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^{13}C NMR Investigation of the Stability of a Resol-Type Phenol–Formaldehyde Resin toward Formalin, toward Base, and toward Nonoxidizing or Oxidizing Acid

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ABSTRACT: A resol-type phenol–formaldehyde (PF) resin was subjected to various treatments: with 1 N sodium hydroxide solution or 1 N sulfuric acid solution under $N_2(g)$ at 65 °C for 3 days, with 36.8% formalin under $N_2(g)$ at room temperature for 1 day, with 36 N sulfuric acid under $N_2(g)$ at room temperature or at 65 °C for 1 day, and with 15 N nitric acid in air at room temperature for 1 day. The effects of these treatments on the structures of PF resins have been elucidated on the basis of ^{13}C CP/MAS NMR spectra and are discussed in terms of fundamental chemical processes.

Introduction

The cured resol-type phenol–formaldehyde (PF) resins[1,2] formed from formaldehyde and phenol are highly cross-linked and versatile materials. They offer good mechanical and thermal properties, are resistant to nonoxidizing inorganic or organic acids at elevated temperatures, and are resistant to moisture as well as various other chemicals. Furthermore, phenolic resins are resistant to attack by fungi and bacteria.[2] With these properties and excellent dimensional stability, phenolic resins find a wide range of applications in a variety of forms. At present, these resins are used mainly in applications related to the wood industry, thermal insulation, and molding.[1] Expansion or refinement of such applications would benefit from the systematic study of the structural effects of certain harsh acid, base, or oxidative treatments.

The high-resolution solid-state ^{13}C NMR technique that consists of the combination of cross polarization[3] with high-power ^{1}H decoupling and magic-angle spinning[4] (CP/MAS)[5] is a powerful tool for elucidating the structural details and the curing processes of resins.[6–15] In this article, we present results of a ^{13}C CP/MAS NMR study of the effects of strong inorganic acid, of base, and of formalin solutions on a cured resol-type PF resin. A ^{13}C CP/MAS NMR study of the thermal decomposition of a PF resin in air or under vacuum up to 400 °C has been reported by Fyfe et al.[16]

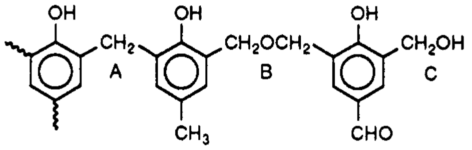
Experimental Section

A. Samples. The preparation of a cured resol-type phenolic resin, labeled PF 50, from a mixture with an initial formal formaldehyde-to-phenol molar ratio of 2.2 and an initial catalyst level of 0.35 mol of sodium hydroxide/mol of phenol was described in a previous article.[8] In the study reported here, the cured PF 50 resin was subjected to the following treatments: (a) 0.8 g of the resin was stirred with 40 mL of 1.0 N aqueous sodium hydroxide solution under $N_2(g)$ at 65 °C for 3 days; (b) 0.8 g of the resin was stirred with 40 mL of formalin (Fisher Scientific, containing 36.8% formaldehyde and 8% methanol) under $N_2(g)$ at room temperature (25 ± 2 °C) for 1 day; (c) 0.8 g of the resin was stirred with 40 mL of a 1.0 N aqueous sulfuric acid solution under $N_2(g)$ at 65 °C for 3 days; (d) 0.8 g of resin was stirred with 40 mL of 36 N sulfuric acid under $N_2(g)$ at room temperature for 1 day; (e) 0.8 g of resin was stirred with 40 mL of 36 N sulfuric acid under $N_2(g)$ at 65 °C for 1 day; and (f) 0.8 g of resin was stirred with 40 mL of 15 N nitric acid at room temperature for 1 day. Following each of these six different treatments, the residues were washed three times with 50-mL portions of distilled water and dried in air, except the residue from treatment b, which was evacuated at 10^{-2} Torr after washing with distilled water.

B. NMR Measurements. All the resin samples specified in section A were investigated by ^{13}C CP/MAS NMR at 15.1 MHz on a modified JEOL FX-60Q spectrometer. The corresponding 50-μs interrupted-decoupling ^{13}C CP/MAS NMR experiment[17] was performed on each sample in order to distinguish hydrogen-bearing carbons in rigid frameworks from those ^{13}C's without directly attached hydrogens or hydrogen-bearing carbons in mobile situations (e.g., rotating methyl groups). The residue obtained from cured PF 50 after the concentrated nitric acid treatment was also investigated by ^{13}C CP/MAS NMR at three higher magnetic fields (corresponding to 90-, 100-, and 200-MHz spectrometers) in order to understand the possible quadrupolar effect of ^{14}N on the ^{14}N–^{13}C dipolar interaction[18–24] and the influence of this effect on the ^{13}C CP/MAS spectra. The liquid portion obtained from the concentrated nitric acid mixture was investigated by liquid-state ^{13}C NMR spectroscopy at 25.1 MHz on a JEOL FX-100 spectrometer.

