Phenol–Formaldehyde Resol Resins Studied by ^{13}C-NMR Spectroscopy, Gel Permeation Chromatography, and Differential Scanning Calorimetry

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ABSTRACT: A series of phenol–formaldehyde resins was produced in the presence of NaOH catalyst. Detailed structural and quantitative information was provided by ^{13}C-NMR spectroscopy. The main interests were the relative quantities of bridge structures, methylol groups, and free phenol. Functionality and linearity of resins were also studied. The effects of the condensation F/P molar ratio on the structure and properties of the resins was studied by gel permeation chromatography (GPC) and differential scanning calorimetry (DSC) in addition to ^{13}C-NMR. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1183–1193, 1997

Key words: quantitative ^{13}C-NMR spectroscopy; phenol–formaldehyde resin; condensation reaction

INTRODUCTION

Resol resins are obtained in the reaction of formaldehyde and phenol under alkaline conditions. Highly crosslinked, versatile, and stabile resins have a wide range of applications in wood working industry, impregnation, thermal insulation, and molding. A low molecular weight phenolic resol resin is used to impregnate paper for laminates to reduce their water absorption. A high molecular weight resol resin needed for plywood glues must wet well, but not penetrate too deeply into porous structure of wood.[1]

The development of resins demands information of the effects of the condensation conditions on the resin structure and properties. ^{13}C-NMR spectroscopy is an useful and informative method to analyze detailed structures of phenol–formaldehyde resins.[2–21] Especially, quantitative NMR analysis gives valuable information in addition to other analytical methods, for example, gel permeation chromatography (GPC),[2–6,22–25] differential scanning calorimetry (DSC),[3,4,26–30] and IR spectroscopy.[2,7–9,31]

In this study a series of phenol–formaldehyde resins was condensed and analyzed by ^{13}C-NMR, GPC, and DSC. The effects of an F/P (formaldehyde/phenol) molar ratio on the structure and the properties of resins were also studied. The large chemical shift range of ^{13}C, the high resolution of the spectra, and the possibility to record the signals of all nonequivalent carbon atoms allowed the identification of many different functional groups by NMR spectroscopy. GPC was used for separation of large molecules and determination of molecular weight distribution. DSC gave information of reactivity of resins by revealing physical or chemical energy changes in DSC curves.

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Table I   The Condensation Conditions of the Resins

Resin Number	F/P Molar Ratio	Condensation Alkalinity (wt %)	Condensation Viscosity (mPa s)
1	1.90	1.25	500
2	1.95	1.25	500
3	2.00	1.20	500
4	2.15	1.25	500
5	2.20	1.20	500
6	2.30	1.22	500
7	2.00	1.85	200

Condensation temperature: 80°C.

EXPERIMENTAL

Resin Preparation

The raw materials, phenol (purchased from J. T. Baker) and formaldehyde (produced by Dynoresin Oy from methanol), were of high purity grade and analyzed further by NMR spectroscopy. Formaldehyde was used as a formalin solution, which contained 45% formaldehyde, water, and some methanol.

A series of six low-molecular resins (1–6, Table I) was condensed in two stages and a high-molecular resin (7, Table I) in one stage with NaOH catalyst (produced by Bayer). The resins were prepared in a 6 dm^3 glass reactor equipped with a stirrer, a condenser, and external cooling and internal heating units. The molar ratio of formaldehyde to phenol varied between 1.90 and 2.30. The condensation viscosity was 200 or 500 mPa s and the condensation temperature was 80°C. The resins were stored frozen at −18°C until analysis.

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, observing ^{13}C at 100.623 MHz and using an inverse gated ^{1}H proton decoupling technique. Typical spectra of resins were run with a 90° pulse of 11.5 μs, a 120 s pulse delay, 600 scans, and a 20-h acquisition time. For the analysis of model compounds (phenol, 4- and 2-methylol phenol, 4- and 2- hydroxydiphenylmethane, obtained from Aldrich Chemical Company) the acquisition time was 4 h and a number of scans 120.

