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## Analysis of phenol-resorcinol-formaldehyde resins

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**Abstract** A method based on high-performance liquid chromatography (HPLC) and proton magnetic resonance (PMR) spectroscopy for analyzing phenol-resorcinol-formaldehyde (PRF) resins is reported. The equations that describe the number-averaged structures of PRF resins in terms of the PMR absorption intensities of acetylated resins have been derived on the basis of the work of Woodbrey et al. and Anderson et al. The P/R molar ratio of the resin calculated from the PMR intensities was in good agreement with the synthetic P/R molar ratio when correction was made for the loss of phenol evaporated during the drying process that preceded the acetylation. The number-averaged molecular weight ( $M_n$ ) of the acetylated resin calculated from the PMR intensities agreed with the  $M_n$  determined by cryoscopy. Unreacted phenol and resorcinol could be determined by analyzing the water-soluble fraction of the resin by use of high-performance liquid chromatography.

**Key words** Phenol-resorcinol-formaldehyde resins · PMR spectroscopic analysis · Phenol/resorcinol molar ratio · Number-averaged molecular weight · Unreacted phenol

### Introduction

Phenol-resorcinol-formaldehyde (PRF) resin is a representative adhesive for manufacturing wood products for structural use, and a large variety of commercial adhesives are named PRF. It is thought that the bonding performance of

a PRF depends on its molecular structure, but there is little information about the relation between the structures and the bonding performance of PRF resins or about the relation between the synthetic procedure and the compositions of resins synthesized. Such being the case, many resin makers have made their PRF products according to their experiences without grasping the molecular structures, and the buyers have used PRF resins without being informed even of the P/R molar ratios of the adhesives. Thus, first we attempted to develop an analytical technique to determine the P/R molar ratios, number-averaged molecular weights, and average numbers of each functional group per aromatic ring of commercial resins. Moreover, as PRF resins contain free phenol, which is thought to remain in the cured resins without taking part in the curing reaction, the method for determining the amount of free phenol was also investigated.

Most analytical tools, such as gas chromatography, paper chromatography, high-performance liquid chromatography (HPLC), infrared spectroscopy, and mass spectroscopy, when applied individually, are not suitable for obtaining information about the structures of the PRF resins. Woodbrey and coworkers<sup>1</sup> have published an article on the application of proton magnetic resonance (PMR) spectroscopy for the determination of number-averaged structures of phenol-formaldehyde (PF) resins; and Anderson and coworkers<sup>2</sup> applied PMR spectroscopy to PRF resins to determine the P/R/F molar ratios.

In this paper we discuss a method for analyzing the PRF adhesives. The method is based on HPLC, ultraviolet (UV) absorption, liquid chromatography–mass spectroscopy (LC-MS), and PMR spectroscopy. In some respects it is a modification of the methods applied by the researchers cited above.

### Theory

The theory is based on consideration of various protons in PRF resins and acetylated PRF resins. As removal of water

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is necessary prior to acetylation for complete acetylation of PRF resins, this theory is also based on consideration of the volatile materials removed during drying.

The resin may exist as a mixture of compounds of the types: Ar-OH, Ar-CH<sub>2</sub>OH, Ar-CH<sub>2</sub>-Ar, Ar-CH<sub>2</sub>-O-CH<sub>2</sub>-Ar, and Ar-CH<sub>2</sub>-O-CH<sub>2</sub>-OH. On acetylation, three types of acetate groups are introduced: Ar-OCOCH<sub>3</sub>-(ArOAc), Ar-CH<sub>2</sub>-OCOCH<sub>3</sub>(ArCH<sub>2</sub>OAc), and Ar-CH<sub>2</sub>-O-CH<sub>2</sub>-OCOCH<sub>3</sub>(ArCH<sub>2</sub>OCH<sub>2</sub>OAc).

Calculation of P/R/F molar ratios from the PMR absorption intensities of acetylated resins

It is possible to determine the P/R molar ratios and number-averaged molecular weights of PRF resins from the absorption intensities of various protons of acetylated PRF resins. First we discuss the equations for the determination of P/R/F molar ratios based on acetylated PRF resins. For acetylated PRF resins, the various PMR absorption intensities are defined as follows.