Results and Discussion

The main types of structures believed to be present in cured resol-type PF resins are characterized by phenolic rings that are bridged by methylene linkages (A) or dimethylene ether linkages (B) at ortho and/or para positions relative to the phenolic hydroxyl groups. Some phenolic rings of PF resins contain attached methylol groups (C) at positions ortho or para relative to phenolic hydroxyl groups. The proportions and positions of methylene linkages (A), dimethylene ether linkages (B), and methylol groups (C) in the phenolic rings of a PF resin depend on details of the synthesis procedure, such as the initial formal phenol-to-formaldehyde molar ratio, pH value, catalyst, and temperature.[1,2,6–9] From the point of view of ^{13}C chemical shift values and ranges, there are three different kinds of methylene linkages, depending on the ring positions of the connection points between two phenolic rings: *o,o'*-methylene linkages, with a ^{13}C NMR chemical shift of ca. 30 ppm; *o,p'*-methylene linkages, with a ^{13}C chemical shift of ca. 35 ppm; and *p,p'*-methylene linkages, with a ^{13}C NMR chemical shift of ca. 40 ppm.[25,26] There are small quantities of methyl groups and formyl groups attached to the ortho or para positions relative to the phenolic hydroxyl groups and other minor linkages in some PF resins.[8,16,27]



I

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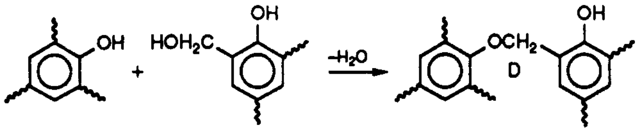
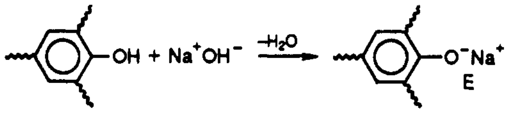
As reported in a previous article,[8] a new type of methylene linkage (D) has been found in cured resol-type PF resins; this type of linkage involves the phenolic hydroxyl oxygen in an ether moiety and is absent in the corresponding uncured resins.[8] The formation of this type of linkage can be visualized as follows:



II

(1)

The ^{13}C NMR chemical shift of an aromatic carbon attached to oxygen in a type-D linkage is ca. 160 ppm; this resonance appears as a shoulder on the main peak at 152 ppm, assigned to the aromatic carbon bearing a phenolic hydroxyl group.[8] Both the shoulder around 160 ppm and the main peak at 152 ppm strongly survive a 50-μs interrupted-decoupling period.[8,17] In a cured PF 50 resin sample prepared from a mixture with a NaOH/phenol molar ratio of 0.35, it is reasonable to assume that some of the phenolic hydroxyl groups in the resin exist in the anionic form[28-30] (E):



(2)

In this kind of system some of the phenolic hydroxyls are ionized and some are not. Because this is an amorphous system, there can be a wide range of structural situations between these two extremes, with various degrees of hydrogen bonding, hydration, and Na^+ complexation; exchanges among these various kinds of structural situations may occur with a wide range of dynamics. It is possible that two or more phenolic hydroxyl groups can be involved in dynamic equilibria with a given NaOH unit; some phenolic hydroxyl groups may not have any sodium hydroxide units in their vicinity. With this picture of the participation of sodium hydroxide in enhancing chemical heterogeneity in the local environment of phenolic hydroxyl sites, it is not difficult to rationalize the fact that the ^{13}C NMR chemical shift of the aromatic ^{13}C attached to oxygen extends from 152 to 168 ppm in the ^{13}C spectra of these resins.[29-31]

In view of the high concentration of sodium hydroxide used in the synthesis of the cured PF 50 resin,[8] it is reasonable to assume that species E and a variety of related species are partially responsible for the 160 ppm shoulder in their ^{13}C CP/MAS NMR spectra. As discussed later in this article, the contribution from species D to the low-shielding (high-frequency) shoulder of the 152 ppm peak can be separated from the contribution of species E and related structures.

Figure 1a shows the ^{13}C CP/MAS NMR spectrum of untreated, cured PF 50 resin. The dominant peak around 130 ppm is assigned to other aromatic carbons not bearing oxygen, the peak around 73 ppm is assigned to methylene carbons of various ether groups (B and D), and the peak around 65 ppm is assigned to the CH_2 carbons of methylol groups.[6-9,26] The peaks at ca. 194, 30–40, and 18 ppm in Figure 1a are assigned to the CHO group,[8,16] various methylene linkages,[6-9,25,26] and methyl groups,[8,16] respectively, in each case attached to phenolic rings at positions ortho or para to a phenolic hydroxyl group. A summary of ^{13}C chemical shifts relevant to this work is given in Table I.

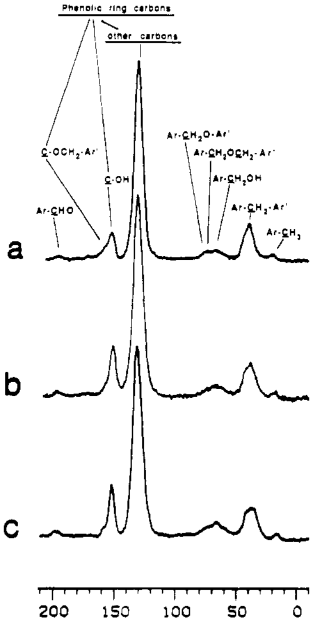


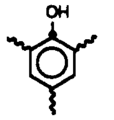
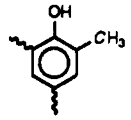
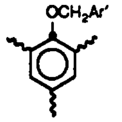
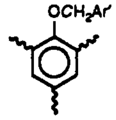
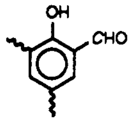
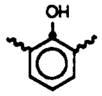
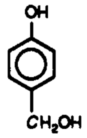
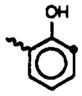
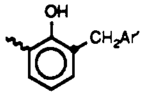
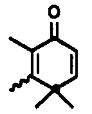
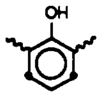
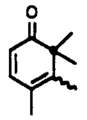
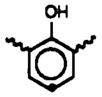
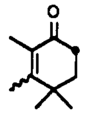
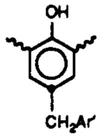
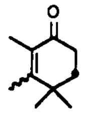
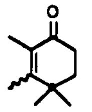
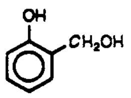
Figure 1. 15.1-MHz ^{13}C CP/MAS NMR spectra of (a) a resol-type PF resin (cured PF 50 resin), (b) cured PF 50 resin after treatment with 1.0 N sodium hydroxide solution under $N_2(g)$ at 65 °C for 3 days, and (c) cured PF 50 resin after treatment with 36.8% formalin under $N_2(g)$ at 25 °C for 1 day. Contact time = 1 ms; repetition time = 1 s.

