Structure of Polycondensates from Hydroxymethylphenols

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ABSTRACT: The structure of oligomers obtained from mono-hydroxymethylphenols in melt condensation at 120°C was determined using ^{13}C NMR spectra in CD_3OD solution. Alongside of methylene region of spectrum, valuable information was obtained from signals of aromatic carbons. Noncatalytic conditions promote the formation of dihydroxydibenzyl ethers in equilibrium with *ortho*- and *para*-benzoquinones of oxymethylene derivatives. The final methylene linked oligomers are formed, mainly, by splitting the ether intermediates with free aromatic positions. In alkaline conditions, highly nucleophilic phenoxide ions of *ortho*-hydroxymethyl compounds are responsible for substitution in free aromatic positions. The most favored reaction in the mixture of both hydroxymethylphenols is the formation of *p,p′*-methylene. In condensation of *para*-hydroxymethylphenol, formation of *p,p′*-methylene groups occurs with simultaneous release of formaldehyde. High content of alkali stabilized *ortho*-hydroxymethyl groups of fully substituted methylene linked oligomers determines the curing behavior of resol phenol–formaldehyde resins. The role of hemiformals in reactions was insignificant. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1226–1234, 2008

Key words: thermosets; resins; polycondensation; NMR; structure

INTRODUCTION

Today, phenol–formaldehyde resins (PF) are essential adhesive binder components in composite materials. Among these, the most important are wood panels (plywood and others), laminates, insulation, and coating materials.[1] Remarkable properties of cured phenoplastics include long term mechanical, thermal and weather stability, fire resistance, insulating capabilities, and low cost at high performance characteristics. At the same time, low curing rate of PF, low alkali resistance, and brittleness of phenolics should be considered.

Model compounds and resol resins, obtained in alkaline conditions, were mainly studied by ^{13}C NMR spectroscopy. Attention was paid to the hemiformal groups in resins,[2] to the assignment of hydroxymethyl(HM)phenol model compounds,[3] and to the functional groups in the prepolymer resins.[4,5] The solid-state NMR analysis was not very promising for characterization of chemical structure in different cure states.[6] Often, high pressure liquid chromatography is accompanied with the ^{13}C NMR study (e.g., Ref. [7]). In all of these studies, the greater reactivity of *para*- as compared to *ortho*-hydroxymethyl or aromatic free position was ascertained.

The practical case, met more frequently, is the strongly alkaline water solution of resol resin synthesized with a great excess of formaldehyde (F/phenol > 2.1), and containing no free aromatic positions for curing.[8] Some of the structures mentioned earlier,[9] formed as the result of participation of phenolic hydroxyl or methylene groups, were not found.

One of the problems, occurring in most cases, is the solubility of resins for NMR study. Very different solvents can be used for PF intermediates with HM and dimethylene ether functionalities.[4] The assignment of methylenes in polycondensates is also possible in the presence of other functionalities. In the case of polycondensation of mono-HM phenols (*o*-HMP and *p*-HMP), the final resins contain only methylene groups because of great excess of aromatic free positions. These resins with predominant content of dihydroxydiphenylmethanes are soluble in pyridine-d_5. This was the best solvent for ^1H NMR study of condensation rate of *o*-HMP and *p*-HMP.[10] The difference in ^1H chemical shifts for *ortho* and *para* HM groups in pyridine-d_5 is greatest among the various solvents (5.16 and 4.81 ppm, respectively). Because of good resolution of different signals, the study of cocondensation of *o*-HMP/*p*-HMP was also successful.[11] At the same time, ^1H NMR was not applicable for the final assignment of clearly resolved signals at 5.31 and 4.92 ppm in

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o-HMP and *p*-HMP condensation, respectively. Probably, attaching to hemiformal structures, supposed usually (e.g., Refs. [2] and [7]), was not the best way in assignment of signals.

Resol resins, obtained in the presence of alkali catalysts, are quite well studied because of their practical importance. In this study, the main attention was paid to the melt condensation of *o*-HMP/*p*-HMP and characterization of products by the ^{13}C NMR spectroscopy, with the hope that the conclusions drawn are of more general character. The spectrum of one typical resol resin for wood panel production is also under discussion. All spectra were taken in CD_3OD solution. Pyridine-d_5 is not a good solvent for ^{13}C NMR study, as the signals for aromatic carbons of pyridine (125–150 ppm) and C2-6 of phenol in the region of 115–135 ppm are overlapped.