A<sub>1</sub>: absorption intensities of aromatic ring protons, ArH

A<sub>2</sub>: absorption intensities of methylene protons in acetoxy-methyl ends of benzyl-type hemiformal acetates, ArCH<sub>2</sub>OCH<sub>2</sub>OAc

A<sub>3</sub>: absorption intensities of methylene protons in hydroxymethyl acetate groups, ArCH<sub>2</sub>OAc

A<sub>4</sub>: absorption intensities of methylene protons in benzyl ends of benzyl-type hemiformal acetates, ArCH<sub>2</sub>OCH<sub>2</sub>OAc, plus those in dibenzyl ether-type bridges, (ArCH<sub>2</sub>)<sub>2</sub>O

A<sub>5</sub>: absorption intensities of diphenylmethane-type methylene protons, Ar-CH<sub>2</sub>-Ar

A<sub>6</sub>: absorption intensities of methyl protons in acetoxy-phenyl groups, ArOAc

A<sub>7</sub>: absorption intensities of methyl protons in acetoxy-methyl groups, ArCH<sub>2</sub>OAc and ArCH<sub>2</sub>OCH<sub>2</sub>OAc

The peaks due to the methyl protons of phenol acetate, hydroxymethyl acetate, and hemiformal acetate frequently overlap to such an extent that an accurate value of A<sub>6</sub> cannot be measured directly. However, the value of A<sub>6</sub> may be obtained by the following procedure. (1) The sum of the absorption intensities for the methylene protons of the hydroxymethyl acetate groups, ArCH<sub>2</sub>OAc, and for the methylene protons in acetoxy-methyl ends of benzyl-type hemiformal acetate, ArCH<sub>2</sub>OCH<sub>2</sub>OAc, is measured. (2) This value is multiplied by 3/2. (3) The resultant figure is subtracted from the value (A<sub>6</sub> + A<sub>7</sub>).

When a resin is formed by the reaction of 1 mol of resorcinol with *x* moles of phenol and *y* moles of formaldehyde, the following relations hold:

$$\begin{aligned} & \text{(Total H in original PRF mixture)} / \text{(total phenol acetate H} \\ & \text{in acetylated resin)} = [A_1 + A_2 + 3(A_3 + A_4)/2 \\ & + 2A_5 + A_6/3] / A_6 = (6 + 6x + 2y) / (6 + 3x) \end{aligned} \quad (1)$$

$$\begin{aligned} & \text{(Total formaldehyde-derived H)} / \text{(total aromatic H} \\ & \text{in original PRF mixture)} = (A_2 + A_3 + A_4 + A_5) / \\ & [A_1 + (A_3 + A_4)/2 + A_5] = 2y / (4 + 5x) \end{aligned} \quad (2)$$

The values of *x* and *y* can be calculated if the relevant absorption intensities, A<sub>1</sub>-A<sub>6</sub>, are measured from the PMR spectrum. Thus, P/R/F molar ratios based on acetylated PRF resins can be calculated. However, because the drying of resins preceding acetylation removes volatile materials, it is necessary to determine the amount of free phenol evaporated during the drying process to obtain more accurate results.

Let us make the weight of dried resin *W* g and the amount of free phenol removed during drying *C* mol. Because the R/P/F molar ratio of the dried resin is 1:*x*:*y*, the *W* g of dried resin was formed by the reaction of *B* mol resorcinol with *xB* mol phenol and *yB* mol formaldehyde. It is convenient to define the following terms:

R<sub>HMAC</sub>: average number of hydroxymethyl acetate groups per aromatic ring

R<sub>MB</sub>: average number of diphenylmethane-type methylene bridges per aromatic ring

R<sub>HFC</sub>: average number of benzyl-type hemiformal acetate groups per aromatic ring

R<sub>EB</sub>: average number of dibenzyl ether-type bridges per aromatic ring

Then the following relations hold:

$$R_{HMAC} = 3A_3(2 + x) / 2A_6(1 + x) \quad (3)$$

$$R_{MB} = 3A_5(2 + x) / 2A_6(1 + x) \quad (4)$$

$$R_{HFC} = 3A_2(2 + x) / 2A_6(1 + x) \quad (5)$$

$$R_{EB} = 3(A_4 - A_2)(2 + x) / 4A_6(1 + x) \quad (6)$$

$$\begin{aligned} B = W / [ & 110 + 94x + (30R_{HMAC} + 12R_{MB} + 60R_{HFC} \\ & + 42R_{EB})(1 + x) ] \end{aligned} \quad (7)$$

Because the amounts of R, P, and F in the dried resin are *B*, *xB* and *yB*, mol, respectively, and the amount of free phenol removed during drying is *C* mol, the following relation holds:

$$R/P/F = B:(xB + C):yB \quad (8)$$

Thus, putting the value of *B* obtained from Eq. (7) and the values of *x* and *y* obtained earlier into Eq. (8), the corrected R/P/F molar ratios can be calculated.