DMSO-d$_6$, 99 atom% deuterated dimethylsulfoxide (purchased from Aldrich), was used as a solvent, an agent to obtain a deuterium lock and an internal chemical shift standard. The ^{13}C signals of resins were referenced to the central resonance line of DMSO with δ value of 39.5 ppm.[10] The solvents containing aromatic groups could not be used because of a possible overlap in the aromatic region and possible reactions with samples. Deuterated water, acetone, and other organic solvents did not dissolve all the resins completely. However, acetone-d$_6$ (purchased from Merck) and methanol-d$_4$ (Riedel-de Haën AG) were tested with one resin, and their central signals were set to 30.2 ppm and 49.5 ppm, respectively.
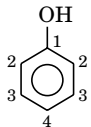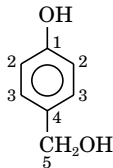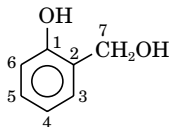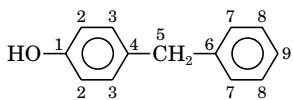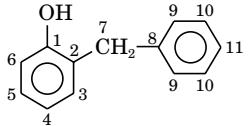
Quantitative Analysis of Resol Resins

All signals in spectrum were integrated, either individually or as a group. The integral value of the phenoxy carbon region was set to 1.00 and all integration results were compared to this setting and are presented per phenolic unit (p.p.u.). The signals of the phenoxy carbon region were also integrated separately. Different signals were identified with the help of model compounds and literature. Only the simplest products can be identified definitely. The higher condensation products can be integrated as a group.

In the analysis of the resin spectrum the F/P molar ratio was obtained by integrating all aliphatic carbon signals versus the phenoxy carbon region with the proportioned integral value 1.00. F/P molar ratio was determined by integration using two different methods. First, each of the aliphatic signals was integrated separately (Integration 1, Table VI), and secondly all together (Integration 2, Table VI). The latter method seems to eliminate the integration errors, be more reliable, and the results agree better with the ones calculated from the amounts of starting materials.

The proportion of free phenol from all phenol carbons was determined by integrating first the group of all phenoxy carbons and methanol, and secondly the single free phenol signal and methanol. Thus, the methanol was used as an internal standard. The sharp and separate carbon signals of the phenoxy region of low molecular weight resins can be integrated accurately. The determination is more difficult for broad signals of high molecular weight resins.

Table II ^{13}C-NMR Assignments for Model Compounds in DMSO Solvent

Compound	Structure	Chemical Shifts (ppm)										
		C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
Phenol		157.10	115.12	129.25	118.70							
4-Methylol phenol		155.94	114.64	127.90	132.57	62.76						
2-Methylol phenol		153.99	127.11	127.11	118.48	128.36	114.32	58.13				
4-Hydroxydiphenylmethane		154.94	114.79	129.20	130.98	a	141.58	127.94	128.12	125.37		
2-Hydroxydiphenylmethane		154.72	127.18	130.12	118.78	126.99	114.86	35.28	141.00	127.96	128.47	125.43

^{a} Not detected, overlapping with the DMSO solvent.

Table III   The Quantitative ¹³C Determination of Methylene Bridges of the Sample Resin in Different Solvents

Methylene Bridges	Solvent		
	Acetone	DMSO	Methanol
o-p′	0.35	0.34	0.31
p-p′	0.20	0.22	0.20
o-p/p-p′ ratio	1.75	1.55	1.55

ᵃ The integral values are related to the value of 1.00 of the phenoxy carbon.

GPC Experiments

The GPC procedure was performed using a chromatography system equipped with a Waters 510 pump, a Rheodyne injector and three styragel columns (1000, 500, and 100 Å, 30 × 0.7 cm) in series. The columns were calibrated with three polystyrene standards (M_w = 1250, 5000, 34500), one dinonylphtalate standard (M_w = 418), and one 1-phenylhexane standard (M_w = 162). Resin samples were diluted to 20 mg/mL into tetrahydrofuran, which was also used as an eluent at a flow rate of 1.0 mL/min. Separated compounds were

detected by means of a Waters 481 UV detector operating at 254 nm.

DSC Experiments

DSC measurements were made using a Perkin–Elmer DSC 7 instrument and thermal analysis software. Liquid resin samples of 18.600 mg were sealed in Perkin–Elmer stainless steel pressure capsules. Samples were heated from 25 to 250°C at a rate of 25°C/min.

