Optimizing the Conditions of Quantitative ^{13}C-NMR Spectroscopy Analysis for Phenol–Formaldehyde Resol Resins

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ABSTRACT: The experimental time of ^{13}C-NMR quantitative analysis of phenol–formaldehyde resins was reduced so that quantitativeness was maintained. The quantitative spectra of 14 model resins were obtained using a gated decoupling technique suppressing the NOE. The paramagnetic additive, $Cr(acac)_3$, was used to shorten relaxation times of carbon atoms. The use of $Cr(acac)_3$ was optimized in two deuterated solvents, DMSO and acetone. To reach short relaxation times and further the measurement times, the concentration of relaxation reagent, the delay time, and the number of NMR scans were optimized. Quantitativeness was proved by analyzing the spectra of accurate mixture of model compounds, and the spectra of the condensed model resins.
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Key words: quantitative ^{13}C-NMR spectroscopy; phenol–formaldehyde resin

INTRODUCTION

Phenolic resins, produced in the reaction of phenol and formaldehyde, have a wide variety of applications as impregnants and adhesives.[1] ^{13}C-NMR is one of the most successful methods to characterize the chemical structure of resins.[2–21] Due to the long spin-lattice relaxation times the measurements of ^{13}C-NMR spectra of phenol–formaldehyde resins are quite time consuming to obtain reasonable signal to noise ratios. The main goal of this study was to optimize the conditions of ^{13}C-NMR analysis for resol resins to reduce the experimental time and still maintain quantitativeness of ^{13}C-NMR spectroscopy.

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EXPERIMENTAL

Model Compounds and Resins

Model compounds used in NMR quantitativeness studies, 4-methylol phenol and 2-hydroxydiphenylmethane, were 99% pure and purchased from Aldrich (Milwaukee, WI).

The raw materials of resins, phenol (purchased from J. T. Baker) and formaldehyde (produced by Dynoresin Oy from methanol), were of high purity grade. Formaldehyde was used as a formalin solution, which contained 45% formaldehyde, water, and some methanol. A series of 14 different resins was condensed with an NaOH catalyst (produced by Bayer). Eight of the resins (numbers 1–8) were impregnation ones having the condensation alkalinity of 1.5 wt % and six resins (numbers 9–14) were adhesives with the condensation alkalinity of 6.0 wt %. The methylation alkalinity of both low- and high-molecular resins

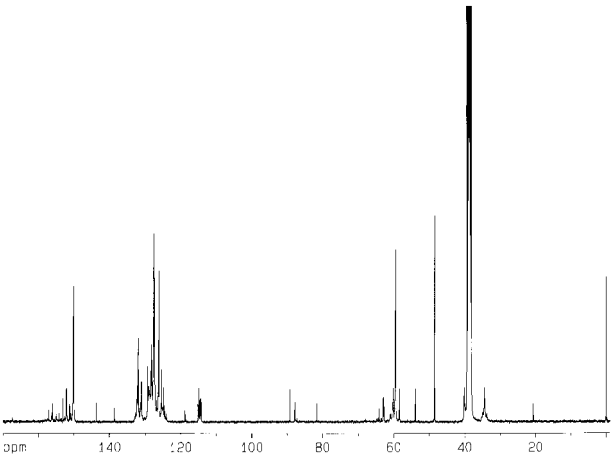


Figure 1 ^{13}C-NMR spectrum of the phenol–formaldehyde impregnant resin 5 in DMSO-d_6 (TMS 0.00 ppm, solvent 38.13–39.38 ppm).