Calculation of number-averaged molecular weights from PMR absorption intensities of acetylated resins

It is convenient to define the following terms for the calculation of number-averaged molecular weights of acetylated resins.

- $R_A$ : average number of aromatic ring protons per aromatic ring  
 $R_{AM}$ : average number of acetoxymethyl (methylol) groups per aromatic ring  
 $R_{EB}$ : average number of dibenzyl ether-type bridges per aromatic ring  
 $R_{MB}$ : average number of diphenylmethane-type methylene bridges per aromatic ring  
 $R_{AHF}$ : average number of acetylated benzyl-type hemiformal (hemiformal) groups per aromatic ring  
 $n$ : average number of aromatic rings per molecule  
 $M_{nAc}$ : number-averaged molecular weights of the acetylated resins

The following relations then hold.

$$R_A = 3A_1(2+x)/A_6(1+x) \quad (9)$$

$$R_{AM} = 3A_3(2+x)/2A_6(1+x) \quad (10)$$

$$R_{EB} = 3(A_4 - A_2)(2+x)/4A_6(1+x) \quad (11)$$

$$R_{MB} = 3A_5(2+x)/2A_6(1+x) \quad (12)$$

$$R_{AHF} = 3A_2(2+x)/2A_6(1+x) \quad (13)$$

$$n = 1/(1 - R_{EB} - R_{MB}) \quad (14)$$

$$M_{nAc} = n \left[ (190 + 131x)/(1+x) + R_A + 73R_{AM} + 44R_{EB} + 14R_{MB} + 103R_{AHF} \right] \quad (15)$$

By using the above equations, number-averaged structures and number-averaged molecular weights of acetylated PRF resins can be determined from the relevant absorption intensities of PMR spectra. However, it is necessary to consider the amount of phenol removed during the drying process. When the amount of phenol removed during drying is  $z$  moles per mole of the sum of phenol and resorcinol found in the dried resin, the following relations hold.

$$R'_A = [3A_1(2+x) + 5zA_6(1+x)]/A_6(1+x)(1+z) \quad (16)$$

$$R'_{AM} = 3A_3(2+x)/2A_6(1+x)(1+z) \quad (17)$$

$$R'_{EB} = 3(A_4 - A_2)(2+x)/4A_6(1+x)(1+z) \quad (18)$$

$$R'_{MB} = 3A_5(2+x)/2A_6(1+x)(1+z) \quad (19)$$

$$R'_{AHF} = 3A_2(2+x)/2A_6(1+x)(1+z) \quad (20)$$

$$n' = 1/(1 - R'_{EB} - R'_{MB}) \quad (21)$$

$$M'_{nAc} = n' \left\{ [190 + 131x + 131z(1+x)]/(1+x)(1+z) + R'_A + 73R'_{AM} + 44R'_{EB} + 14R'_{MB} + 103R'_{AHF} \right\} \quad (22)$$

Thus the number-averaged molecular weights of acetylated PRF resins corrected can be calculated. The number-

averaged molecular weights of nonacetylated PRF resins can be calculated from the following equation.

$$M'_{nOH} = n' \left\{ [106 + 89x + 89z(1+x)]/(1+x)(1+z) + R'_A + 31R'_{AM} + 44R'_{EB} + 14R'_{MB} + 61R'_{AHF} \right\} \quad (23)$$

## Materials and methods

A resin synthesized in our laboratory and a commercial resin were examined.

### Synthesis of PRF resin

Phenol (0.67 mol), formaldehyde (1.33 mol, aqueous 37% solution), and sodium hydroxide (0.065 mol, aqueous 30% solution) were placed in a reaction flask. The reaction was carried out at 30°C for 24 h. One mole of resorcinol was added, and the reaction was carried out at 30°C for 24 h. The resin was then analyzed.

### Drying of resin

Removal of water was necessary prior to acetylation for complete acetylation of the resin. Resin (30 g) was dried using a rotary evaporator, with the vacuum created by a water pump. Temperatures of the waterbath and the condenser were 40°C and 0°C, respectively. The drying operation was continued until a constant weight was obtained. Substantial amounts of water and free phenol were removed during the drying operation. This water fraction was collected and analyzed by LC-MS. The amount of phenol was determined from the UV absorption intensity.

