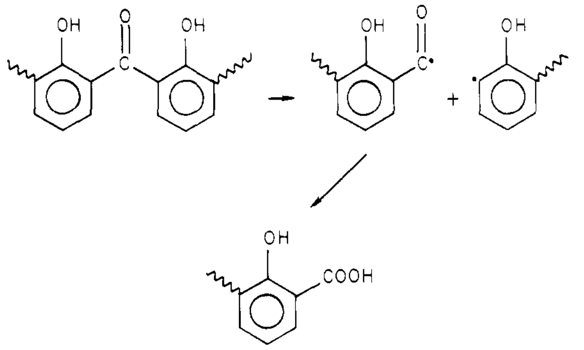
In addition, there is the somewhat surprising formation of methyl groups, as indicated by the absorption at $\delta = 15$. This is observed in all of the samples and is a major pathway when the reaction is carried out under vacuum and will be discussed subsequently. (It should be noted that there is evidence even in the spectrum of the starting resin cured at 180 °C for this formation of minor amounts of the aldehyde and methyl functionalities.) Thus, at these temperatures, little degradation and, in particular, oxidation of the structure have taken place. Further heating at 220 °C causes the complete loss of the methylol groups and an increase in the amount of oxidation, indicated by the appearance of small peaks in the 150–190-ppm range (not shown).

At 300 °C, the oxidative degradation of the sample is rapid and substantial (Figure 2C–H). After only 15 min there is the complete loss of the methylol groups but only a small amount of oxidation (weight loss ~7%), indicating that the substantial oxidation which takes place subsequently (Figure 2E–H) cannot be via methylol moieties. As heating at 300 °C is continued, there is a marked decrease in the intensity of the methylene resonance with the simultaneous formation of a number of carbonyl absorptions in the range 150–195 ppm. These are assigned to acid and ketone functionalities as indicated in the figure from the chemical shift values of reference compounds (hydroxybenzoic acid and dihydroxybenzophenone). It should be noted that the peak at $\delta = 172$ is now due mainly to an acid carbonyl function, as it appears clearly in the spectra recorded using the nonprotonated carbon selection experiment (Figure 2F,H) and that there is a "carbonyl" peak (indicated by arrows) in the same shift range as the hydroxyl-bearing phenolic carbon, evidenced by the increase of the spectral intensity in this range. As previously postulated form IR data[15] these groups can be formed as in eq 3 and 4 although, as indicated above, the spectra rule out their formation from methylol groups. The relative intensities of the carbonyl absorptions are constant with time, indicating that the formation of the two types of functionalities occurs at comparable and constant rates, leading to a "uniform" oxidized structure for the material.

The weight loss at this stage is only moderate (10% after 60 min) but it would appear that a gradual ablation of the sample is taking place from a limiting "oxidized" structure. As noted previously, these spectra discriminate in favor of functionalities derived from the formaldehyde-based protion of the resin and against such species as quinones derived from the phenol, but spectra of unenriched samples indicate that formation of these is not a *major* oxidation pathway, although small amounts may well be formed.

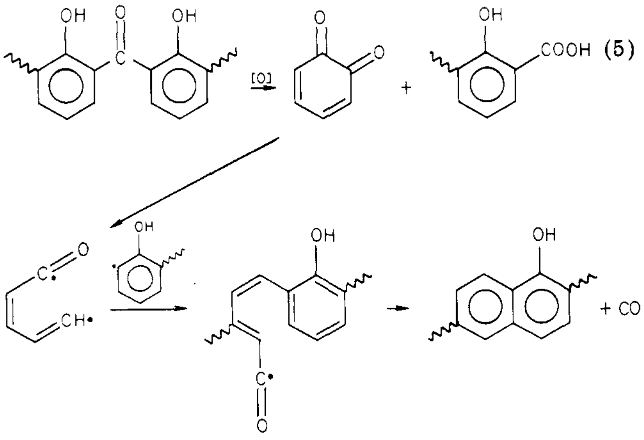


(3)



(4)

At higher temperatures (400 °C) there is rapid degradation and decomposition of the sample. There is considerable loss of material (43% after 15 min and 52% after 30 min) and drastic changes in the spectra as shown in Figure 2I,J. There has again been almost complete loss of the methylene resonance but there are no carbonyl functionalities present and the absorption due to the hydroxyl-bearing phenolic carbons appears to be reduced. The spectra indicate the loss of almost all linking groups and the formation of an essentially aromatic species. Comparison with the spectra of a nonenriched resin indicates that about 10% of the aromatics are formed from the linking groups. This is in agreement with the formation of polycyclics, suggested by the IR data as in eq 5, but the shift is also compatible with the direct elimination of CO bridges forming biphenyl-type units as shown in eq 6.