EXPERIMENTAL

Synthesis

p-HMP was synthesized by the reduction of *p*-hydroxybenzaldehyde with $NaBH_4$ aqueous alkaline solution by cooling. After neutralization with H_2SO_4 and filtration, *p*-HMP was recrystallized several times from ethyl acetate/hexane (3/1). A commercial grade *o*-HMP was recrystallized several times from benzene/ethyl alcohol (20/1). *o*-HMP and *p*-HMP were characterized by melting temperature (87 and 121°C, respectively) and by ^{13}C NMR spectra. Melt condensation of *o*-HMP, *p*-HMP and their equimolar mixture was carried out at temperature 120°C ± 1°C for 2 h. The mixtures *o*-HMP/NaOH and *o*-HMP/*p*-HMP/NaOH with molar ratios of 1/0.1 and 1/1/0.1 were, after thorough mixing, heated in the melt at the temperature 120°C ± 1°C for 1 h.

Industrial grade phenol, 45% formaldehyde aqueous solution, and 25% NaOH aqueous solution were used for the synthesis of the resol-type PF resin. Molar ratio of phenol/formaldehyde/NaOH was 1/2.3/0.7. Half of the NaOH solution and melted phenol were charged into the stirred reactor (1 L). After cooling to 30°C, formaldehyde solution was added by portions, maintaining the temperature under 45°C. After that, the reaction mixture was stirred at the temperature 50–55°C for 1.5 h. Thereafter, the temperature was raised to boiling point and the mixture was refluxed for 40 min. The other portion of NaOH solution was added, and the resin was stirred at 80–85°C for 1.2 h, followed by cooling. The resin was characterized by standard methods (viscosity = 750 mPa s; dry solids content = 48.9%; the content of free phenol = 0.07%; the content of free formaldehyde = traces; the content of NaOH = 7.8%).

^{13}C NMR spectroscopy

^{13}C NMR spectra of synthesized products were obtained on a Bruker AMX500 NMR spectrometer with ^{13}C frequency at 125.77 MHz at 25°C from CD_3OD solutions by 5 mm $^{13}C—^{1}H$ dual probehead. Spectra were accumulated into 32K data points and processed using exponential multiplication, with 2 Hz line broadening into 128K spectra. Scans (10,000–15,000) were accumulated for the resulting spectra. All spectra were accumulated in identical conditions, using power gated Waltz decoupling, with 25° measurement pulse and 1 s prepulse delay. Quantitative information on changes of different structural elements was obtained by the manual integration routine of XWINNMR 2.1 software.

RESULTS AND DISCUSSION

General reaction route in noncatalytic condensation

Bifunctionality of F in electrophilic substitution reaction is revealed, actually, in subsequent reactions of different mechanisms. In this work, *ortho*- and *para*-HMP as the first-formed addition species were used to eliminate the influence of mixtures of hydroxymethylated phenols on interpretation of complicated polycondensation reactions. Condensation of HMP occurs by two different reactions. The substitution in aromatic *ortho* and *para* positions of HMP leads directly to the formation of dihydroxydiphenylmethanes and oligomers. The condensation between hydroxymethyl groups can also proceed. Despite the fact that the condensation of *o*-HMP and *p*-HMP occurs in the presence of great excess of aromatic free positions(2/1), the tendency to formation of dihydroxydibenzyl ethers is great in noncatalytic reaction (Table I).

The conditions of melt condensation were chosen so that about 20% of hydroxymethyl groups remained unreacted to the moment of the run of ^{13}C NMR spectra of reaction products. As HM groups are also involved as end groups of condensation products, the additional signals, somewhat different from these for *o*-HMP and *p*-HMP, appear in spectra (e.g., Fig. 1). The formed dimethylene ether and methylene groups belong to several species, and are revealed in spectra by multiple signals. It is presumed in this discussion that the covalent bond between aromatic positions and (oxy)methylene is resistant to any rearrangement reaction. One has seen no reason for the substitution of *o*,*p*′-methylenes with *p*,*p*′-methylenes in the polycondensation route.[7] Certainly, dimethylene ether derivative is not a final species in reaction and releases from one F. The products of long-time noncatalytic condensation of *o*-HMP and *p*-HMP contain only methylene groups

TABLE I
Molar Distribution (%) of Methylene Containing Functional Groups in Reaction Products of Heat Treatment of Hydroxymethylphenols

Assignment	Typical signal (ppm)	*ortho* HMP	*para* HMP	*o* HMP/*p* HMP (1/1)
Hydroxymethyls				
ortho CH_2OH	61.2	18.2	0.5	12.7
para CH_2OH	65.0	0	21.5	8.9
Dimethylene ethers				
ortho,ortho′	69.5 (68.5–70.7)	65.5	0.6	13.5
para,para′	72.3 (71.9–72.8)	0	29.7	9.4
ortho,para′	68.4/73.0	0	0	25.8
Methylenes				
ortho,ortho′	30.8–31.5	4.1	0	2.6
ortho,para′	35.2–36.5	7.2	26.4	7.8
para,para′	40.7–41.0	0	4.5	5.1
Others				
$-CH_2O-CH_2OH$	83–91	0.3	1.3	0
$Ar(H)-CH_2O-$				
ortho	66.6–66.8	4.7	0	4.4
para	70.8–71.0	0	15.5	9.8

mostly in dihydroxydiphenylmethanes and are soluble in pyridine-d_5.[11]

The reaction products are characterized quantitatively by the content of methylene-containing functional groups (Table I). Useful information can be obtained also from the region of 150–160 ppm for the hydroxyl-bearing aromatic carbon C1, despite the fact that the intensity of that is about 35% of that of methylene carbon (Table II). The signals in the region of 115–135 ppm for C2-6 aromatic carbons can be used also for identification of reaction products. The intensity in that region is about 80% from the intensity calculated on the basis of methylene region.