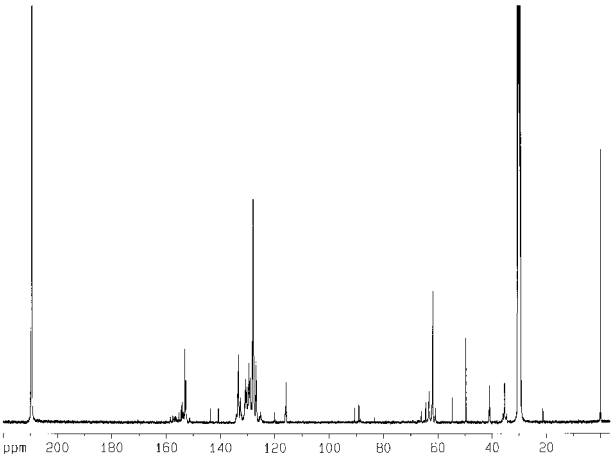


Figure 2 ^{13}C-NMR spectrum of the phenol–formaldehyde impregnant resin 5 in acetone-d_6 (TMS 0.00 ppm, solvent 29.42–30.64 ppm and 209.66 ppm).

varied between 0.5 and 3.5 wt %. The molar ratio of formaldehyde to phenol was 2.2 in all the resins. The resins 5–8 were neutralised with *p*-toluene sulfonic acid to the low condensation alkalinity of 1.5. The resins were stored frozen at −18°C until NMR analysis.

NMR Reagents

DMSO-d_6, 99 atom% deuterated dimethylsulfoxide (purchased from Riedel-de Haën AG), acetone-d_6 (99.8%, purchased from Cortec) and methanol-d_4 (99.8%, Cortec) were used as solvents, agents to obtain a deuterium lock and internal chemical shift standards. The ^{13}C signals of resins were referenced to the central resonance line of DMSO-d_6 with the δ value of 39.5 ppm, of acetone-d_6 with the δ value of 32.5 ppm or methanol-d_4 with 49.3 ppm. Also, chloroform-d (99.8%, purchased from Cortec) and D_2O (99.8%, Merck) were tested as NMR solvents.

$Cr(acac)_3$, of 97% purity and purchased from Aldrich, was used as 5–30 m*M* solutions as the relaxation reagent.

NMR Experiments

The resins and model compounds were characterized by NMR spectroscopy. Quantitative ^{13}C-NMR spectra were recorded with a Bruker AMX-400 spectrometer at 20°C, observing ^{13}C at 100.623 MHz and using an inverse gated ^{1}H decoupling technique to eliminate Nuclear Overhauser effect. Typically spectra of resins were run with a 90° pulse of 11.5 μs. DMSO-d_6, acetone-d_6, and methanol-d_4 were the solvents and $Cr(acac)_3$ was used as a relaxation reagent. Digital resolution was 0.309 corresponding to a spectral width of 20218 Hz, and a data size of 64 k.

RESULTS AND DISCUSSION

Choosing a Solvent for the NMR Analysis of Phenol–Formaldehyde Resol Resins

The suitability of five different solvents, DMSO-d_6, acetone-d_6, methanol-d_4, chloroform-d, and

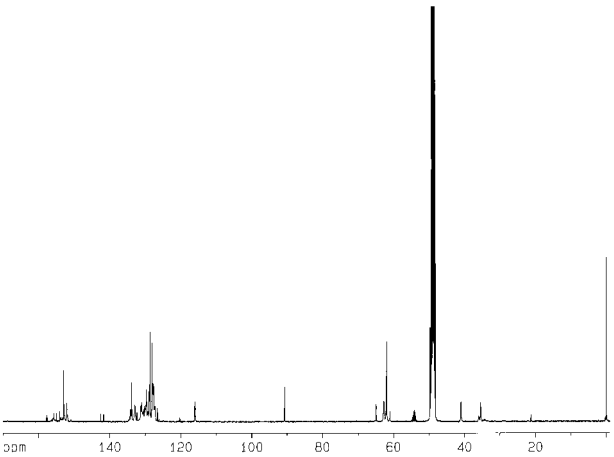
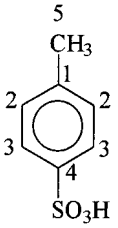


Figure 3 ^{13}C-NMR spectrum of the phenol–formaldehyde impregnant resin 5 in methanol-d_4 (TMS 0.00 ppm, solvent 48.29–49.77 ppm, deuterium exchange in hemiacetal of formalin at 54.23 ppm).