### Acetylation of dried resin

The dried resin was dissolved in 100 g acetic anhydride under cooling. When the resin was dissolved completely, 30 g pyridine was added to the reaction mixture. The reaction was then carried out at 5°C for 1.5 h. During this period the mixture was stirred continuously while strictly maintaining the temperature at 5°C until there was a lightening in the solution's color. The mixture was then allowed to warm to room temperature, and the reaction was carried out for 12 h at 25°C. During this period the mixture was stirred continuously. Acetylation was followed by addition of cold water, extraction with ether, and washing with dilute aqueous hydrochloric acid, dilute aqueous sodium bicarbonate, and water. The aqueous layer was removed, and water-insoluble products were thoroughly dried using a vacuum evaporator.

### PMR characterization

Acetylated resin was analyzed by PMR spectroscopy. The acetylated resin (100 mg) was dissolved in 1 ml 100% CDCl<sub>3</sub>

(Wako Pure Chemicals Industry). Tetramethyl silane was used as the internal standard. The spectrum was recorded on a JEOL-GSX 400 spectrometer. Two values were recorded for each absorption intensity and the average taken. Chemical shift data are reported in this paper as  $\delta$  values.

Determination of number-averaged molecular weight of acetylated resin by cryoscopy

The number-averaged molecular weight of acetylated resin was determined by cryoscopy and compared with that obtained from PMR spectroscopy. Phenol was used as the solvent. Acetylated resin (1.5 g) was dissolved in 40 g of phenol, and the depression of the freezing point was measured. The coefficient of the freezing point for phenol was 7.1 (K/mol) which was confirmed with the use of resorcinol as a solute.

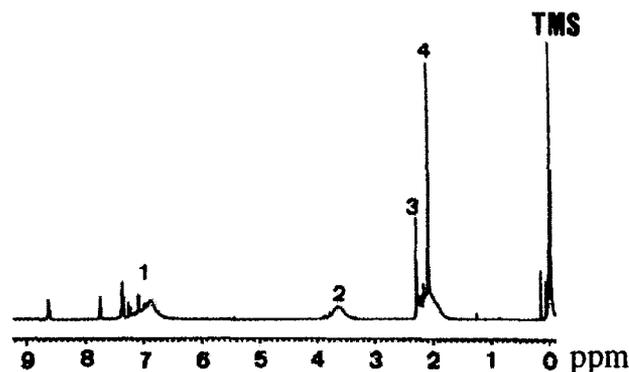
Determination of free phenol and resorcinol in the resin

It was impossible to fractionate total PRF resins by HPLC or to separate PRF resins by isocratic elution. In the case of gradient elution, the column became blocked. It is believed that the PRF resins coagulated in the column during gradient elution. Hence, the following procedure was used for determining free phenol and resorcinol.

Resin (30 g) was dissolved in 400 ml of water. The mixture was then acidified to pH 5–6 by adding acetic acid with stirring. The mixture was kept standing until the soluble fraction separated from the precipitate, after which another 400 ml water was added to the precipitate with stirring. Again, the soluble fraction was separated from the precipitate. This operation was repeated several times. The water-soluble fractions collected were placed in a 2-l measuring flask. Water was then added to make 2 l of solution. This water-soluble fraction was then analyzed by HPLC and LC-MS. HPLC analyses were carried out with a Hitachi chromatograph (Auto Sampler L-7200; Column Oven L-7300; UV detector L-7400; pump L-7100; integrator D-7500). An Inertsil ODS-3 column (4.6  $\times$  250 mm) was used, and the UV wavelength was set at 280 nm. The mobile phase of methanol/water was used with an elution gradient of 30:70 to 70:30 over 60 min. The amounts of phenol and resorcinol were determined from the peak areas on the HPLC chromatogram using calibration curves prepared with the use of authentic samples. A Hitachi M-1200AP/ES mass spectrometer was used for the LC-MS analysis.

## Results and discussion

The PMR spectrum for the acetylated PRF resin synthesized in our laboratory is shown in Fig. 1. The absorption intensities for the various types of protons can be measured in the following regions of the PMR spectrum: A<sub>1</sub> 7.40–6.58 ppm; A<sub>2</sub> 5.28–5.17 ppm; A<sub>3</sub> 5.10–4.90 ppm; A<sub>4</sub> 4.63–4.48 ppm and 4.55–4.27 ppm; A<sub>5</sub> 4.03–3.40 ppm; A<sub>6</sub>