Stereosensitivity of aromatic carbons to chemical environment is obvious. Generally, the signals for *para* carbons in comparison with *ortho* carbons appear in lower field. The shielding effect depends on H-bond formation (e.g. *o*-HMP), the amount, position, and structure of substituents. Thus, the contents of aromatic unsubstituted *ortho* and *para* carbons as compared to substituted carbons show higher values. So, the approximation of constitutions by C1 and methylene regions of spectra is more promising. C1 signals for compounds with oxygen containing functional groups appear in lower field. The upfield shift is caused by methylene substituents and multiple substitution with functional groups

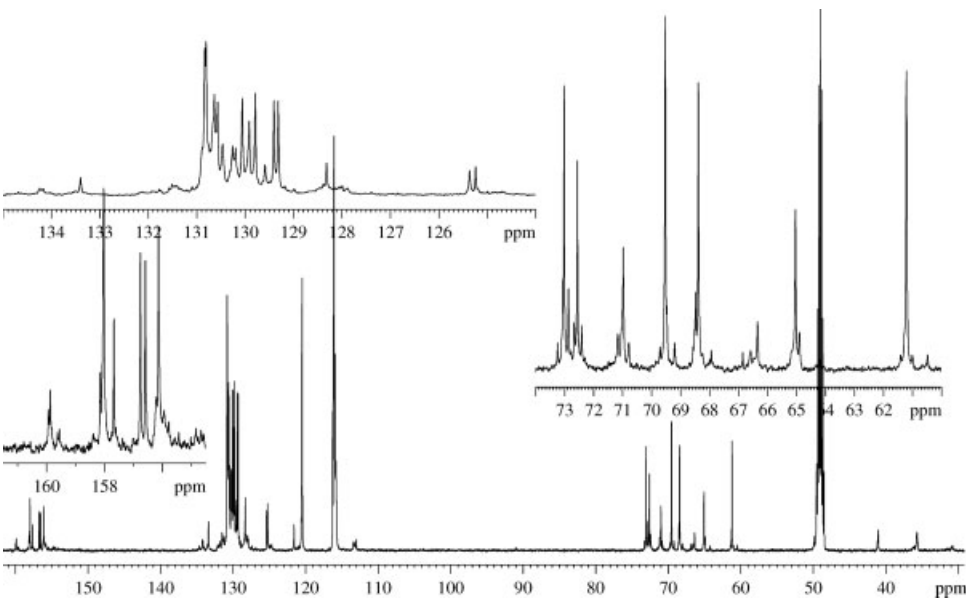


Figure 1 ^{13}C NMR spectrum in CD_3OD of equimolar mixture of *ortho*- and *para*-hydroxymethylphenol after condensation in the melt at 120°C for 2 h.

TABLE II
Molar Distribution (%) of Aromatic Carbons in Reaction Products of Heat Treatment of Hydroxymethylphenols

Assignment	Typical signal (ppm)	*Ortho*-HMP	*para*-HMP	*o*-HMP/*p*-HMP (1/1)
C1 region				
para Benzoquinone	159–160	0	10.0	13.3
ortho-Benzoquinone	158.1	4.3	0	4.2
Compounds with *o*-HM-group	155.9–156.1	20.7	0	10.3
Compounds with *p*-HM-group	157.4–157.6	0		7.9
p,p′-Dimethylene ether	156.8–157.0	0	43.6	9.3
o,o′-Dimethylene ether	156.6–156.7	61.9	0	10.0
o,p′-Dimethylene ether	156.1; 158.0	0	0	30.0
Compounds with methylenes	154–155.5		32.9[a]	
	151–154	13.1	13.5	15.0
C2-6 region				
Free *o*-positions	115.8–16.2	22.6	39.8	32.0
Free *p*-positions	120.3–121.6	21.4	0	9.8
Substituted *o*-positions in ethers	124.8–125.4	5.8	0	3.4
Substituted *o*-positions in HM and methylene compounds	127.5–128.5	4.9	5.1	4.9
m-Positions in HM compounds	129.3–129.8	9.4	9.1	8.7
m-Positions in ethers and methylene compounds	129.9–131.5	35.0	35.1	35.5
p-Positions	131.5–135	0.9	10.9	5.7

[a] Compounds substituted also with HM groups.