Table I ^{13}C Chemical Shifts (ppm) of the Phenol–Formaldehyde Resol Resin in Three Different Solvents[a]

Assignment of the Carbons	DMSO	Acetone	Methanol
Ortho–para methylene bridges	33.82–34.98	34.58–35.93	35.02–36.07
Para–para methylene bridges	40.12–40.29	40.98–41.09	41.06–41.13
Solvent	38.13–39.38	29.42–30.64, 209.66	48.29–49.77
Methanol	45.55	49.66	[b]
Hemiacetal of formalin	53.91, 89.22	54.82, 90.68	54.23, 90.69
Ortho methylol	58.36–60.25	60.96–62.02	60.97–62.76
Para methylol	62.73–64.76	63.29–66.16	64.85–64.95
Phenolic hemiformals	67.97, 87.20–87.83	88.54–89.18	—
Oxymethylene of formaldehyde oligomers	81.68	83.32	—
Free *ortho*	114.34–115.11	116.00–116.26	115.92–116.10
Free *para*	118.72	120.06	120.31
Meta, substituted *ortho,* substituted *para*	124.79–132.23	126.87–133.74	126.55–134.12
Phenoxy region	150.13–156.01	152.76–158.51	151.88–157.58
Para toluene sulfonic acid,[c] C5	20.66	21.25	21.26
C4	138.62	140.77	141.69
C1	143.73	143.85	142.51



[a] TMS as the internal reference at 0.00 ppm.
[b] Overlapped with the solvent methanol signal.
[c] Used in neutralization, C2 and C3 signals overlapped with those of the free *meta,* substituted *ortho,* and substituted *para* groups.

D_2O for ^{13}C-NMR analysis of phenol–formaldehyde resol resins was studied. The use of D_2O as a NMR solvent was restricted by quite low water tolerance of the resins when an opacity or a precipitate was formed in mixing a resin and a heavy water solvent. Chloroform-d was unsuitable as a solvent for the resins, forming two phases in NMR samples.

Fairly good NMR spectra for the analyzed model resin 3 with the methylation alkalinity of 1.2 wt % and the condensation alkalinity of 1.5 wt % were acquired in deuterated solvents, DMSO, acetone, and methanol (Figs. 1–3). All the spectra could be assigned according to previous studies[2] and literature.[2–5] Solvent effects can be seen in the spectra measured in different solvents (Table I). More fine structure is found in the signals of different free *ortho* aromatic carbons at 114–116 ppm and of *para* aromatic carbons at 118–120 ppm in DMSO-d_6 solvent than in acetone-d_6 or in methanol-d_4. When deuterated methanol was used as a solvent there were no signals of phenolic hemiformals or oxymethylene of formaldehyde oligomers observed as in the two other solvents. Thus, methanol-d_4 solvent does not seem to be completely inert in ^{13}C-NMR measurement, and the analysis of methanol content of resin is naturally impossible. In DMSO-d_6 even a trace amount of phenolic hemiformals was detected as the signal at 67.97 ppm assigned to the carbon of methylene group connected to aromatic carbon. The other signal of phenolic hemiformal, the carbon of terminal methylene group, was observed at 87.2–87.7 ppm in DMSO-d_6, and it was also found in acetone-d_6 at 88.5–89.2 ppm. The intensive signal of DMSO-d_6 at 40.1 ppm partially overlaps the signal of *para–para* methylene bridges of a phenolic resin at 40.8–41.0 ppm.

Also, chemical shifts of different structural groups deviate slightly from each other in different solvents. The signal of free phenol at 150–153 ppm is more deshielded in acetone-d_6 solvent than in DMSO-d_6 or methanol-d_4. ^{13}C chemical shifts of phenolic region are found to be strongly affected by magnetically anisotropic acetone-d_6 solvent in which mutual orientations between solvent and phenolics are possible.[3] Furthermore, the methylene bridge signals as well as the aromatic carbon signals, are most shielded in DMSO-d_6 solvent.