Figure 1b shows the ^{13}C CP/MAS NMR spectrum of the residue of cured PF 50 resin after alkaline hydrolytic treatment (1 N NaOH solution at 65 °C for 3 days). Overall, the intensity in the 150–165 ppm region has been sharpened and concentrated around 152 ppm in the spectrum of the treated resin sample (Figure 1b), compared to the spectrum of the untreated sample (Figure 1a). The dominant portion of phenolic hydroxyl groups in this washed sample is in the neutral form,[28,29] and the aromatic carbon bearing the phenolic hydroxyl group therefore has a ^{13}C NMR signal at 152 ppm. Some fraction of the hydroxyl groups in these samples is ionized, and this fraction is responsible for a small portion of the shoulder at 159 ppm; however, the intensity centered at ca. 159 ppm in Figure 1b can largely be assigned to the aromatic carbons bearing a phenolic hydroxyl group that has been "etherized" to species D.[8] The etherification of the phenolic hydroxyl group (O-alkylation) has been used to improve alkali resistance of PF resin.[33] Species D is stable toward hydrolytic treatment under alkaline condition, and it is reasonable to assign the major portion of the 159 ppm peak in Figure 1b to the aromatic carbons attached to linkage D.

Urea–formaldehyde (UF) resins are reported to have substantial solubilities in formalin.[34] Because cured UF resins contain methylene linkages, dimethylene ether linkages, and methylol groups and the dissolution process probably involves these groups, it was of interest to see if treatment with 36.8% formalin has any influence on the structure of cured PF 50 resin. One obvious observation was that the cured PF 50 resin is not markedly soluble in formalin (0.8 g of resin/50 mL of formalin after stirring under nitrogen at room temperature for 1 day). Figure 1c is the ^{13}C CP/MAS NMR spectrum of the sample prepared by treatment of the cured PF 50 resin with formalin, followed by washing three times with 50-mL portions of distilled water and then freeze-drying under vacuum for 12 h. The pH value of the 36.8% formalin solution is 4.5, so it is an effective neutralization agent for the alkaline-cured PF 50 resin, in contrast to a 1 N NaOH/H_2O wash

Table I

^{13}C Chemical Shift Regions for Various Carbon Types Found in Phenol–Formaldehyde Resins and Parent Structures of Their Possible Reaction Products

structure	^{13}C chem shift,[a] ppm	ref	structure	^{13}C chem shift,[a] ppm	ref
		A. From Solid-State NMR			
	150 152	7 8		18 15	8 16
	160 159	8 this work		75	this work
	194 190	8 16			
		B. From Liquid-State NMR			
	153.1–158.7	25		65.5	26
	152–168	29–31	ArCH$_2$Ar′		
			o,o′ [b]	30.8–31.4 29.2	25 26
			o,p′ [b]	35.5–35.9 34.9	25 26
	115.4–116.0	25	*p,p′* [b]	41.0 39.7	25 26
	127.6–130.6	25		39.5–39.8	32
	127.4–132.3	25		49.3	32
	119.9–120.9	25		34.3	32
	132.1–133.9	25		37.4–37.6	32
ArCH$_2$OCH$_2$Ar′	70.8	26		35.8–35.9	32
	61.4–62.3	26			

[a] Chemical shifts are relative to liquid tetramethylsilane, larger numbers corresponding to lower shielding. Values refer to carbons indicated by dots or italics. [b] The positions of methylene linkages in the phenolic rings relative to the OH groups.

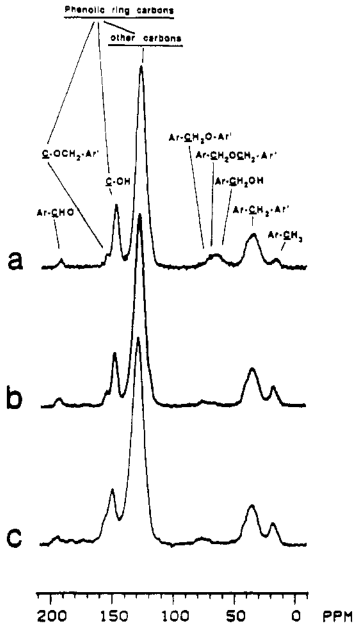


Figure 2. 15.1-MHz ^{13}C CP/MAS NMR spectra of three residues of cured PF 50 resin after treatment with sulfuric acid under N_2(g) and three different conditions: (a) 1.0 N sulfuric acid solution at 65 °C for 3 days; (b) 36 N sulfuric acid at 25 °C for 1 day; (c) 36 N sulfuric acid at 65 °C for 1 day. Contact time = 1 ms; repetition time = 1 s.

treatment; therefore, the peak around 152 ppm of Figure 1c is sharpened further in comparison to the case seen in Figure 1b and the shoulder at ca. 159 ppm is separated somewhat better from the 152 ppm peak in Figure 1c. In addition to the neutralization effects, the other effects of treating the cured PF 50 resin with formalin (Figure 1c) are small increases in the intensities corresponding to methylol groups (65 ppm) attached to the ortho or para positions and the *p,p'*-methylene linkages (40 ppm) connecting two phenolic rings relative to the intensities corresponding to phenolic hydroxyl groups. The increased amounts of methylol groups and *p,p'*-methylene linkages are generated by the methylolation of phenolic rings in the cured PF 50 resin by formalin. There is no evidence in Figure 1c of methoxy groups (55 ppm)[15] formed from a reaction between methylol groups attached to phenolic rings and the 8% methanol present in formalin; neither is there any evidence of poly(oxymethylene) chains, $-(CH_2O)_n-$, at ca. 87–92 ppm, formed from a reaction between methylol groups attached to phenolic rings and methylene glycol constituents in formalin. According to the spectrum of Figure 1c, the methylene glycol in formalin also does not react with phenolic hydroxyl groups to produce $ArOCH_2OH$ moieties, for which the ^{13}C chemical shift would be ca. 87 ppm.

