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Structure and curing mechanism of resol phenol–formaldehyde prepolymer resins

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Abstract. Prepolymer resol resins with different phenol/formaldehyde/NaOH molar ratios were synthesized and characterized by technical analysis as well as by ^{13}C NMR spectra for samples in CD_3OD solution. Larger amounts of NaOH promoted the binding of formaldehyde and *para* substitution including the formation of benzoquinone rings with two *o,p'*-methylene groups in the *para* position. The polycondensation between *ortho*-hydroxymethyl groups and one-substituted aromatic *para* positions as the main thermosetting curing process continued in the heat treatment of resol resins. The self-condensation between *ortho*-hydroxymethyl groups, the release and oxidation of formaldehyde, and the formation of hemiformals are processes of low significance in curing resol resins. The assignment of ^{13}C NMR resonances depending on the presence of phenolic hydroxyl groups, phenoxide ions, and substituted quinone rings is discussed.

Key words: polymer chemistry, thermosets, resol resins, ^{13}C NMR, molecular structure, curing mechanism.

INTRODUCTION

The oligomers from alkaline polycondensation between phenol and formaldehyde (PF) are excellent adhesive resins for wood lamination (plywood, oriented strand-board, veneer lumber) [1]. After temperature promoted curing long-term mechanical, thermal, and weather stability of adhesively bonded wood panels is remark-able. The need for a high content of alkali in resin (up to 8.5%) is substantiated by a sufficient pot life and hydro-phility of resin. At the same time it lowers the curing rate of resin at the similar content of hydroxymethyl groups [2], leading to higher pressing time of panels. On the contrary, a resin of enhanced viscosity due to more thorough polycondensation in synthesis has a shorter curing time. For adjusting wetting and avoiding excessive penetration, mineral ($CaCO_3$) and organic (corn, coconut shell, or wood flour) fillers are added [3]. The addition of curing accelerators, such as resorcinolic [2] or alkylresorcinolic resins [4], is also well known.

The method usually applied for the characterization of the chemical structure of PF resins is ^{13}C NMR spectroscopy [e.g. 5]. Dihydroxydibenzyl ethers as the main reaction products were identified only in heat treatment of hydroxymethyl phenols [6]. Their further change to methylene derivatives occurs mainly by split-ting with free aromatic positions [7]. Assignments of ^{13}C chemical shifts in model hydroxymethyl (HM) phenols and dihydroxydiphenylmethanes [6,8] were usually obtained by combining with high-performance liquid chromatography and used for the study of the structure of alkali catalysed resole resins [8,9,10]. The identification of products simplifies as an alkaline poly-condensation excludes the formation of *o,o'*-methylene and dimethylene ether groups [9,10]. Sometimes [5,10] the role of hemiformals in reaction products was emphasized. The general rule is that in an alkaline region a higher pH promotes hydroxymethylation, but at a lower pH polycondensation is favoured [11]. As compared to mono-hydroxymethylation, all further

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reactions occur at higher rates. A great difference is that *ortho*-HM phenol prefers to continue hydroxymethylation, but *para*-HM phenol is very prone to polycondensation [12,13]. Also the hydroxymethylation of dihydroxydiphenylmethanes proceeds at a higher rate in comparison with phenol [14]. The formation of dimers with *p,p′*-methylene in condensation between HM phenols is the reaction occurring at the highest rate in the synthesis of resol resins. The *para* position of *o,o′*-di-HM phenol is the most reactive [9]. Despite an alkaline catalysis and free aromatic *ortho* positions, the self-condensation between *para*-HM groups with release of F proceeds as well [9,12].

Stereosensitivity of aromatic carbons to the chemical environment is not sufficient for quantitative calculations [7]. Most valuable information is obtained from resonances of unsubstituted *ortho* and *para* positions [15]. In case of great excess of F, nearly all reactive aromatic positions are occupied [11].