The purpose of a relaxation reagent, $Cr(acac)_3$, is to shorten the carbon spin-lattice relaxation times considerably and at the same time to enhance sensitivity, to improve the signal-to-noise ratio, and to maintain the quantitative NMR spectrum.[22] Insolubility of $Cr(acac)_3$ into deuterated water restricts the use of this combination in NMR measurements. Also, the resins analyzed in this study could not be dissolved in water due to low water tolerance. $Cr(acac)_3$ dissolved into DMSO-d_6, acetone-d_6, and methanol-d_4 as about 0.05 *M* solutions, which are suitable for the NMR analysis. If the NMR sample dissolves in chloroform, the content of $Cr(acac)_3$ could be, if required, even 10 times higher, 0.5 *M*, in chloroform than in DMSO-d_6, acetone-d_6, or methanol-d_4.

Because chloroform and water were excluded from potential solvents in the ^{13}C-NMR spectroscopy of phenolic resins because of solubility problems, only deuterated DMSO, acetone, and methanol were used in final solubility tests. All the 14 resins (F/P 2.2, condensation alkalinity of resins 1–8 1.5 wt %, and of resins 9–14 6.0 wt %) dissolved in deuterated DMSO–$Cr(acac)_3$ and methanol–$Cr(acac)_3$ solutions. The resins 9–14 having the high condensation alkalinity of 6.0 wt % did not dissolve in deuterated acetone.

As a conclusion, DMSO-d_6 proved to be the best common solvent for the ^{13}C-NMR spectroscopy of the whole series of 14 phenol–formaldehyde resol resins. Also, acetone-d_6 was used as a proper NMR solvent for the first eight resins of lower condensation alkalinity.

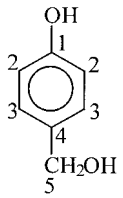
Optimizing the Concentration of Relaxation Reagent, the Delay Time, and Number of Scans of NMR Analysis with Model Compounds

Before the optimizing with real resins the accurately weighed mixture of model compounds, 4-methylol phenol and 2-hydroxydiphenylmethane, was measured with ^{13}C-NMR spectroscopy, both in deuterated DMSO and acetone. The chemical shifts for the model compounds in both solvents have been given in Table II. The signals of the two model compounds, which were not overlapping and were able to be integrated separately, were exploited in quantitative studies.

The weighed and actual mass ratio of 4-methylol phenol to 2-hydroxydiphenylmethane was 0.37. The NMR analyzed mass ratios both in deuterated acetone and DMSO solvents with different concentration of the relaxation reagent, $Cr(acac)_3$, delay times, and number of scans are represented in Tables III and IV.

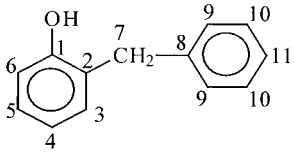
Table II ^{13}C Chemical Shifts (ppm) of the Model Compounds

4-methylol phenol



Carbon	Acetone	DMSO
C1	157.87	156.38
C2[a]	116.23	114.91
C3[a]	129.50	128.51
C4	134.70	132.88
C5	64.94	62.84

2-hydroxydiphenylmethane



Carbon	Acetone	DMSO
C1	156.37	155.14
C2	129.12	127.49
C3	131.89	130.46
C4	120.89	119.07
C5	128.61	127.32
C6[a]	116.38	115.13
C7	36.64	35.23
C8	142.90	141.45
C9[a]	129.61	128.31
C10	130.20	128.80
C11	126.99	125.77

[a] The signals not included in quantitativeness studies due to the overlapping.