One of the excellent properties of PF resins is their apparent resistance to nonoxidizing inorganic or organic acids, even at elevated temperatures.[1,2] In order to examine any structural effects of nonoxidizing acids on the cured PF 50 resin, the samples obtained after treatment with 1 N aqueous sulfuric acid solution under N_2(g) at 65 °C for 3 days or 36 N sulfuric acid under N_2(g) at room temperature or at 65 °C for 1 day were investigated by ^{13}C CP/MAS NMR; the results are shown in Figure 2a–c. Compared to Figure 1b, Figure 2a shows a sharper 152 ppm peak, with a slight shift to higher shielding, and a distinctly sharper 159 ppm peak; these patterns are in agreement with the fact that 1 N sulfuric acid solution is a highly effective neutralizing agent for the alkaline-cured PF 50 resin. The ^{13}C NMR results indicate that the *only* effect of 1 N sulfuric acid solution on the alkaline-cured PF 50 resin is neutralization.

The effects of concentrated sulfuric acid (36 N) on cured PF 50 resin give rise to some new structural features. As indicated by Figure 2b, treatment with 36 N sulfuric acid under N_2(g) at room temperature for 1 day results in several changes: (a) simplification of the structural distribution of phenolic hydroxyl groups by elimination of the anionic form,[28,29] as indicated by the sharpened 159 and 152 ppm peaks in the spectrum of Figure 2b compared to that in Figure 1a (however, a new shoulder appears on the high-shielding (low-frequency) side of the 152 ppm peak); (b) demethylolation, as indicated by the substantial disappearance of intensity around 65 ppm (methylols, C) from the spectrum of Figure 2b; (c) a decrease in the proportion of dimethylene ether linkages (B, 73 ppm); (d) increases in the proportions of CHO (194 ppm) and CH_3 (18 ppm) groups attached to phenolic rings at positions ortho or para to a phenolic hydroxyl group; and (e) a new shoulder on the high-shielding (low-frequency) side of the 130 ppm peak (at 117–122 ppm) in the spectrum of Figure 2b. This new shoulder on the 130 ppm peak in Figure 2b does not survive a 50-μs interrupted-decoupling period[17] (spectrum not shown here) and, hence, arises from a hydrogen-bearing aromatic carbon. As the methylol groups (C, 65 ppm) are depleted from phenolic rings, the newly created unsubstituted aromatic carbons appear with an 11–13 ppm increase in shielding (low-frequency shift) relative to carbon-substituted aromatic carbons[31] and are responsible for the new shoulder on the low-frequency side of the 130 ppm peak in the spectrum of Figure 2b.

It is well-known that concentrated sulfuric acid can sulfonate phenolic rings;[35] at 15–20 °C the sulfonation mainly occurs at ortho positions relative to a phenolic hydroxyl group, whereas at 100 °C the sulfonation goes mainly to the corresponding para position. We expect that at room temperature (25 ± 2 °C) concentrated sulfuric acid can sulfonate some of the aromatic carbons ortho to the phenolic hydroxyl group in the resin system of this study. Then, if the additivity rule for substituent effects[36–41] can be assumed to be valid in this case, the ^{13}C NMR chemical shift of the ipso and ortho positions relative to the sulfonic acid group should experience a low-shielding (high-frequency) shift of 14.5 ppm and a high-shielding shift of 2.7 ppm, respectively,[31] and the aromatic carbon bearing the phenolic hydroxyl group and ortho to the sulfonic acid group should experience a 2.7 ppm high-shielding (low-frequency) shift in comparison to the corresponding aromatic COH carbon without a sulfonic acid group in the ortho position. According to the above speculation, the small shoulder on the high-shielding side of the 152 ppm peak in Figure 2b can be explained at least partially by the sulfonation of phenolic rings at the position ortho to the phenolic hydroxyl group at room temperature by concentrated (36 N) sulfuric acid.

As suggested by Zinke[27] and confirmed by ^{13}C CP/MAS NMR spectroscopy in a previous article,[8] a dimethylene ether linkage (B, 73 ppm) in a PF resin can be cleaved to form a methyl group (18 ppm) and a formyl group (194 ppm). When the cured PF 50 resin was treated with 36 N sulfuric acid at room temperature, most of the dimethylene ether linkages disappeared and some of them probably formed $Ar'CH_3$ methyl groups (18 ppm) and Ar-CHO formyl groups (194 ppm); this is indicated by a substantial decrease in intensity in the region around 73 ppm and increases in intensities around 18 and 194 ppm in the spectrum of Figure 2b in comparison to intensities in Figure 1a. According to the predictions of substituent-effect additivity of chemical shifts,[36-41] when a methyl group is attached to the position para to the phenolic hydroxyl group, it should cause a high-shielding shift of ca. 3 ppm[31] in the ^{13}C NMR chemical shift of the aromatic carbon bearing the phenolic hydroxyl group; therefore, if the $ArCH_3$ moiety formed from cleavage of $ArCH_2OCH_2Ar'$ had the methyl group attached to a carbon atom para to the phenolic hydroxyl group, it could partially account for the high-shielding shoulder of the 152 ppm peak in the spectrum of Figure 2b. Concentrated (36 N) sulfuric acid did not markedly affect the methylene linkages of the cured PF 50 resin at room temperature, as indicated by the similarity of the 30–40 ppm region in the spectra of Figures 1a and 2b, even though this treatment caused a depletion of most of the methylol groups (C, 65 ppm) and of the dimethylene ether linkages (B, 73 ppm). Treatment with 36 N sulfuric acid at room temperature did not eliminate the $ArOCH_2Ar'$ linkages in the cured PF 50 resin, at least during the 1-day period of treatment, as indicated by retention of intensity at 159 and 75 ppm in the spectrum of Figure 2b.