(Table II). In C2-6 region, higher content of *meta* carbons shows that the resolution from signals of *ortho* and *para* carbons is not complete. Signals of *meta* carbons can be assigned to different HM and dimethylene ether derivatives. The signals of *meta* carbons for methylene compounds are overlapped by other signals. The shielding effects reveal differently for *ortho* and *para* carbons. In addition to the influence of oxygen in a functional group, the neighborhood of the methylene group is essential. Thus, the chemical shift of *para* carbon is different in *p,p′*- and *o,p′*-methylene linked derivatives.

It can be concluded from the data in Table I that the role of hemiformals is very small. Usually, it is supposed that the formation of methylene group proceeds by the release of F from the intermediate dimethylene ether group. It is clear that this reaction is of minor importance in this case. First-formed dihydroxydibenzyl ethers are unstable compounds and their splitting is promoted by free aromatic positions. Accelerated decomposition to hydroxymethyl derivatives with subsequent reaction with aromatic positions is one variant. Direct splitting with aromatic positions to methylenes by the condensation mechanism is the other possibility.

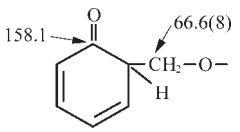
Condensation of *ortho* -hydroxymethylphenol

The formation of *o,o′*-dihydroxydibenzyl ether is favored in this condensation (Table I). The appearance of multiple signals in the region of 68.5–70.7 ppm shows that about 20% of ether groups belong to compounds containing other functionalities as well. The absence of *para* functionalities proves that F release from dimethylene ether groups is insignificant. The reaction of free *ortho* and *para* aromatic positions of ether with *o*-HMP gives the oligomers containing both dimethylene ether and methylene groups. The signals for dimethylene ether functionalities appear in lower field because of *para* substitution (69.7–70.7 ppm) and in higher field because of *ortho* substitution (68.5–69.2 ppm). It means also that methylene substitution in ether as compared to *o*-HMP is favored. Full disappearance of dimethylene ether groups occurs in the long-time condensation.[10] It is clear that free aromatic positions have the decisive role in splitting the ether functionalities. The reactions with *para* positions are preferred and by the end of quantitative methylene formation, the ratio of *o,p′*- and *o,o′*-methylenes increases to 2.3.

The main constituent, *o,o′*-dihydroxydibenzyl ether, can be identified by the following chemical shifts (ppm): $C(CH_2)$, 69.5; C1,1′, 156.7; C2,2′, 125.2; C3,3′, 130.4; C4,4′, 120.3; C5,5′, 130.0; C6,6′, 116.2.

The contents of various species, obtained from methylene and C1 regions, are quite similar (Tables I and II). C2-6 region with the signals whose intensities are influenced by different shielding effects is suitable mostly for identification of structural elements. Apparently, low content of substituted *ortho* carbons in dimethylene ethers is obtained. The signal at 66.6–66.8 ppm appears only in systems with *o*-HMP, and can be assigned to *ortho* oxymethylene functionality, usually supposed to be the constituent of hemiformal attached to aromatic C2. The proper amount of the end HM group cannot be seen

because of low intensity in the region of 83–91 ppm (Table I). The appearance of a new signal for C1 (158.1 ppm) of proper intensity verifies the presence of equilibrium bensoquinone structure (Table II).



The C2-6 signals of that are overlapped by dominating signals of dihydroxydibenzyl ether. The participation of bensoquinone intermediates in heat curing is not surprising.[12] It can be supposed that *para* bensoquinones should be more typical intermediates in HMP polycondensation (p. 3).

Condensation of *para*-hydroxymethylphenol

p,p′-Dihydroxydibenzyl ether is the main intermediate compound in the melt condensation of *p*-HMP. The first step is the very fast disappearance of HM group from the reaction mixture[10] that occurs because of ether formation. This is assured also in the thermoanalysis of *p*-HMP by the exotherm, with peak maximum at 62°C due to the formation of the equilibrium amount of *p,p′*-dimethylene ether. After that, the melting endotherm splits with appearing a shoulder (~107°C) before the melting of *p*-HMP (121°C). The further reactions with participation of *p,p′*-dimethylene ether are faster than those with *o,o′*-dimethylene ether of greater stability. It can be supposed that the maximum amount of *p,p′*-dimethylene ether was higher[10] but by the moment of spectrum run it was reduced by secondary reactions. Low amount of *p,p′*-methylene groups (Table I) proves that the release of F is not the main route of disappearance of the dimethylene ether group. That is in accordance with the low content of *ortho* derivatives in the reaction mixture. It is not possible in the beginning to exclude entirely the reaction between free *ortho* positions of *p,p′*-dimethylene ether with *p*-HMP, but more probable is the splitting of dimethylene ether groups by free aromatic *ortho* positions. That leads to the formation of *o,p′*-methylenes that end in final methylene linked pyridine-soluble oligomer with great (4.5/1) predominance over *p,p′*-methylenes.[10]