Table III The Ratios of Model Compounds Measured in Acetone-d_6 Solvent Comparing to the Actual Mass Ratio of 0.37

NS/D1 (s)	4	6	10	20	60	120
$Cr(acac)_3$ 0 m*M*						
100	0.16	0.16	0.21	0.18		
300	0.15	0.19	0.19	0.23		
600					0.19	0.26
$Cr(acac)_3$ 10 m*M*						
100	0.32	0.33	0.35	0.34		
300	0.33	0.34	0.35	0.34		
600					0.34	
$Cr(acac)_3$ 20 m*M*						
100	0.34	0.35	0.35	0.35	0.34	
300	0.34	0.35	0.36	0.35		
600					0.34	
$Cr(acac)_3$ 30 m*M*						
100	0.34	0.35	0.34	0.35		
300	0.35	0.34	0.34	0.34		
600					0.35	

NS, number of scans; D1, delay time (s).

When no relaxation reagent was added in the NMR sample in acetone-d_6, the analyzed mass ratio of model compounds varied between 0.16 and 0.26, depending on delay times (4, 6, 10, 20, and 120 s), and the number of scans (100, 300, and 600 scans). In some cases the pulse delay may be long enough to result in a complete relaxation of all nuclei. Relaxation times were not measured, but according to literature[4] values (0.1–15 s) the pulse delay times were set at least to the value of $5T_1$, which is long enough in the gated decoupling pulse technique to obtain quantitative spectra. Only in the measurements without relaxation reagent were some delay times, shorter than 5 times the longest relaxation time, tested. The concentration of 10 m*M* of $Cr(acac)_3$ was enough to increase the analyzed ratio of model compounds near to the actual one, because the value of 0.35 was found with 100 and 300 scans and with the delay time of 10 s. The best result of 0.36 was achieved when the concentration was 20 m*M*, the number of scans 300 and the delay time 10 s. The mass ratio of 0.36 is considered to be acceptable, because the error can be 2–4% in these types of determinations.[23,24] Increasing the concentration of the relaxation reagent to 30 m*M* did not improve the results to a higher value than 0.35. Totally, the significance of the relaxation reagent was enormous, because when using $Cr(acac)_3$ in acetone-d_6 all the mass ratios were between 0.32 and 0.36.

When the mixture of model compounds with the actual mass ratio of 0.37 was dissolved in DMSO-d_6, the analyzed mass ratios varied from 0.31 to 0.36. Even without any relaxation reagent the ratios of 0.33–0.34 were found independently, with the number of scans between 100 and 600, and delay times between 5 and 120 s. DMSO-d_6 is a viscous solvent, unlike acetone-d_6, and could increase a relaxation rate.[24] Adding $Cr(acac)_3$ in different concentrations of 5, 20, and 30 m*M* improved the result only in one experiment, when the mass ratio of 0.36 was achieved in the conditions of 5 m*M* of $Cr(acac)_3$, delay time of 10 s and 100 scans.

Table IV The Ratios of Model Compounds Measured in DMSO-d_6 Solvent Comparing to the Actual Mass Ratio of 0.37

NS/D1 (s)	5	10	20	120
$Cr(acac)_3$ 0 m*M*				
100	0.33	0.33	0.34	
300	0.33	0.33	0.34	
600				0.33
$Cr(acac)_3$ 5 m*M*				
100	0.32	0.36	0.31	
300	0.33	0.31	0.31	
$Cr(acac)_3$ 20 m*M*				
100	0.32	0.31	0.32	
300	0.32	0.32	0.32	
$Cr(acac)_3$ 30 m*M*				
100	0.32	0.33	0.33	
300	0.32	0.34	0.33	

NS, number of scans; D1, delay time (s).

As a result, the concentration of relaxation reagent of 20 m*M* can be chosen for the further studies of the resins in both solvents. Also, the highest studied number of scans of 600 could be the best to obtain a good signal-to-noise ratio.

Optimizing the Delay Times of NMR Analysis of Phenol–Formaldehyde Resins

The main idea to optimize the delay times is to reduce the experimental NMR time and at the same time maintain the quantitativeness of the analysis. As the concentrations of many compounds in resin samples are quite low, the number of scans should be high, and therefore, the experimental time increases easily even to 20 h.