Figure 2c shows the ^{13}C CP/MAS NMR spectrum of the residue of the cured PF 50 resin after treatment with 36 N sulfuric acid under $N_2(g)$ at 65 °C for 1 day, followed by washing with distilled water. In comparison to the spectrum shown in Figure 2b, the spectrum of Figure 2c shows generally larger line widths for the peaks in the aromatic carbon region. As mentioned above, at 15–20 °C the sulfonation of phenolic rings occurs at the ortho position relative to the phenolic hydroxyl group, whereas at 100 °C the sulfonation occurs at the corresponding para position.[35] Therefore, the sulfonation of phenolic rings at 65 °C with 36 N sulfuric acid may be expected to occur at ortho and/or para positions relative to the phenolic hydroxyl group. When a sulfonic group is attached to the para position of a phenolic hydroxyl group, the SO_3H-substituted carbon experiences a 14.5 ppm low-shielding (high-frequency) shift, while the hydroxyl-bearing carbon suffers a 3.3 ppm low-shielding shift;[31] this can be expected to cause some broadening in the low-shielding side of the 152 ppm peak. One can also expect some broadening of the intense 130 ppm peak, especially on the low-shielding side, because of the low-shielding shift of aromatic carbons bearing the sulfonic groups. As mentioned above, sulfonate substitution at the ortho position relative to the phenolic hydroxyl group gives rise to a shoulder on the high-shielding side of the 152 ppm peak, whereas the elimination of methylol groups (C, 65 ppm) and dimethylene ether linkages (B, 73 ppm) from phenolic rings of the cured PF 50 resin causes an increase in the intensity of the shoulder on the high-shielding side of the 130 ppm peak. With a combination of sulfonation of phenolic rings at ortho and para positions relative to the phenolic hydroxyl group and the elimination of methylol groups and dimethylene ether linkages, we expect intensity on both sides of the peaks at 152 and at 130 ppm, i.e., broadening. Except for the increased occurrence at 65 °C of sulfonation at the alternate para positions, the residue of cured PF 50 resin treated with 36 N sulfuric acid under $N_2(g)$ at 65 °C is not substantially different from that obtained by room temperature treatment.

The esterification of phenolic hydroxyl groups of novolak resins with inorganic polybasic acids has been exploited to increase the heat and flame resistance of phenolic resins.[42] Because sulfuric acid is a dibasic acid, the possibility of esterification of phenolic hydroxyl groups of cured PF 50 resin by 1 N or 36 N sulfuric acid is not ruled out by this ^{13}C study.

After exploring the behavior of the cured PF 50 resin toward a nonoxidizing inorganic acid, we thought it would be interesting to study the behavior of this resin toward an oxidizing inorganic acid. For this purpose we have chosen a treatment with 15 N nitric acid in air at room temperature for 1 day. With a concentration below 2 N, nitric acid is only a relatively weak oxidizing agent; however, concentrated nitric acid (such as 15 N) is a powerful oxidizing agent.[43] Therefore, 15 N nitric acid can function as a mineral acid, a nitration agent for many organic compounds, or a strong oxidizing agent.[43] In the previously reported ^{13}C CP/MAS NMR study of the thermal decomposition of a PF resin in air or under vacuum at temperatures up to 400 °C, several possible decomposition reactions were suggested.[16] In the following section, we try to understand the behavior of the cured PF 50 resin toward the combination of chemical functions of 15 N nitric acid at room temperature as a mineral acid, a nitration agent, and a strong oxidizing agent.

Various side chains like methyl groups, methylene linkages, dimethylene ether linkages, methylol groups, and CHO groups that may be attached to phenolic rings in PF resins, primarily at positions ortho or para relative to the phenolic hydroxyl group, may undergo nitration or oxidation by nitric acid to some extent. Some possible reactions are presented below for the methyl group:

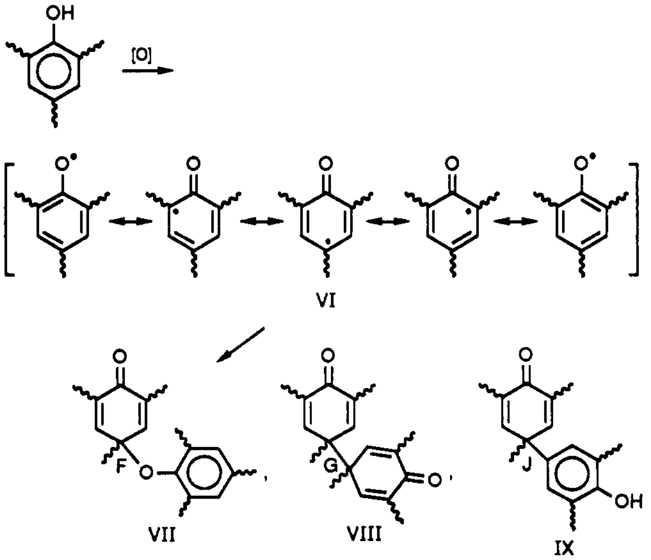
$$ArCH_3 + HNO_3 \rightarrow \underset{\text{III}}{ArCH_2NO_2} + H_2O \tag{3}$$

$$ArCH_3 + 6HNO_3 \rightarrow \underset{\text{IV}}{ArCOOH} + 6NO_2(g) + 4H_2O \tag{4}$$