**Fig. 1.** Proton magnetic resonance (PMR) spectrum of the acetylated phenol-resorcinol-formaldehyde (PRF) resin synthesized in our laboratory. 1, (7.40–6.58 ppm) Ar-H; 2, (4.03–3.40 ppm) Ar-CH<sub>2</sub>-Ar; 3, (2.33–2.25 ppm) ArOAc; 4, (2.07–1.80 ppm) ArOAc

**Table 1.** Results of the analysis of a model resin<sup>a</sup>

Analysis	Result
P/R/F molar ratio	
Obtained from PMR analysis of the acetylated resin	0.62:1.00:1.11
Corrected, with the evaporated phenol being taken into account	0.66:1.00:1.11
At synthesis of the resin	0.67:1.00:1.33
Number-averaged molecular weight of the acetylated resin	
Obtained by PMR analysis	567
Obtained by cryoscopy	567–575
Free phenol/total phenol (%)	36
Free resorcinol/total resorcinol (%)	29

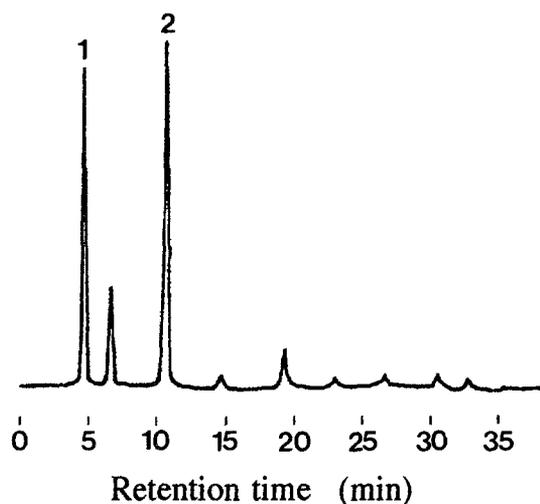
P/R/F, phenol/resorcinol/formaldehyde; PMR, proton magnetic resonance

<sup>a</sup>The resin synthesized in our laboratory

2.33–2.25 ppm (ArOAc on monomeric phenols) and 2.18–2.13 ppm (ArOAc on polymeric phenols); A<sub>7</sub> 2.07–1.80 ppm.

In view of the high reactivity of resorcinol, it was not expected that large amounts of labile formaldehyde, in the form of hemiformals or polyformals, would be present. The spectra, in fact, were found to contain no peaks attributable to acetate derivatives of hemiformals, polyformals, or polyoxymethylene oligomers; nor were PMR peaks characteristic of benzyl ether bridges observed. Three types of peak (aromatic ring protons, Ar-H; diphenylmethane-type methylene protons, Ar-CH<sub>2</sub>-Ar; methyl protons of acetoxyphenyl groups, ArOAc) were observed in the PMR spectrum for the resin. The relative absorption intensities of aromatic protons, diphenylmethane-type methylene protons, and methyl protons of acetoxyphenyl groups were 4.496, 2.033, and 7.231, respectively. This resin was found to contain no hydroxymethyl phenols, hemiformals, or dibenzyl ethers.

Investigation of volatile materials removed during the drying process were carried out by UV absorption spectroscopy and LC-MS. It was found that 30 g of resin synthesized in our laboratory contained 0.00425 mol of free phenol. The results of the P/R/F molar ratio and number-averaged molecular weight of acetylated resin synthesized in our laboratory are summarized in Table 1. These results show

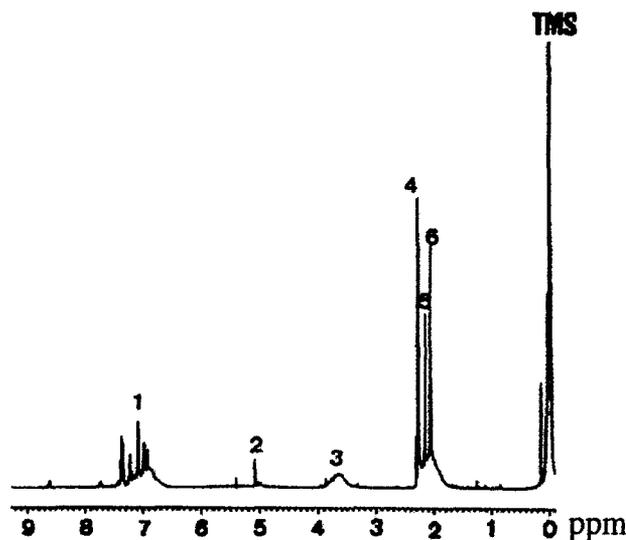


**Fig. 2.** High-performance liquid chromatography (HPLC) chromatogram of the water-soluble fraction of the PRF resin synthesized in our laboratory. 1, resorcinol; 2, phenol

that when the amount of free phenol evaporated during the drying process is combined with the result of the P/R/F molar ratio obtained from acetylated PRF resin by PMR analysis, the P/R/F molar ratio can be determined accurately. However, a discrepancy was observed between the measured and expected formaldehyde contents. The reason has not yet been clearly understood. The number-averaged molecular weight of the acetylated resin calculated from PMR analysis agrees with that evaluated by cryoscopy.