Two different regions were used to determinate whether the resin spectrum was quantitative. First, the ratio of the integration value of the phenolic carbon to the integration value of the other aromatic carbons should theoretically be 1 : 5. The other way to determine the quantitativeness of the NMR analysis was to compare the integration values of the two sharp signals of hemiacetal of formalin monomer, $\underline{C}H_3O\underline{C}H_2OH$, at 54–55 ppm and 89–91 ppm. Because these two signals originate from the single carbons of the same compound, the integrals should have the same values.

The model resin 3 was dissolved in the solution of $Cr(acac)_3$ in deuterated acetone or DMSO. The concentration of the relaxation reagent was 20 m*M* in the NMR samples, the delay time varied between 10 and 60 s, and the number of scans was 600. For the reference analysis the same resin was measured without the relaxation reagent in acetone-d_6 with the delay time of 200 s and in DMSO-d_6 with the delay time of 120 s. The results are collected in Table V.

The method where signals other than phenolic carbons were integrated separately seemed to be most accurate, whereas the combined integral value increases the proportion of nonphenolic carbons. The ratio of the phenolic carbon to the other carbons attached to the phenyl ring varied in acetone-d_6 solvent between 1 : 5.01 and 1 : 5.08 (or when integrated together between 1 : 5.13 and 1 : 5.21), and in DMSO-d_6 between 1 : 4.79 and 1 : 5.08 (or 4.98 and 5.22). In the reference analyses with the longer delay time and without the relaxation reagent the ratio was 1 : 5.01 (1 : 5.16) in acetone-d_6 and 1 : 5.00 (1 : 5.10) in DMSO-d_6. The enhancement of delay time from 10 to 60 s does not seem to decrease the ratio closer to 5.0 in acetone-d_6. As another indication of quantitativeness, the ratio of signals of hemiacetal of formalin varied between 1.04 : 1 and 1.17 : 1 in acetone-d_6 and between 0.95 : 1 and 1.14 : 1 in DMSO-d_6.

The main goal of this study was to reduce the NMR experimental time. Therefore, the delay time of 10 s with 600 scans was chosen for further studies in DMSO-d_6 solvent. The results with this shortest delay time of 10 s proved to be as acceptable as with the longer delay times. The total experimental time decreases now below 2 hs. In nonviscous acetone-d_6 solvent relaxation is slower and the delay time of 30 s could be the best choice in resin analysis, which results in the 5-h total experimental time. The short spectrometer times obtained might be an essential factor in cost and time saving of NMR analysis.

Quantitativeness of ^{13}C-NMR Analysis of Resol Resins

The quantitativeness of the ^{13}C-NMR analysis of the series of phenol–formaldehyde resol resins was studied with the optimized conditions. The resins 1–8 were analyzed both in DMSO-d_6 and acetone-d_6, and the resins 9–14 in DMSO-d_6. The former optimized NMR conditions, 20 m*M* $Cr(acac)_3$ in the sample, 600 scans, and the delay time of 10 s in DMSO-d_6 and 30 s in acetone-d_6, were utilized and again tested in these NMR measurements.

The ratios of the phenolic carbon to the other carbons attached to the benzene ring and the ratios of hemiacetal of formalin signals are collected in Table VI. The indications of quantitativeness, the ratio 1 : 5 and the other optimum ratio 1 : 1, seem to be fulfilled quite accurately in both solvents. The proportion of the nonphenolic aromatic carbons of the resins 5–8 could not be detected, because the neutralization agent, *p*-toluene sulfonic acid, has overlapping signals in the phenolic region. The most significant deviations of both test ratios are about 7%, and the most common deviations 1–4%. Again, the sum of the separately integrated signal gives better results than the group integration, which obviously takes into account more noise from the region of 114–132 ppm than from the phenolic region. To get reliable data for quantitativeness studies the spectra of high-molecular resins 9–14 must be integrated extremely carefully, whenever it is even possible due to broad phenolic signals. Also, the absence or negligible size of formalin hemiace-

Table V The Ratios of the Phenolic Carbon to the Other Aromatic Carbons (1 : 5) and the Ratios of Signals of Hemiacetal of Formalin (1 : 1) of the Model Resin 3 in Acetone-d_6 and in DMSO-d_6 Solvents with Different Delay Times[a]