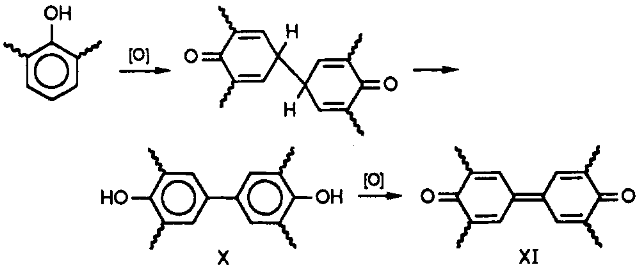
$$ArCH_3 + 4HNO_3 \rightarrow \underset{\text{V}}{ArCHO} + 4NO_2(g) + 3H_2O \tag{4'}$$

For methylene linkages (A in I), oxidation to either an aromatic carboxylic acid or a ketone, ArC(O)Ar′ is possible.[16] The dimethylene ether linkages (B of I) and ring-attached methylol groups (C of I) can react by nitration or oxidation, as well as cleavage, as in the cases discussed for treatment by 36 N H_2SO_4.

The aromatic rings of the cured PF 50 resin can react with 15 N nitric acid according to the following modes: (a) nitration at positions ortho or para relative to the phenolic hydroxyl group; (b) oxidation to produce various kinds of species discussed below; and (c) nitration of species resulting from oxidation vis-à-vis (b). The types of products that can be expected to result from oxidation of phenolic rings in PF resins include the following:[44]

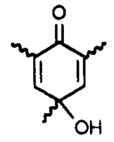


and isomers of VII, VIII, and IX and



X XI

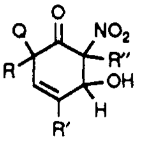
With the presence of water, species of type XII can be formed as well.



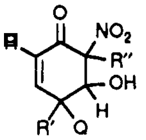
XII

All the species VII–XII can undergo nitration, as mentioned above.

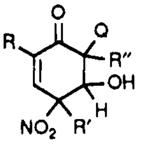
In addition to these oxidation reactions and ring nitration (an electrophilic *substitution* reaction), a possible electrophilic *addition* reaction involving nitronium ion (NO_2^+) to species VII–IX, XII, and their isomers can produce products such as XIII, XIV, and XV, with Q = O or Ar and with R, R′, R″ = H or CH_2.



XIII



XIV



XV

A 25.1-MHz ^{13}C NMR spectrum was obtained on the liquid portion of the mixture of 50 mL of 15 N nitric acid and 0.8 g of cured PF 50 resin after stirring at room temperature for 1 day; there is no observable signal in this spectrum. Figure 3 shows the 50.3-, 22.6-, and 15.1-MHz ^{13}C CP/MAS NMR spectra and the corresponding 15.1-MHz 50-μs interrupted-decoupling[17] ^{13}C CP/MAS spectrum of the residue of the cured PF 50 resin after the 15 N nitric acid treatment at 25 °C for 1 day. The main new features in Figure 3 that are not apparent in Figures 1 and 2 are the large peaks centered at 79 and 94 ppm. In addition, close inspection of Figure 3 reveals the existence of a significant "shoulder" intensity extending to about 102 ppm in the spectra. Possible candidates for assignment of these three peaks include, respectively, species III; $ArCH(NO_2)Ar'$ (XVI), formed through the nitration of various methylene linkages (IA); and species XIII–XV. The nitro group causes a low-shielding shift of ca. 60 ppm[45] on the chemical shift of a ^{13}C nucleus at a substituted alkane site and a low-shielding shift of ca. 48 ppm[46] at a substituted site next to the ketonic carbon of cyclohexanones; therefore, the carbon bearing the nitro group should have a ^{13}C chemical shift of ca. 78 ppm for species III, ca. 90–100 ppm for XVI, ca. 90 or 105 ppm for species XIII and XIV, respectively, and ca. 85 or 100 ppm for species XV (with the R's being H or CH_2 for species XIII–XV).

The detailed character of the 70–110 ppm intensity patterns seen in the spectra in Figure 3c could a priori be due at least partially to splittings that arise from the effect of the quadrupolar ^{14}N on the ^{13}C resonance[18–24] through the ^{14}N–^{13}C dipolar interaction. This neighboring ^{14}N effect is well-known to decrease in importance as the Larmor frequency is increased. One can see small differences in the 70–110 ppm spectral patterns among the three spectra in Figure 3a–c; however, the main features are largely independent of the static magnetic field strength.

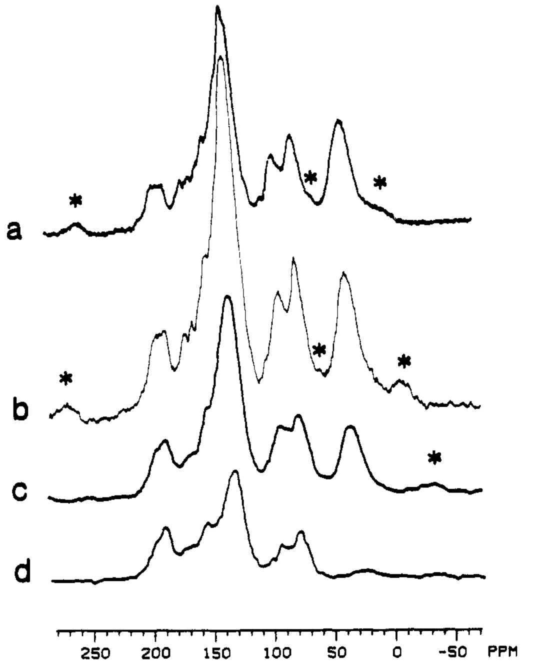


Figure 3. ^{13}C NMR spectra of the residue of cured PF 50 resin after treatment with 15 N nitric acid in air at 25 °C for 1 day (contact time = 1 ms; repetition time = 1 s): (a) 50.3-MHz CP/MAS spectrum; (b) 22.6-MHz CP/MAS spectrum; (c) 15.1-MHz CP/MAS spectrum; (d) 15.1-MHz 50-μs interrupted-decoupling CP/MAS spectrum. Spinning sidebands are indicated by asterisks.