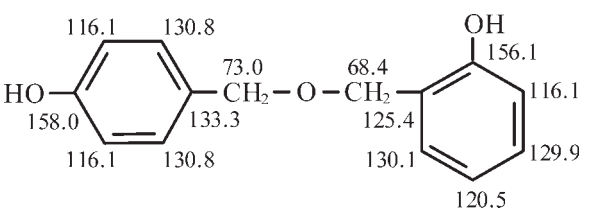
p,p′-Dihydroxydibenzyl ether is characterized by the following chemical shifts (ppm): C(CH_2), 72.3; C1,1′, 157.0; C2,2′,6,6′, 116.1; C3,3′,5,5′, 130.5; C4,4′, 134.2.

Also, in this case, the lower shielding effect results in higher content of unsubstituted *ortho* carbons (Table II). The multiple C1 signals for *p,p′*-dimethylene ether and *para* HM compound overlap. The other most occurring species with *o,p′*-methylene group beside the multiple signal for methylene at 35–36.5 ppm is characterized also by signals for C1. The greatest upfield shift (e.g., 153.5 ppm) is typical for carbons in aromatic rings of multiple substitution with methylenes. In lower field, the C1 signals in aromatic rings substituted with *para* methylenes and with end *para* HM groups of oligomers are not fully resolved. Lower content of *para* carbons is caused by shielding effects and overlapping with signals of *meta* carbons. The signal for *para* carbon substituted with methylene group appears at 131.5–132 ppm.

The signal at 70.8–71.0 ppm of quite great intensity in the methylene region of spectrum is typical only for the reaction mixture with *p*-HMP (Table I). It can be assigned to *para* oxymethylene group. In comparison with condensation of *o*-HMP, the role of that kind of functionality is more than three times higher (Table I), and analogically to the previous conception, it is not the constituent of hemiformal. The appearance of signals for C1 at 159.1–159.4 ppm proves the presence of *para* bensoquinone equilibrium structure. It is not possible to assign the C4 signal for that intermediate because of overlapping of various signals in C2-6 region of spectrum.

Condensation of equimolar mixture of *ortho*- and *para*-hydroxymethylphenols

In comparison with condensations proceeding separately, some retarding of *o*-HMP reaction and accelerating of *p*-HMP reaction occurs. Cocondensation in this case is revealed in high tendency to formation of unsymmetrical dihydroxydibenzyl ether (Table I). The whole amount of ethers is similar to the mean of amounts obtained in separate condensations, but the participation of *p*-HMP in comparison with *o*-HMP is clearly increased. *o,p′*-Dihydroxydibenzyl ether is identified by the following chemical shifts (Fig. 1).



The change in chemical environment is responsible for the appearance of new signals for oxygen-adjacent methylenes of unsymmetrical ether, allowing an unambiguous assignment of that in the presence of symmetrical dimethylene ethers. Good resolution in C1 region (Fig. 1) allows to get a similar quantitative constitution of the condensation product (Table II). Only in calculation of the content of unsymmetrical ether, the intensity of C1 signal from *para* substituted

TABLE III
Molar Distribution (%) of Structural Elements in Reaction Products of Heat Treatment of Hydroxymethylphenols in the Presence of NaOH

Assignment	Typical signal (ppm)	*ortho*-HMP	*o*-HMP/*p*-HMP (1/1)	Resol resin
Methylene region				
Hydroxymethyls				
ortho-HMP	61.2	32.9		0
ortho-CH_2OH in oligomer	61.4–63.3	21.9	41.5	62.5[a]
para-CH_2OH	65.0–65.6	0	8.3	2.7
Dimethylene ethers				
ortho,ortho′	69.5	1.9	0	0.8
para,para′	72.3	0	0	0
ortho,para′	68.4/73.0	0	0	0
Methylenes				
ortho,ortho′	30.8–31.5	5.5	0	0
ortho,para′	35.0–36.5	37.8	25.2	22.6
para,para′	40.7–41.0	0	25.0	11.1
Others				
$-CH_2O-CH_2OH$	83–91	0	0	0.3
C1 region				
Phenoxide ion	≥158 (mostly 163)	0	0	61.9
p-HMP	157.6	0	6.5	0
ortho,ortho′ Ethers	156.7	2	0	0
o-HMP	156.1–156.5	31.0	12.1	
Rings with methylenes	155.6–155.9	31.6	45.4	22.8
	154–155	20.1	19.4	
	153–154	15.3	16.6	15.3
C2-6 region				
Free *o*-positions	115.8–116.2	21.4	30.4	
Free *p*-positions	120.3–120.5	15.6	4.8	0.9
Substituted *o*-positions	126.0–128.5	16.7	9.8	
m-Positions in HM compounds	129.0–129.8	20.3	9.1	66.6
m-Positions in methylene compounds	129.8–130.8	12.3	13.5	
m-Positions in methylene compounds	130.8–131.5	7.5	18.4	
Substituted *p*-positions	131.5–134.5	6.2	14.0	32.5