RESULTS AND DISCUSSION

¹³C-NMR Spectroscopy of Phenol–Formaldehyde Resins

Model Compounds

The NMR spectra of model compounds, phenol, 4-methylolphenol and 2-methylolphenol were comparable to the NMR data represented in the literature.[9,14–16] Also, the spectra of 4-hydroxydiphenylmethane and 2-hydroxydiphenylmethane were analyzed (Table II). The information obtained from model compounds was utilized in the inter-
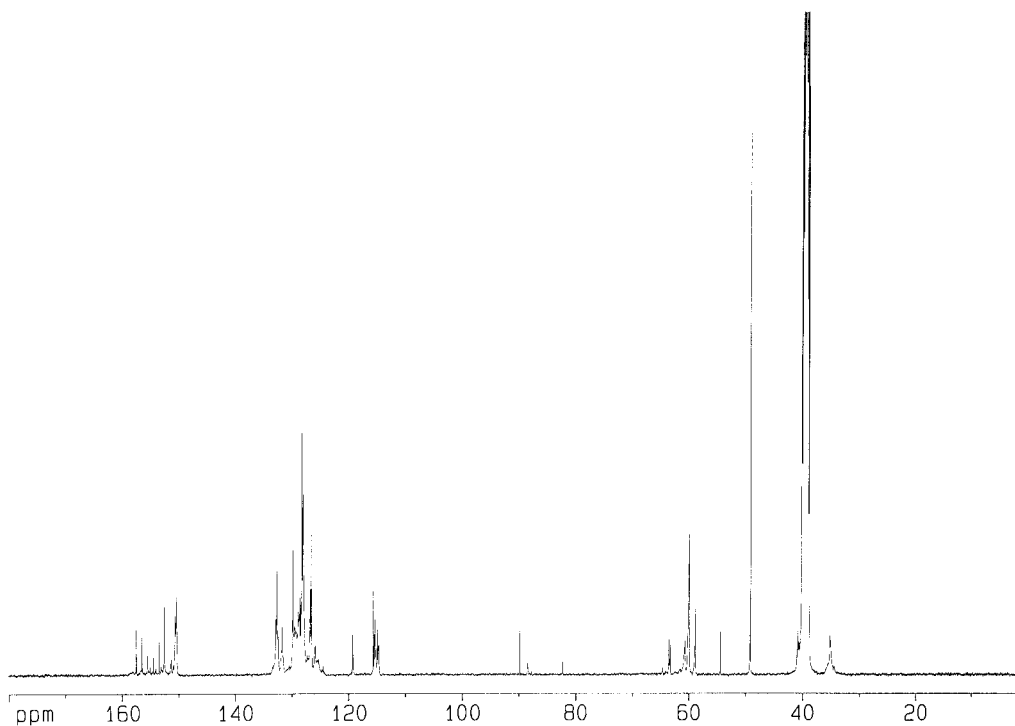

Figure 1   ¹³C-NMR spectrum of the low molecular weight resol resin.

Table IV ^{13}C Chemical Shifts of a Low Molecular Weight
Phenol–Formaldehyde Resin

Chemical Shift (ppm)	Assignment of the Carbons
34.27–36.00	*ortho–para* methylene bridges
40.83–41.00	*para–para* methylene bridges
38.87–40.12	DMSO-d$_6$ solvent
49.80	methanol
54.70, 89.90	hemiacetal of formalin
59.00–62.00	*ortho* methylol
63.00–65.00	*para* methylol
65.00–70.00, 86.00–88.60	phenolic hemiformals
82.00–91.00	oxymethylene of formaldehyde oligomers
114.70–115.10	free *ortho*
119.20–119.50	free *para*
124.66–133.50	meta, substituted *ortho*, substituted *para*
150.40–157.50	phenoxy region
154.8–156.1	phenoxy, alkylated in *ortho* position
156.5–156.8	phenoxy, alkylated in *para* position

pretation of the spectra of resins and used in checking the quantitativity of the method.