Because of the directly attached proton, the magnetization arising from the carbon nucleus bearing a nitro group in species III or XVI, with ^{13}C chemical shifts around 78 or 90–100 ppm, cannot survive to detection in a 50-μs interrupted-decoupling ^{13}C CP/MAS experiment. This behavior is in contrast to what is expected for the signals that arise from the carbons bearing nitro groups in species XIII (with R″ = CH_2), XIV (with R″ = CH_2), or XV (with R′ = CH_2) with ^{13}C chemical shifts expected at 105, 105, or 100 ppm, respectively. In the spectrum of Figure 3d, more than half of the 79 ppm peak and about half of the 94 and 102 ppm peaks in the spectra of Figure 3a–c survive the 50-μs interrupted-decoupling period; this assessment is based on comparisons with the carbonyl peak at ca. 188 ppm. On this basis we can conclude that the NO_2-bearing sp^3 carbons discussed above can at most account only partially for the 79 and 94 ppm peaks in the spectra of Figure 3a–c. The hydroxyl-bearing carbon of species XII should have a chemical shift of ca. 79 ppm,[32,47a] and the ether-bearing carbon (F) of species VII is expected to have a ^{13}C chemical shift of ca. 88 ppm;[32,47b] the ^{13}C NMR signals of both of these sites should survive in the 50-μs interrupted-decoupling experiment. The sp^3 carbons (G or J) of species VIII or IX and their isomers are expected to have ^{13}C resonances at ca. 56–70 ppm;[32] therefore, these structures can be excluded as possible constituents in the sample yielding the ^{13}C spectra of Figure 3. The hydroxyl-bearing sp^3 carbons of species XIII, XIV, or XV are expected (on the basis of taking into account the substituent effect of a neighboring nitro group)[45] to have ^{13}C chemical shifts in the vicinity of 80 ppm,[32,47a] and their signals cannot survive in the 50-μs interrupted-decoupling

^{13}C CP/MAS NMR experiment. Therefore, species XIII, XIV, and XV are possible constituents in the sample represented in Figure 3.

The 18 ppm peak in all the spectra shown in Figures 1 and 2 is absent in the spectra shown in Figure 3. This peak has been assigned to methyl groups attached to phenolic rings at positions ortho or para relative to the phenolic hydroxyl group. The absence of the 18 ppm peak in Figure 3 indicates that these methyl groups may undergo the following kinds of reactions under treatment with concentrated HNO_3/air: nitration to CH_2NO_2 (with a ^{13}C NMR chemical shift around 78 ppm) or oxidation to CHO (194 ppm) or COOH (about 168 ppm).[47c] In view of the presence of the 78, 168, and ~194 ppm peaks in the spectra of Figure 3, we cannot rule out any of these three possibilities. From the fact that the peak extending from ~20 to ~50 ppm in the spectra of Figure 3 has a relative intensity (referenced to the total intensity of the entire spectrum) that is not substantially reduced in comparison to that of the peak extending from ~30 to ~45 ppm in the spectra shown in Figures 1 and 2, we can conclude that most of the methylene linkages (A) connecting two phenolic rings in the cured PF 50 resin are immune to attack by 15 N nitric acid in air; i.e., only a small amount of nitration or oxidation takes place at these methylene linkages. However, the width of the peak centered between 20 and 50 ppm is considerably larger in Figure 3 than the corresponding peak in the spectra shown in Figures 1 and 2. This observation suggests an increase in the degree of chemical structural heterogeneity of the methylene linkages accompanying the concentrated HNO_3/O_2 treatment, e.g., production of the species VII and X–XV.

There is almost no intensity in the region between 56 and 70 ppm in the spectra of Figure 3. Therefore, almost all of the methylol groups (IC, 65 ppm) attached to phenolic rings of the cured PF 50 resin must undergo some changes under concentrated HNO_3/O_2 treatment. The several conversions one can envision include the following: (1) the effects of strong acid treatment similar to those discussed above for 36 N sulfuric acid treatment (production of $ArCH_2ONO_2$ by HNO_3 being excluded as a reaction product on the basis of its chemical shift, ~66 ppm); (2) oxidation of methylol groups to CHO groups (194 ppm) or COOH groups (168 ppm); (3) nitration of CH_2 moieties to $CH(NO)_2OH$ groups (~125 ppm),[45] each of which may undergo further nitration or oxidation, as discussed above. At present, we know only that most of the dimethylene ether linkages and methylol groups are indeed eliminated from the cured PF 50 resin upon concentrated HNO_3/O_2 treatment at room temperature for 1 day. As mentioned above, VIII, IX, and their isomers have been excluded as major oxidative products of the cured PF 50 resin on the basis of the absence of a ^{13}C NMR signal between 56 and 70 ppm in the spectra of Figure 3a–c.

The phenolic rings of cured PF 50 resin have ^{13}C NMR chemical shifts in two main regions, 130 and 152 ppm, as shown in the spectra of Figures 1 and 2. The phenolic rings can be oxidized to species of the types VII or X–XII or can be transformed into structures of the types XIII–XV, as discussed above. The carbonyl ^{13}C chemical shifts of species VII, XI, or XII and their isomers or of species XIII–XV should be in the region 180–206 ppm;[32] these values are consistent with spectral patterns displayed in Figure 3a–c. Almost all the intensity at ~190 ppm and a large fraction of the intensity at ~199 ppm in the spectrum of Figure 3a survive in the 50-μs interrupted-decoupling experiment (Figure 3d) and therefore cannot originate from CHO groups. A portion of the peak at ~199 ppm in the spectrum in Figure 3a that did not survive in the 50-μs interrupted-decoupling experiment (Figure 3d) can be assigned to the CHO group attached to phenolic rings. Hence, the surviving portion of these two regions in Figure 3d can be assigned to the carbonyl groups of species VII, XI, or XII and their isomers or species XIII–XV. The non-carbonyl sp^2 carbons of species VII and XI–XV are expected to have ^{13}C chemical shifts in the range of 126–161 ppm;[32] this range is consistent with intensity patterns displayed in the spectra of Figure 3a–c.