[a] Shifted to 62.5–65.0 ppm due to influence of phenoxide ion.

aromatic ring (158 ppm) is taken as a half from the whole content because of the coincidence of C1 signals for *ortho* substituted rings of ether and *ortho* HM derivative at 156.1 ppm. The resolved signals for *meta* carbons in *para* substituted rings of *o,p′*-dimethylene ether (130.8 ppm) and *p,p′*-dimethylene ether (130.5 ppm) are obtained. A number of other signals for *meta* carbons in the region of 129.3–130.5 ppm are seen and can be assigned to different hydroxymethyl and dimethylene ether derivatives.

The stability of unsymmetrical ether as compared to *p,p′*-dimethylene ether is higher and splitting with free aromatic positions to methylene compounds becomes retarded. It follows that the formation of unsymmetrical ether is only kinetically preferred and the rearrangement to symmetrical ethers before splitting is also probable. The main difference from condensation of *p*-HMP only is the appearance of a new possibility of splitting of *p,p′*-dimethylene ether with reactive *para* positions of *o*-HMP. This reduces essentially the prevalence of *o,p′*-methylenes over *p,p′*-methylenes (1.8/1) in the methylene linked final polycondensate.[11]

On the background of changes in the spectrum (Fig. 1), because of the formation of unsymmetrical dimethylene ether, the signals of typical *ortho*- and *para*-bensoquinone equilibrium structures of oxymethylene derivatives are recorded. No hemiformals were found. As expected, *para*-bensoquinones predominate over *ortho*-bensoquinones. The intensities of signals in methylene and C1 regions for bensoquinone structures are comparable (Tables I and II).

Alkali catalyzed condensation of *ortho*- and *para*-hydroxymethylphenols

The used molar ratio of NaOH to phenol (0.1/1) is thought to be suitable to characterize the changes in the condensation mechanism. This amount of NaOH is essentially lower than that of resol PF resins for manufacturing of wood panels (next part). High rate of alkali promoted condensation excludes the experiment with *p*-HMP only for obtaining an oligomer soluble in CD_3OD.

As compared to noncatalytic conditions, the role of dimethylene ether formation in *o*-HMP condensation is insignificant (Table III). It means that direct

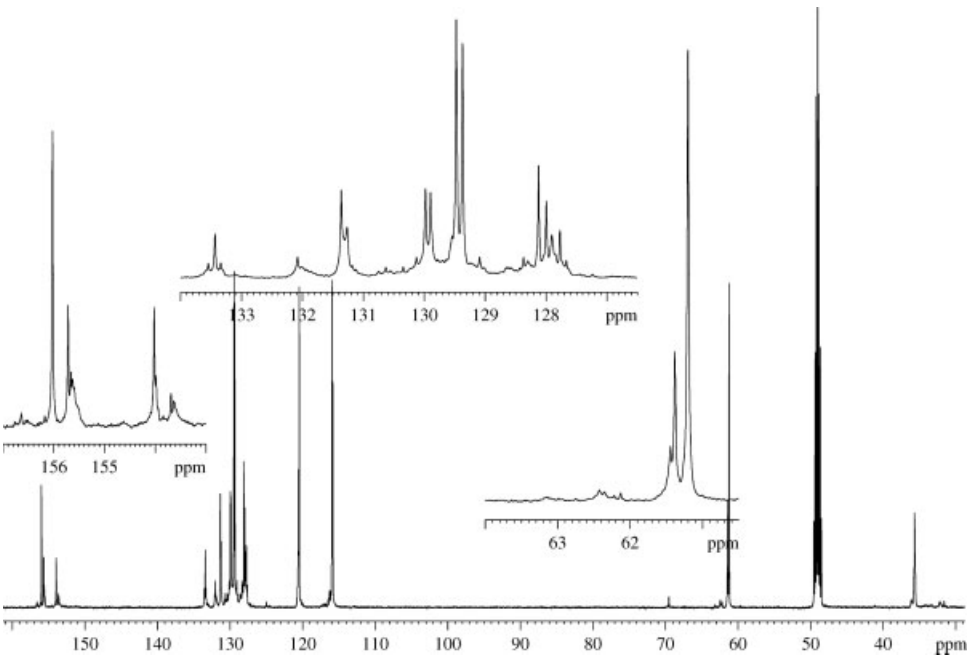
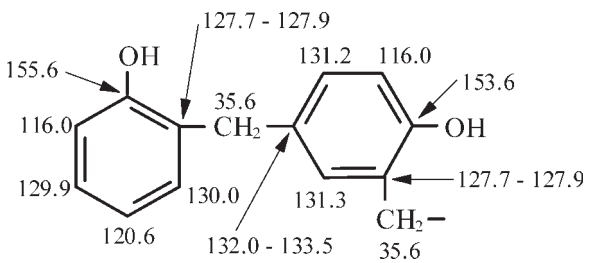