The broadening of the resonances in the solid-state NMR spectra due to loss of molecular mobility enables only to ascertain that methylene formation (25–50 ppm) is the curing reaction of resols [16]. It is believed that the process of the formation of *o,p′*-methylenes in liquid resins [11] continues also in the solid state [17,18]. In the case of trihydroxymethylphenol [19] or substituted HM phenols [20] the absence of other possibilities promotes the formation of dimethylene ethers including also *o,o′*-ether. Alkali is a good catalyst for F release from all dimethylene ethers [20]. It is not consistent with the very low amount of F emitted in curing resol resins [1] but can be founded with subsequent oxidation of F in alkaline conditions [18].

In any case, there is a contradiction between the absence of unsubstituted *para* positions and the formation of *o,p′*-methylenes in ageing and curing resol resins. Also the F binding depending on the alkali content needs some additional study. Clarification of these problems can improve our understanding of the mechanism of heat promoted curing of resol resins.

EXPERIMENTAL
Synthesis

Industrial grade phenol (P), 43.7–44.2% aqueous solution of formaldehyde (F), and 47.2–47.6% aqueous solution of NaOH were used for the synthesis of resol resins with four different molar ratios of F/P (2.4, 2.2, 2.0, 1.8) at two different NaOH contents (4.5% and 7.0%) in final resins. The amounts of the initial reagents were changed in the following limits:

P	5.17 kg
NaOH solution	1.39–2.94 kg
F solution	6.76–9.04 kg
additional water	1.8–2.71 kg.

Melted P, NaOH solution, and additional water were loaded into a stirred glass reactor (30 L) and cooled to 35–40 °C. The F solution was added slowly maintaining the temperature under 50 °C. After that, the reaction mixture was stirred at 55–65 °C for 1.5 h, then the temperature was raised to boiling and the mixture was refluxed for various times (about 0.5–1 h) depending on the NaOH and F content. The advancement of polycondensation was evaluated by the change in viscosity, and after obtaining its suitable level, the resin was cooled. The final resins and in some cases also the intermediates were characterized by standard methods and ^{13}C NMR spectra.

Analysis

Viscosity was measured by a Höppler-type viscometer at 25 °C and reported in mPa · s. The content of dry solids was determined with 1.0 g of resin on a metal plate as the residue after heating at 105 °C for 3 h. The content of free P was determined after water steam distillation by the bromination method. The content of free F was determined by the hydroxylamine method. Gel time of resin was evaluated with 2 g of resin in the test tube at 100 °C by the time needed for loss of fluidity.

The ^{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$_3$OD solutions with a 5 mm ^{13}C–^{1}H dual probehead. The spectra were accumulated into 32K data points and processed using exponential multiplication with 2 Hz line broadening into 128K spectra. For the resulting spectra 25 000–45 000 scans were accumulated. All spectra were accumulated in identical conditions, using power gated Waltz decoupling with 25 degree 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
Comments on technical characteristics of resins

The amounts of reagents in the synthesis were changed in the limits most probably used in the resins for producing wood panels. Considering also the results of our previous study [11], two more characteristic mass contents of alkali in final resins were chosen (Table 1). It should be noted that as various amounts of F are used the molar ratio of NaOH/P changes causing different catalytic activity of phenoxide ions. It is expressed also in the different pH values of resins. The time necessary for condensation under reflux depends strongly on the NaOH content, which is substantiated by the stabilizing influence of phenoxide ions on the first-formed HM

Table 1. Technical characterization of resol resins synthesized with different amounts of NaOH and formaldehyde

Characteristic	NaOH content, % in resin							
	4.5				7.0			
	NaOH/phenol, mole ratio							
	0.37	0.35	0.33	0.31	0.64	0.59	0.56	0.53
	Formaldehyde/phenol, mole ratio							
	2.4	2.2	2.0	1.8	2.4	2.2	2.0	1.8
Dry solids, 105 °C, 3 h, %	47.4	50.0	50.6	52.7	46.7	47.9	49.1	50.8
pH, 25 °C	10.6	10.4	10.4	10.3	11.6	11.5	11.5	11.4
Viscosity, 25 °C, mPa · s	3944	2151	1996	2109	2235	2904	2457	1927
Gel time, 100 °C, min	13	19	24	27	24	24	30	36
Free formaldehyde, %	1.93	0.48	0.14	0.03	0.1	0.08	0.09	0.05
Free phenol, %	0.12	0.11	0.28	0.85	0.04	0.08	0.18	0.42
Approximate condensation time, min	28	32	35	40	51	55	56	62

compounds (Table 1). This influence strengthens in the case of larger amounts of F.