The phenolic rings of cured PF 50 resin may undergo a nitration reaction to introduce nitro group(s) at positions ortho and/or para relative to the phenolic hydroxyl group. Using simple additivity rules for substituent effects on ^{13}C chemical shifts,[31,47d] one can predict that the nitro-bearing carbon of the nitrated aromatic ring of cured PF 50 resin will have a chemical shift of ca. 135 ppm when ortho to a phenolic oxygen or ca. 140 ppm when para to a phenolic oxygen; the ^{13}C NMR signals of such carbons can survive in an interrupted-decoupling experiment. According to the spectra of Figure 3, there is some degree of nitration of the phenolic rings of the cured PF 50 resin after treatment with 15 N nitric acid in air at room temperature for 1 day.

The 155 ppm shoulder on the main 133 ppm peak in the spectra of Figure 3a–c can be assigned either to the aromatic carbon bearing the phenolic hydroxyl group or to the non-carbonyl sp^2 carbons of the species VII and XI–XV. Judging from the strong intensity in Figure 3a–c in the regions of 190 and 199 ppm (most of which is asigned to carbonyl groups of species VII and XI–XV) and the fact that all these species (VII and XI–XV) originate from oxidation of the phenolic rings of the cured PF 50 resin by 15 N nitric acid, it seems reasonable that at least some portion of the intensity in the ~155 ppm region can be attributed to non-carbonyl sp^2 carbons of species VII and/or XI–XV, and the rest of the 155 ppm intensity can be attributed to the remaining hydroxyl-bearing aromatic carbons. The region from 165 to 172 ppm in the spectra of Figure 3a–c can be assigned to COOH groups attached to ring positions ortho or para relative to the phenolic hydroxyl groups.

On the basis of the ^{13}C CP/MAS NMR spectra shown in Figure 3 and the discussion above, one can conclude that most of the methylene linkages (IA) in the cured PF 50 resin are stable toward 15 N nitric acid in air, at least at room temperature for 1 day, whereas the other side chains of phenolic rings and the phenolic rings themselves undergo some degree of nitration and/or oxidation under this treatment. How large an effect is due simply to the strong acidity of 15 N nitric acid is not yet clear, nor is the fate of $ArOCH_2Ar'$ species under these conditions.

Conclusions

The ^{13}C CP/MAS NMR technique provides a valuable means of elucidating the effects of base, formalin, nonoxidizing acid, or oxidizing inorganic acid on a resol-type PF resin. The major changes in a cured resol-type resin after treatment with 1 N sodium hydroxide solution or nonoxidizing 1 N sulfuric acid solution under N_2(g) at 65 °C for 3 days or with 36.8% formalin under N_2(g) at room temperature for 1 day is simply neutralization of the resin, bringing the phenolic hydroxyl groups of an alkaline resin into the neutral form. Some of the dimethylene ether linkages (IB) that connect two phenolic rings of the cured PF 50 resin are cleaved by 1 N sodium hydroxide solution to produce two corresponding methylol groups, whereas the dimethylene ether linkages are stable toward treatment with 1 N sulfuric acid or 36.8% formalin. Treatment with 36.8% formalin methylolates some of the phenolic rings of cured PF 50 resin to produce more methylol groups attached to phenolic rings at positions ortho or para with respect to the phenolic hydroxyl group and *p,p'*-methylene linkages between two phenolic rings. Methylene linkages, methylol groups, CHO groups, and CH_3 groups attached to phenolic rings of cured PF 50 resin, as well as $ArOCH_2Ar'$ species, are stable toward these three types of treatments.

Almost all of the methylol groups and dimethylene ether linkages in cured PF 50 resin are eliminated by treatment with concentrated (36 N) sulfuric acid under $N_2(g)$ at room temperature or at 65 °C for 1 day. Some of the dimethylene ether linkages are cleaved[8,27] by concentrated sulfuric acid to produce CHO and CH_3 moieties, whereas methylene linkages, CHO groups, CH_3 groups, and $ArOCH_2Ar'$ moieties in the resin are stable toward this strong, nonoxidizing 36 N sulfuric acid, at least under $N_2(g)$ at room temperature or at 65 °C for 1 day. Concentrated sulfuric acid sulfonates some of the aromatic carbons at positions ortho to the phenolic hydroxyl groups of cured PF resin at room temperature[35] and sulfonates some of the aromatic carbons ortho and/or para to phenolic hydroxyl groups of the resin at 65 °C.

Some major changes in the structure of cured PF 50 resin are brought about by 15 N nitric acid. Some of the phenolic rings of the resin are oxidized to cyclic ketones[44] and some of the phenolic rings are nitrated after treatment with 15 N nitric acid in air at room temperature for 1 day. Most of the methylene linkages and CHO groups in cured PF 50 resin are stable toward 15 N nitric acid at room temperature, at least up to 1 day. Methylol groups and CH_3 groups in cured PF 50 resin are eliminated, becoming nitrated or oxidized.

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Registry No. (P)(F) (copolymer), 9003-35-4; NaOH, 1310-73-2; H_2SO_4, 7664-93-9; HNO_2, 7697-37-2; formaldehyde, 50-00-0.