Figure 2 ^{13}C NMR spectrum in CD_3OD of *ortho*-hydroxymethylphenol/NaOH 1/0.1 after condensation in the melt at 120°C for 1 h.

substitution in free aromatic positions of *o*-HMP by methylene groups occurs. Because of preferred influence of alkali on *para* positions, the *o,p′*-methylene linked oligomer is predominant. The quite simple spectrum (Fig. 2) allows to identify this oligomer on the background of unreacted *o*-HMP (ppm): ($C(CH_2)$, 61.2; C1, 156.1; C2, 128.1; C3, 129.4; C4, 120.4; C5, 129.3; C6, 115.9).



The presence of multiple signals shows that a mixture of different oligomers is formed. It follows from the content of methylene groups and *ortho* HM groups in oligomer (Table III) that the oligomer with three aromatic rings is statistically more probable. The constitutions of polycondensate by methylene and C1 regions (Table III) are in good accordance. Three predominant substitution variants in aromatic ring can be assigned (Fig. 2). C2-6 region suffers a greater content of free aromatic *ortho* and *para* carbons as compared to substituted carbons, but the whole amount of *meta* carbons with resolved signals for HM and methylene derivatives is remarkable (Fig. 2). The signal of *para* carbon resolves depending on substituents in neighboring aromatic rings. The influence of alkali in final polycondensate, soluble in pyridine-d_5, is revealed in high excess of *o,p′*-methylenes over *o,o′*-methylenes (9/1).[10]

In the mixture of *o*-HMP/*p*-HMP, *p*-HMP reacts preferably, but the oligomer remains soluble in CD_3OD. At the first approach, it seems that this experiment characterizes mostly *p*-HMP condensation without involving *o*-HMP (Table III). The common feature of systems with *p*-HMP is their great tendency to form *p,p′*-methylenes. In condensation of *p*-HMP, despite the presence of alkali, *p,p′*-dimethylene ether formation is favored. Unlike noncatalytic reaction (Table I), F is released followed by its subsequent reaction with free aromatic *ortho* positions.[10] Otherwise, in the mixture of *o*-HMP/*p*-HMP/NaOH, free *para* position of *o*-HMP causes the preferable formation of *p,p′*-methylene. Growing excess of free aromatic *ortho* positions over *p*-HMV group (initially 3/1) promotes *o,p′*-methylene formation as well. About 40% of free *para* positions remain for the condensation with *ortho* HM groups. It can be calculated that in exhaustion of *para* positions, the formation of *o,o′*-methylenes can amount to 30% of all methylenes.[11] Excluding *o,o′*-methylenes (Table III), only on the level of dihydroxydiphenylmethanes four variants of substitution are possible. It means that *ortho* HM groups are mostly linked to oligomers (~61.4 ppm). Considering also the ^{13}C chemical shifts for *p*-HMP (ppm): ($C(CH_2)$, 65.0; C1, 157.6; C2,6, 116.0;

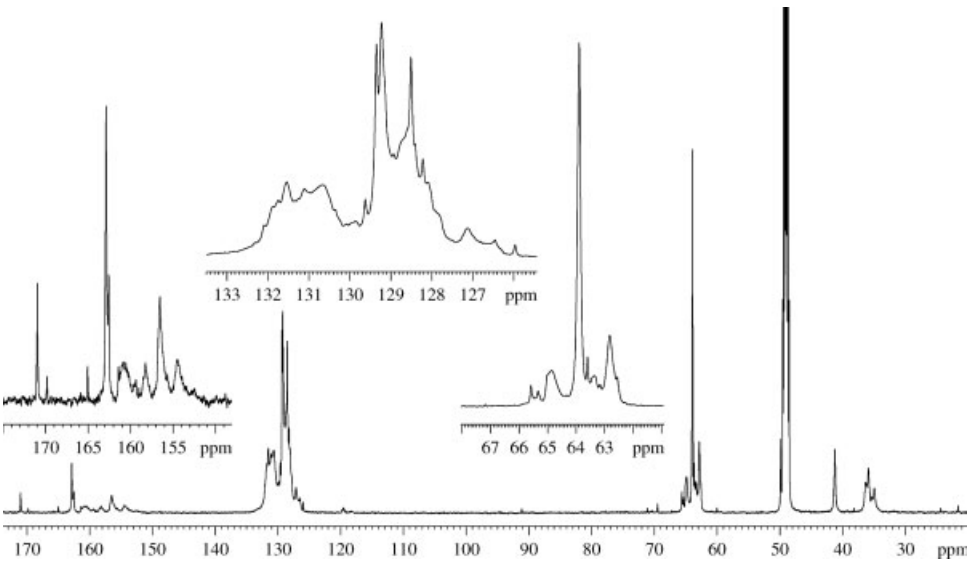
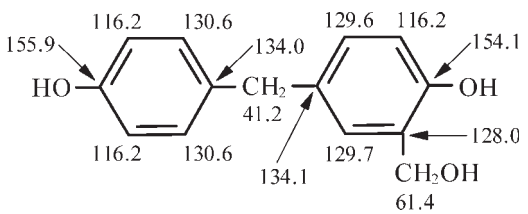