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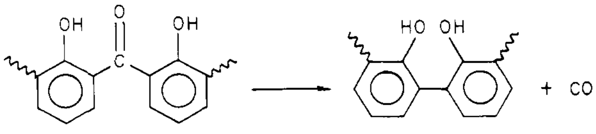


(6)

From both the weight loss and spectral data it is obvious that severe and extensive sample degradation of the sample occurs at this temperature. The spectra themselves identify only the nature of the products and do not imply a particular mechanism for their formation. However, a quite different situation involving little decomposition prevails when the reaction is carried out under vacuum (see following section), which implies that the decompositions are via oxidized intermediate species as indicated in eq 5 and 6.

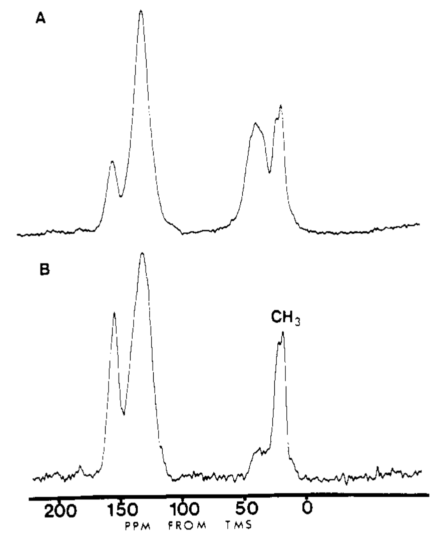
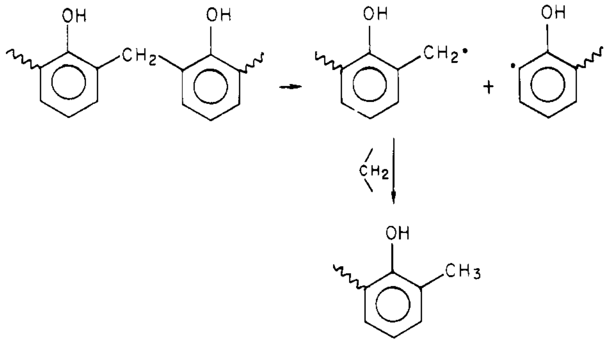


Figure 3. ^{13}C/MAS spectra of cured resole heated under vacuum to 400 °C for 60 min. Resins prepared with 5% ^{13}C-enriched formaldehyde P/F/NaOH = 1/2/0.01. (A) Spectrum using 1-ms contact and 1-s recycle delay, 3600 scans; (B) same sample as (A), only nonprotonated carbon selection, 3600 scans.

Degradation under Vacuum. When the reaction is carried out at 400 °C under vacum, quite different results are obtained, as shown in Figure 3. There has been loss of the methylol functionalities and the formation of substantial amounts of methyl groups but little structural change in the sample. The methyl groups may be formed via reaction 7, where no oxygen is needed for the reaction.



(7)

There are two methyl signals observed, due probably to ortho and para substitution with respect to the hydroxyl group, and the relative narrowness of the absorptions indicates that the sample is much more homogeneous in nature than the air-cured resins. The sample is thus much more stable under vacuum, confirming the oxidative nature of the degradation process. When the sample is cooled and then heated in air at 300 °C, it follows the same oxidation sequence described in Figure 2, confirming that the oxidized functionalities are not from methylol groupings.

Conclusions

The application of high-resolution ^{13}C CP/MAS NMR spectroscopy to the decomposition reactions of solid cured phenolic resins at elevated temperatures provides considerable structural information on the solid species formed and the nature of the degradation processes. At elevated temperatures in air, substantial degradation takes place: Methylol groups are lost but the main processes are thought to be oxidative in nature, in agreement with previous IR data involving at 300 °C the formation of acid and ketone carbonyl functionalties from the bridging methylene groups, with moderate and gradual weight loss. At 400 °C there is rapid and substantial weight loss and the formation of a highly aromatic char with no carbonyl functionalities but again by an oxidative mechanism.

In the absence of oxygen, there is loss of methylol groups and methyl group formation but the methylene groups remain intact and the structural and chemical integrity of the resin is largely preserved.

We are currently carrying out further investigations of these systems in an attempt to better understand the mechanisms of these oxidative decomposition processes.

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Registry No. Formaldehyde–phenol copolymer, 9003-35-4.

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