The chemical shifts of phenoxy carbons (C$_1$—OH) are between 153 and 158 ppm. The C$_1$ signals of phenolic rings, in which the reaction has taken place at *ortho* positions, have lower chemical shift values than the ones reacted to *para* positions. Free *ortho* and *para* carbons, the important signals in ^{13}C-NMR spectroscopy of resins, occur at 115 ppm and 119 ppm, respectively. Substitution with a methyl group (—CH$_2$OH) causes a downfield shift of the *ortho* and *para*
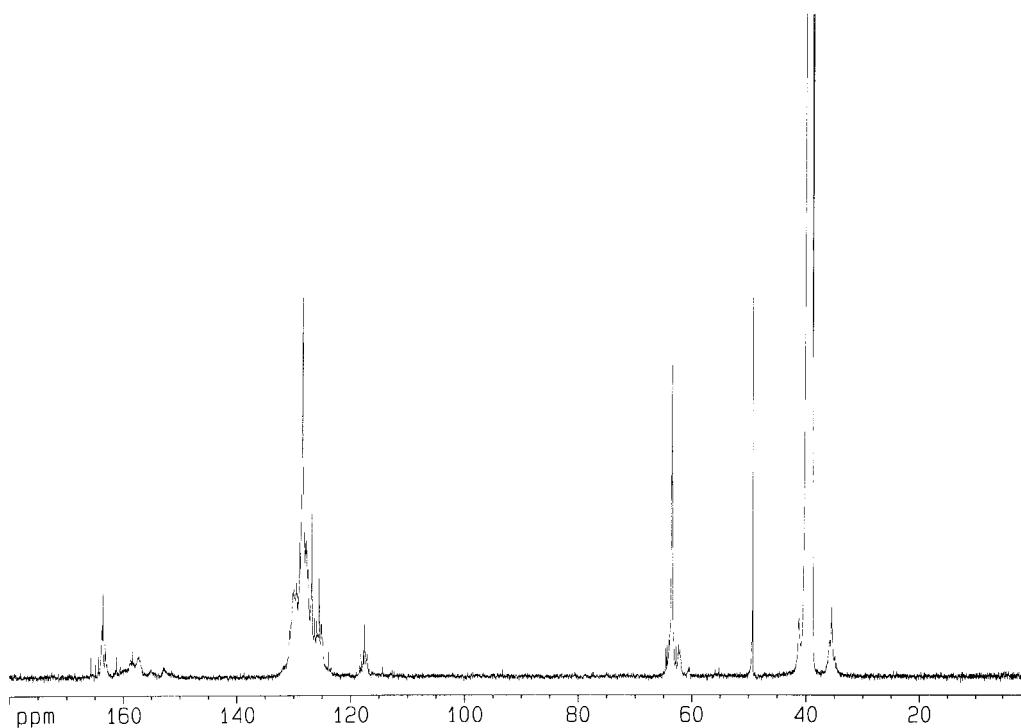

Figure 2 ^{13}C-NMR spectrum of the high molecular weight resol resin.

Table V NMR Results of the Analyzed Resins, Part 1

Resin Number	F/P Molar Ratio	Aromatic Carbons				Formalin Hemiacetal		Formalin Oxymethylene	Formalin Sum	Phenolic Hemiformals	Methylol Groups		Methylene Bridges	
		Phenoxy	Free para	Free ortho	Other	C1	C2				ortho	para	p-p'	o-p
1	1.90	1.00	0.066	0.458	4.626	0.034	0.032	0.012	0.077	0.027	0.955	0.127	0.214	0.394
2	1.95	1.00	0.062	0.436	4.722	0.038	0.039	0.011	0.087	0.015	0.984	0.108	0.266	0.451
3	2.00	1.00	0.050	0.386	4.715	0.041	0.047	0.011	0.099	0.035	1.005	0.124	0.250	0.405
4	2.15	1.00	0.034	0.304	4.920	0.070	0.084	0.021	0.175	0.042	1.079	0.123	0.276	0.466
5	2.20	1.00	0.037	0.318	4.768	0.079	0.086	0.023	0.188	0.066	1.023	0.124	0.214	0.456
6	2.30	1.00	0.020	0.218	4.789	0.109	0.113	0.027	0.250	0.092	1.053	0.123	0.314	0.389
7	2.00	1.00	0.063	0.216	5.192	0.005			0.005	0.037	1.174	0.033	0.201	0.490

The integral values are related to the value of 1.00 of the phenoxy carbon.

carbon resonances to 127 ppm and 132 ppm, respectively. Methylol groups themselves give signals between 58 and 63 ppm and methylene bridge groups ($-CH_2-$) between 35 and 41 ppm.

The Effect of Solvent

The solvent can affect the ^{13}C resonances of functional groups. To find out the importance of the solvent, ^{13}C-NMR spectra of the sample resin were recorded in DMSO-d$_6$, methanol-d$_4$, and acetone-d$_6$. The important signals of free ortho and para aromatic carbons at 115 ppm and 119 ppm, respectively, are more clearly visible in DMSO and acetone solvents than in methanol. The solvent has also effect on the chemical shifts of various carbons.

Only in the DMSO solvent the presence of oxymethylene (82–91 ppm), hemiacetals of formaldehyde (54.7 ppm, 89.9 ppm) and phenol hemiformals (65–70 ppm, 86–88.6 ppm) can be detected completely. On the other hand, the ^{13}C signal of acetone solvent at 30 ppm does not overlap with the signals of *ortho–para* or *para–para* methylene bridges, but does overlap with the resonances of possible *ortho–ortho* bridge structures. The *p–p'* signal has to be integrated extremely carefully when situating next to the DMSO signal. The quantitative ^{13}C determination of methylene bridges of the sample resin in different solvents is seen in Table III.