Acetone Delay Time (s)	10	20	30	40	60	200[b]
1 : 5[c]	1 : 5.07	1 : 5.01	1 : 5.04	1 : 5.04	1 : 5.08	1 : 5.01
1 : 1	1.17 : 1	1.07 : 1	1.04 : 1	1.06 : 1	1.15 : 1	1.10 : 1
DMSO Delay Time (s)	10	20	30	40	60	120[b]
1 : 5[c]	1 : 5.03	1 : 5.08	1 : 4.84	1 : 5.07	1 : 4.79	1 : 5.00
1 : 1	1.01 : 1	0.95 : 1	1.11 : 1	1.14 : 1	0.95 : 1	1.01 : 1

[a] Number of scans 600; [$Cr(acac)_3$] = 20 m*M*.
[b] Reference, no $Cr(acac)_3$.
[c] The aromatic signals other than phenolic integrated separately.

tal signals in the spectra of high-molecular resins 9–14 make the calculation of quantitative ratios impossible.

The sharp and separate signal of methanol at 49.5–50.0 ppm is also a good criterion to demonstrate quantitativeness of measurements in different solvents. Table VII presents the integration values of methanol. There is no significant difference that would be caused by the chosen solvent. The difference is not greater than the error (2–4%) in NMR integration.

CONCLUSION

In addition to the pulse program, the experimental conditions, the concentration of a relaxation reagent, the delay time between scans, and the number of scans, affect quantitativeness of ^{13}C-NMR spectroscopy of phenol–formaldehyde resins. Acetone-d_6 and especially DMSO-d_6 were found to be proper solvents. Especially, the phenolics in deuterated acetone give the most downfield signals. The optimized combination of the number

Table VI The Ratios of the Phenolic Carbon to the Other Aromatic Carbons (1 : 5) and the Ratios of Signals of Hemiacetal of Formalin (1 : 1) of the Series of Model Resins in Acetone-d_6 and in DMSO-d_6 Solvents[a]

Acetone[b] Resin	1	2	3	4	5	6	7	8
1 : 5[d]	1 : 5.05	1 : 5.00	1 : 5.10	1 : 5.17				
1 : 1	1 : 1.05	1 : 1.03	1 : 1.02	1 : 1.05	1 : 1.07	1 : 1.05	1 : 1.02	1 : 1.00
DMSO[c] Resin	1	2	3	4	5	6	7	8
1 : 5[d]	1 : 4.98	1 : 5.05	1 : 4.95	1 : 5.09				
1 : 1	1 : 1.05	1 : 1.15	1 : 0.97	1 : 1.01	1 : 1.07	1 : 0.98	1 : 1.02	1 : 1.06
DMSO[c] Resin	9	10	11	12	13	14		
1 : 5[d]	1 : 5.23	1 : 5.21	1 : 5.22	1 : 5.21	1 : 5.21	1 : 5.30		

[a] Number of scans 600; [$Cr(acac)_3$] = 20 m*M*.
[b] Delay time 30 s.
[c] Delay time 10 s.
[d] The aromatic signals other than phenolic integrated separately.

Table VII Methanol Content of Model Resins Measured in Either Acetone-d_6 or DMSO-d_6 Solvents[a]

Resin	Acetone	DMSO
1	0.204	0.206
2	0.206	0.207
3	0.215	0.222
4	0.217	0.213
5	0.205	0.204
6	0.205	0.219
7	0.194	0.200
8	0.212	0.220

[a] The actual integral values, related to the value of 1.00 of the phenoxy carbon.

of scans of 600 and the delay time of 10 s in viscous DMSO-d_6 and 30 s in acetone-d_6 provides quantitative spectra in the presence of 20 m*M* of the relaxation reagent, $Cr(acac)_3$, when the series of resins were analyzed. The optimizing definitely reduces the total spectrometer time and maintains, or even improves, the accuracy.

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