Free phenol and resorcinol present in resins were determined from HPLC analysis. Figure 2 shows the chromatogram of the water-soluble fraction of the PRF resin. The two peaks (peak 1 is resorcinol, peak 2 is phenol) were identified by LC-MS using authentic samples. The absence of overlapping peaks also was confirmed. HPLC analysis showed that 30 g of resin synthesized in our laboratory contained 0.02774 mol of free phenol and 0.03128 mol of resorcinol. Moreover, 20.45 g of dried resin was obtained from 30 g of undried resin. Putting the values of the PMR absorption intensities of acetylated resin into Eq. (1) and (2), the value of  $x$  was determined to be 0.62. Substituting the value of  $x$  in Eq. (3) and (4) with 0.62, the values of  $R_{\text{HMAC}}$  and  $R_{\text{MB}}$  were calculated. From Eq. (7), the value of  $B$  was determined to be 0.1079. Thus, the amounts of resorcinol and phenol in this amount of resin became 0.1079 and 0.0669, respectively. Addition of the amount of phenol evaporated during the drying process makes the quantities of resorcinol and phenol 0.1079 and 0.07112 mol, respectively. Thus, the ratio of free phenol to total phenol and that of free resorcinol to total resorcinol were calculated. The free phenol/total phenol and resorcinol/total resorcinol ratios (percentages) are 36% and 29%, respectively.

A commercial resin was also analyzed. Figure 3 shows the PMR spectrum of the acetylated resin, and Table 2 shows the analytical results. Hydroxymethyl phenols were present in this commercial resin. Neither hemiformals nor



**Fig. 3.** PMR spectrum of a commercial PRF resin acetylated. 1, (7.40–6.58 ppm)  $\text{Ar}\text{H}$ ; 2, (5.10–4.90 ppm)  $\text{Ar}\text{-CH}_2\text{OAc}$ ; 3, (4.03–3.40 ppm)  $\text{Ar}\text{-CH}_2\text{-Ar}$ ; 4, (2.33–2.25 ppm)  $\text{ArOAc}$ ; 5, (2.18–2.13 ppm)  $\text{ArOAc}$ ; 6, (2.07–1.80 ppm)  $\text{ArOAc} + \text{Ar-CH}_2\text{OAc}$

**Table 2.** Results of the analysis of a commercial resin

Analysis	Result
P/R/F molar ratio	0.65:1.00:1.06
Number-averaged molecular weight	251
No. of hydroxymethyl groups per aromatic ring	0.09
No. of methylene bridges per aromatic ring	0.55
Free phenol/total phenol (%)	58
Free resorcinol/total resorcinol (%)	13

benzyl ether bridges were present. Because the materials that had gelled during storage are present in some other commercial PRF resins, it is believed that most of the commercial resins contain methylol groups. The results in Table 2 show that the average number of diphenylmethane-type methylene bridges per aromatic ring is relatively small for the commercial resin analyzed. Consequently, the number-averaged molecular weight of this resin is relatively small. This commercial resin contained a large amount of free phenol. The free phenol/total phenol ratio (percentage) is 58%, whereas the amount of free resorcinol is relatively small. It is assumed that during synthesis of PRF resins resorcinol was added in such a condition that the methylation of phenol was not sufficient and large amounts of formaldehyde remained unreacted. The resin analyzed here demonstrated good bonding performance. It is thought that the unreacted phenol remains as free phenol in resins without taking part in the curing reaction. Free phenol is not only the wastage of phenol but remains as a poisonous material in the resin. Ideally, it is desirable to synthesize resins of low free-phenol content.

## Conclusion

The P/R molar ratios and number-averaged molecular weights of PRF resins can be determined by PMR analysis

of acetylated resins with correction of the amounts of phenol evaporated during the drying process before acetylation. The amounts of free phenol and resorcinol can be determined from HPLC analysis of the water-soluble fractions of PRF resins.

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