The Low Molecular Weight Resol Resin

Figure 1 is a typical ^{13}C-NMR spectrum of a low molecular weight resol resin (resin 1, Table I). The signals are assigned in Table IV by means of model compounds and the literature.[2–21]

Differences in the chemical structure of the phenol ring next to a methylene bridge cause broadening to the observed signals at 34–41 ppm. Every methylene bridge, which has a different chemical environment, has a different chemical shift. The possibilities of different structures next to *ortho-para* methylene bridges are larger than those of para-para methylene bridges. Because of this, the signal corresponding to *o–p'* bridges seems to be broader than the signal due to *p–p'* bridges. Possible methylene bridges in *ortho–ortho* positions could be observed at 30 ppm.

The phenoxy carbon region from 150 to 158 ppm is important from an analytical standpoint. The amount of free phenol, the concentration, and

Table VI NMR Results of Analyzed Resins, Part 2

| Resin Number | F/P Molar Ratio | | | Free Phenol (%)[c] | Methanol[d] | o-p/p-p' Ratio | Higher Condensation Products (%)[c] |
	in Synthesis	Integration 1[a]	Integration 2[b]				
1	1.90	1.87	1.87	4.22	0.119	1.84	45.6
2	1.95	2.00	1.94	3.29	0.413	1.69	44.1
3	2.00	2.02	2.04	2.56	0.439	1.62	47.8
4	2.15	2.34	2.18	1.37	0.233	1.69	54.3
5	2.20	2.26	2.23	2.09	0.287	2.13	54.5
6	2.30	2.48	2.34	1.22	0.186	1.24	54.8
7	2.00	1.94	2.13		0.367	2.44	50.4

[a] Separate integration of each aliphatic signals.
[b] Group integration of aliphatic signals.
[c] Percent from total phenolic units.
[d] The integral values are related to the value of 1.00 of the phenoxy carbon.

types of end groups and the concentration of branched centers can be determined by means of these signals. The chemical shifts of ortho alkylated end phenolic groups are between 154.8 and 156.1 ppm, which is clearly separated from the corresponding signals of para alkylated groups between 156.5 and 158.8 ppm.

The High Molecular Weight Resol Resin

Figure 2 represents a typical ^{13}C-NMR spectrum of a high molecular weight resol resin (resin 7, Table I), which differs from that of low molecular weight resin. Due to higher alkalinity the signals have shifted to the lower field. The effect of the high molecular weight compounds can be observed as broad signals.

Both methylene bridges can be seen, and the amount of $o–p'$ methylene bridges is high and $p–p'$ is low. Many *ortho* methylol structures are present, but the amount of *para* methylol is low. Almost no hemiformal, oxymethylene, or hemiacetal structures can be detected. The free *para* carbons cannot be identified, and the amount of free *ortho* carbon is small. Different groups of the phenoxy region are difficult to analyze and integrate reliably.

The Effects of the F/P Molar Ratio on the Structure and the Properties of the Resin

NMR Analysis

To study the effect of the formaldehyde to phenol ratio on the structure and the properties of the resin, the low molecular resins 1–6 (Table I) were

synthesized in the molar ratios from 1.90 to 2.30. Condensation viscosity was 500 mPa s, temperature 80°C, and the alkalinity 1.20–1.25 wt %. NMR data of the studied resins is collected in Tables V and VI. The large quantitative NMR data make possible a versatile analysis. Kim et al. have even presented the theoretical equations to calculate the degree of polymerisation and the molecular weights of resins.[5]

For resins 1–6 the free *ortho* and *para* positions decrease as a function of F/P molar ratio (Fig. 3). The unsubstituted *ortho* positions decrease even more rapidly than the *para* ones. The addition of formaldehyde seems to cause only a slight increase in amounts of *ortho* methylol groups and $p–p'$ methylene bridges, whereas the amounts of *para* methylols and $o–p'$ bridges stay constant (Fig. 4). The number of all hemiformal structures increases as a function of F/P molar ratio. The proportion of formalin hemiacetals and phenolic
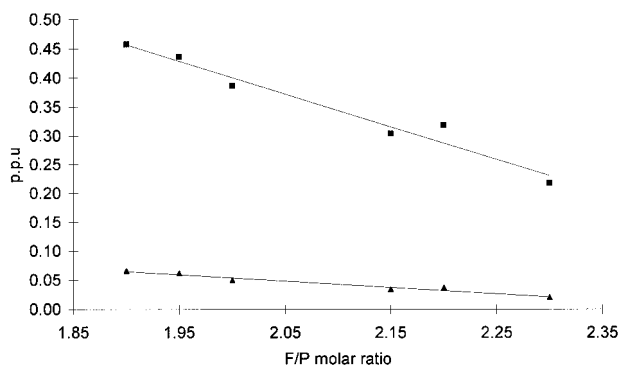