Figure 3 ^{13}C NMR spectrum in CD_3OD of resol phenol-formaldehyde resin.

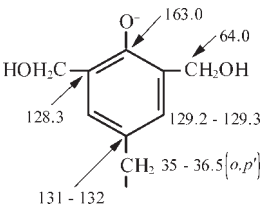
C3,5, 129.8; C4, 133.3), the identification of *p,p′*-methylene compound should be a not very great speculation (ppm):



Structure of resol PF resin

This resin, obtained with high molar excess of F over phenol (2.3) in the presence of a great amount of NaOH (7.8%), is of special constitution (Table III). Because of higher reactivity of *para* functionalities, nearly all aromatic *para* positions are attached to methylenes during resin synthesis. In the methylene formation, only 26% of aromatic *ortho* positions are bound despite their excess. The remaining reactive positions are substituted almost entirely by the *ortho* HM groups. This structure also shows that the high level of hydroxymethylation is obtained without any remarkable role of hemiformals.

The methylene region of the spectrum (Table III) allows to calculate that statistically the structure of the resin corresponds to the tetramer with the determined ratio of *o,p′*- and *p,p′*-methylenes (2/1) and nearly full substitution with *ortho* HM groups. Phenolic hydroxyls are mainly dissociated to phenoxide ions. It is proved by the appearance of new signals of C1 in lower field (e.g., 163 ppm) (Fig. 3), as well by downfield shift of strongly multiple signal of *ortho* HM groups. The most frequent structure can be pictured in the following way (ppm):



The intensities of carbon signals by methylene region and C2-6 region are in good accordance, but shielding effects and overlapping cause quantitative distortions. Despite the fact that the more shielded *ortho* carbons show lower intensity, the typical signal at 128.3 ppm is particularly pronounced in this case due to high content of *ortho* HM groups. The signals of *meta* carbons of aromatic rings are not fully resolved from signals of *para* carbons. The signals at 129.2–129.3 and 130–131 ppm for *meta* carbons appear because of two different substitution models with methylene and HM groups in aromatic rings. C1 signals of those differently substituted undissociated aromatic rings at 156.5 and 154 ppm can be assigned as well.

The described structure predetermines the relatively low curing rate of resin. Any *o,o′*-methylene formation in curing should cause F release. This is not in good accordance with low F emission at manufacturing of wood panels.[8] It was shown in the condensation of *o,o*- and *o,p*-disubstituted HMP that in the absence of other possibilities, the alkaline catalyst promotes the formation of dimethylene ethers among which *o,o′*-ethers are more stable.[13] On the other side, the released F can be scavenged by oxida-

tion. The role of benzoquinones is insignificant, hence the phenoxide equilibrium counter-parts prevail in the presence of alkaline catalyst. It is supposed that the formation of additional methylene groups is not the essential reaction in curing of resol resin.

CONCLUSIONS

1. High tendency of formation of unsymmetrical dihydroxydibenzyl ether (typical oxygen-adjacent methylene signals at 68.4 and 73.0 ppm, respectively) alongside of symmetrical ethers (69.5 and 72.3 ppm, respectively) was ascertained in the noncatalytic cocondensation of *ortho*- and *para*-hydroxymethylphenol in the melt.
2. Splitting of dihydroxydibenzyl ethers with free aromatic positions is the favored reaction route as compared to formaldehyde release from first-formed ethers in the formation of final methylene-attached polycondensates.
3. *Ortho* and *para* substituted oxymethylene derivatives characterized by signals at 66.6–66.8 and 70.8–71.0 ppm in the methylene region and 157.6–158.1 and 159.1–159.9 ppm in the aromatic region of spectra are identified as *ortho*- and *para*-benzoquinone equilibrium structures of oxymethylene intermediate species. Very little role of hemiformals in polycondensation reaction has been established.
4. The mechanism of reaction and structure of resol resin in alkaline conditions are dependent on phenoxide ions, excluding benzoquinone intermediates and promoting the direct formation of methylene linked polycondensates. The structure and curing behavior of commercial resol resins are determined by high content of phenoxide ions of oligomers substituted with *ortho* hydroxymethyl groups.

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