Figure 3 The amounts of (■) free *ortho* and (▲) free *para* positions as a function of an F/P molar ratio.
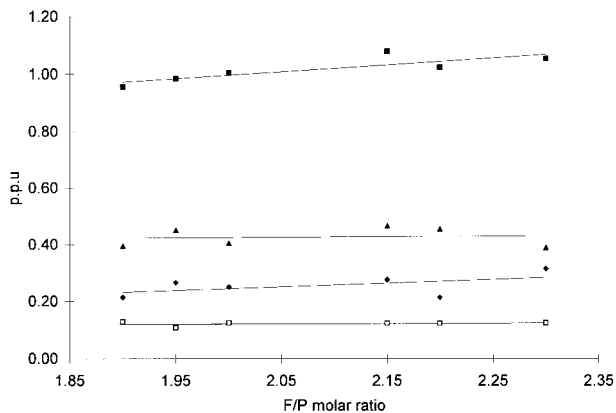
Figure 4 The amounts of (■) *ortho* methylol, (□) *para* methylol, (♦) *p–p'* methylene bridges, and (▲) *o–p'* methylene bridges as a function of an F/P molar ratio.

hemiformals increases most, and the proportion of oxymethylene groups slightly less (Fig. 5).

A proportion of higher condensation products (spectra in Fig. 6, values in Table VI) can be determined from the integrals of broad phenoxy carbon signals at highest field 150–151 ppm. The amount of the higher molecular weight products increases rapidly as a function of an F/P molar ratio until the F/P value 2.15 in which the maximum amount of higher condensation compounds are produced. The amount of free phenol (spectra in Fig. 6, values in Table VI) decreases as a function of an F/P molar ratio.
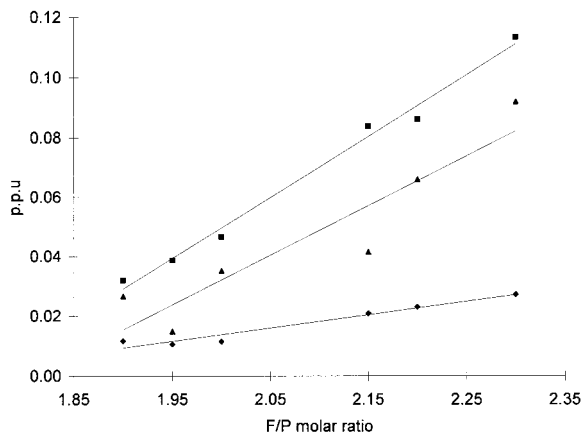

Figure 5 The amounts of hemiformal structures as a function of an F/P molar ratio; (■) formalin hemiacetal, (▲) phenolic hemiformals, and (♦) formalin oxymethylene.
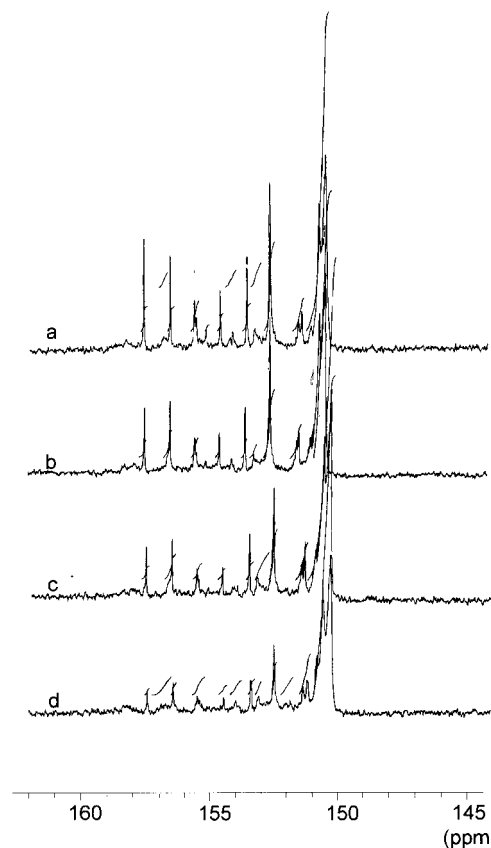

Figure 6 The phenoxy carbon regions of ^{13}C-NMR spectra of the resins condensed with different F/P molar ratios: (a) resin 1 in Table I (F/P 1.90), (b) resin 3 (F/P 2.00), (c) resin 5 (F/P 2.20), and (d) resin 6 (F/P 2.30).

GPC Analysis

Gel permeation chromatography gives relatively fast information of molecular weight distribution. Figure 7 illustrates gel permeation chromatograms of low molecular weight phenolic resins (1–6 in Table I) condensed with different molar ratios. The wide signal between 15.5 and 19.5 min is due to the first eluted largest oligomers, after which dimers (19.5–24.5 min), monomers, for example, *p*- and *o*-methylol phenol (24.5–27.5 min), and free phenol (27.5–28.5) give the corresponding signals in the order of increasing retention times. The relative amounts of different dimers increase and the relative amounts of monomers decrease as a function of an increasing molar ratio, which could also be concluded from the NMR spectra. The GPC curve of a high molecular weight resin differs from the one of a low molecular weight resin so that it rises more quickly, is
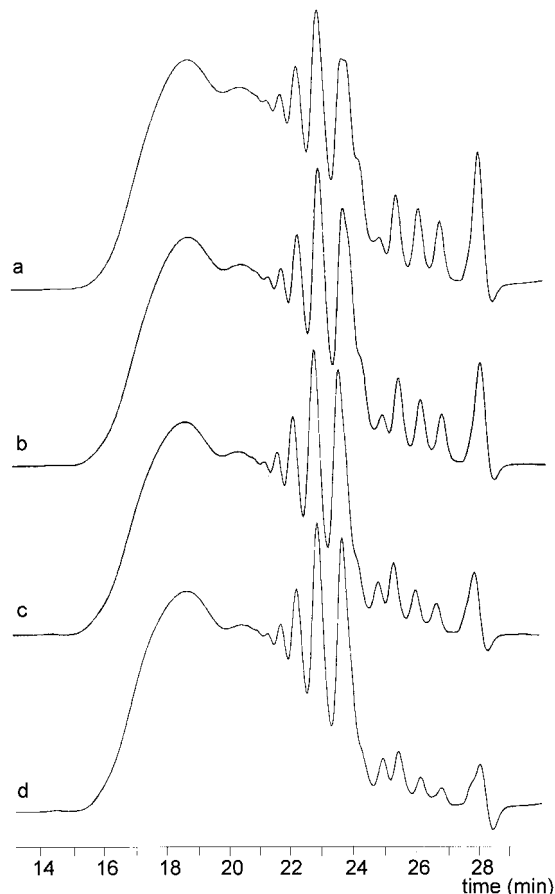
Figure 7 The GPC curves of resins condensed with different F/P molar ratios: (a) resin 1 in Table I (F/P 1.90), (b) resin 3 (F/P 2.00), (c) resin 5 (F/P 2.20), and (d) resin 6 (F/P 2.30).
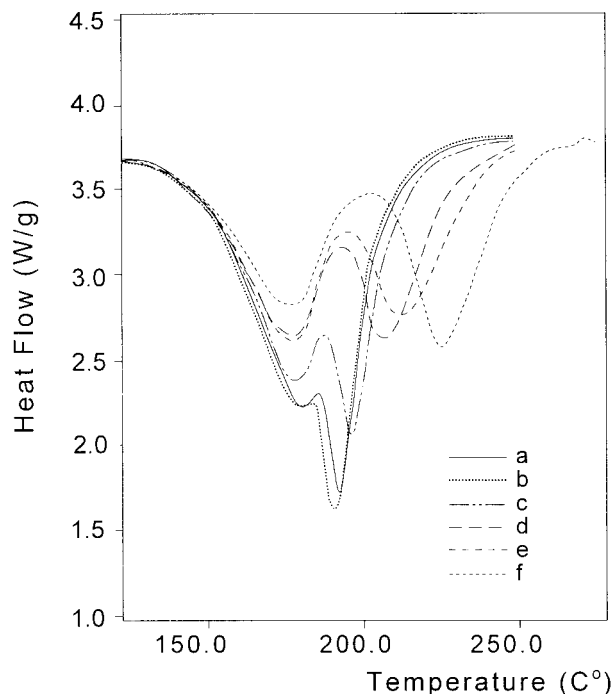

Figure 8 The DSC curves of resins condensed with different F/P molar ratios: (a) resin 1 in Table I (F/P 1.90), (b) resin 2 (F/P 1.95), (c) resin 3 (F/P 2.00), (d) resin 4 (F/P 2.15), (e) resin 5 (F/P 2.20), and (f) resin 6 (F/P 2.30).

broader and naturally contains fewer signals of small molecules.

Average molecular weights (M_n and M_w) and polydispersity index (M_w/M_n) calculated from the GPC results are presented in Table VII. The number-average molecular weight, M_n, increases al-

Table VII   Molecular Weights of Resins with Different F/P Molar Ratios Analysed by GPC

Resin Number	F/P	M_n	M_w	M_w/M_n
1	1.90	781	2717	3.48
2	1.95	815	3019	3.70
3	2.00	839	2900	3.46
4	2.15	887	2931	3.30
5	2.20	906	3102	3.42
6	2.30	954	3113	3.26

most linearly as a function of a molar ratio. Also, the highest weight-average molecular weight values, M_w, are found with the highest F/P molar ratios. The polydispersity index seems to decrease according to the increasing molar ratio, which means that molecular weight distribution narrows as the amount of formaldehyde increases.

DSC Analysis

DSC curves of low molecular weight resins (1–6 in Table I) condensed with different molar ratios are shown in Figure 8, and the calculated results are collected in Table VIII. The DSC curve gives valuable information of the exothermic curing of a resin, for example, the temperature range and the heat of reaction (the area of both peaks) indicating reactivity. The shapes of the DSC signals change as the F/P molar ratio increases. At lower molar ratios (from 1.90 to 2.00) two DSC signals are overlapping, while at higher F/P ratios (from 2.15 to 2.30) the signals are well separated from each other. As the F/P molar ratio increases, the temperature of the first signal, T_1, decreases

Table VIII   DSC Analysis of Resins with Different F/P Molar Ratios

Number Resin	F/P	ΔH (J/g)	T_1 (°C)	T_2 (°C)	$\Delta(T_1-T_2)$ (°C)
1	1.90	171.6	181.8	192.5	10.7
2	1.95	178.0	180.7	190.5	9.8
3	2.00	168.6	179.4	196.7	17.3
4	2.15	165.0	177.9	208.4	30.5
5	2.20	168.8	177.2	213.2	36.0
6	2.30	154.9	177.3	226.5	49.2

slightly, while the temperature of the second signal, T_2, increases after the F/P value of 1.95. The first signal of DSC curve is caused by the condensation of methylol groups with phenol to form methylene bridges, and by the condensation of two methylol groups to form dibenzyl ether bridges.[4,26] The second signal of the thermogram represents the further reactions of the resin, for example, the condensation of the dibenzyl ether bridges to methylene bridges eliminating formaldehyde.[4,26]

The increasing F/P value enhances the concentration of methylol groups. This results in the increasing amount of methylene and ether bridges and further in the rigid resin structure, which makes condensation of dibenzyl ether bridges more difficult. This is probably the reason for the shift of the second exotherm to the higher temperature range according to the increasing F/P value. The difference of peak temperatures, $\Delta(T_1-T_2)$, is considerably higher for the resins condensed with higher F/P molar ratios. The total area of the DSC signals, corresponding to ΔH, does not change significantly.

CONCLUSIONS

Quantitative ^{13}C-NMR spectroscopy proved to be a valuable technique in a detailed analysis of resins. Chemical shifts of basic model compounds and synthesized phenol–formaldehyde resins could be assigned and the signals integrated to get a quantitative data. Each resin gave an informative spectrum, which was used as a basis to analyze the effects of condensation conditions on the resins structure and properties.

On the basis of NMR results, the amounts of free *ortho* and *para* positions decrease, and *ortho* methylol groups, *p–p'* methylene bridges and

hemiformal structures increase as a function of the increasing F/P molar ratio. M_n and M_w values calculated from GPC curves and the amount of dimers increase as a function of molar ratio. Polydispersity index M_w/M_n and the amount of monomers decrease according to an F/P ratio. As the F/P molar ratio increases, the shapes of the DSC signals change from the overlapping signals to the separate ones and the temperature of the first signal decreases slightly, while the second exotherm shifts to the higher temperature range.

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