For better comparison we attempted to synthesize resins with similar viscosity. Only in one case, despite a lower content of dry solids, a somewhat higher viscosity than in other cases was obtained. The reasons were that the same stabilizing effect causes a lower curing rate of resin with a higher content of alkali and the simultaneous decrease in the F amount leads to a resin with an excessively low curing rate evaluated by higher gel time (Table 1).

The content of free P in the resin logically remains greater when F excess decreases. A higher NaOH content improves the bonding of P, especially if its amount is greater. It is seen (Table 1) that alkali is a useful constituent for achieving more complete binding of F in the synthesis. At the same time it is not very easy to understand why the quite high content of free F (1.93%) disappears from the resin when the alkali amount increases. In any case, ^{13}C NMR studies can clarify the problem.

Formaldehyde distribution between functional groups

The assignment of methylene carbon signals occurs in accordance with the previous study [11]. It is useful to calculate also the mole quantities of F bound to different groups as the molar ratio of F/P was changed considerably in the synthesis of resins (Table 2). The structure of polycondensates is mainly determined by the high *para*-activating influence of alkali. This means that *para* substitution is quantitative despite the different F/P molar ratios in the synthesis. Both the *para*-HM group and aromatic *para* position are prone to *p,p′*-methylene formation. A lower amount of F increases the role of *p,p′*-methylenes in the methylene distribution (Table 2). At the same time a higher alkali content improves the F

binding, leading also to a slightly greater amount of *p,p′*-methylenes. So the dimers with *p,p′*-methylene are in great excess. Their formation mostly (more than 80% of the final content) occurs at lower than reflux temperature. The further oligomerization of the dimer can proceed only with the formation of *o,p′*-methylenes as no *o,o′*-methylenes (30–31 ppm) can be detected in resol resins. This means also that every oligomeric molecule can contain no more than one *p,p′*-methylene group. An essential part of the *o,p′*-methylenes (about 40–50% of the final amount) arises also at lower than the reflux temperature, mainly in the reaction between *p,p′*-methylene containing the dimer and the *para*-HM group of HM compounds.

A higher content of alkali increases the amount of *o,p′*-methylenes (Table 2) mainly because of better F binding at a greater excess over P (2.2–2.4). Alkali promotes also the condensation between the *ortho*-HM group and *para* position. Different F/P ratios do not change considerably the part of *o,p′*-methylenes in methylene distribution. This means that the amount of *o,p′*-methylenes decreases at a smaller F excess.

In comparison with mono-hydroxymethylation, the multiple hydroxymethylation of *ortho*-HM phenol or oligomers (dimers) occurs at a higher rate [12–14]. A higher alkali content promotes these reactions and the polycondensation rate is lower (Table 1). A lower content of alkali accelerates the polycondensation of intermediates. The P that did not react in the initial stage has a small chance to take part in further reactions. Actually, the content of free P is low. In the worst case (P/F/NaOH = 1/1.8/0.31) it is up to 2.5% of P, increasing the molar ratio of the reacted F/P to 1.84 (Table 1). Depending on the succession of reactions, *o,p′*-methylene formation can occur with the participation of both HM groups. Due to the favoured exhaustion of the *para* position (over half of *p,p′*-methylene), it can be supposed that *o,p′*-methylene formation proceeds mainly

Table 2. Molar distribution (%) of methylene containing functional groups and some other calculated quantities obtained from the ^{13}C NMR study of resol resins

Assignment	NaOH 4.5%; Mole ratio F/P				NaOH 7.0%; Mole ratio F/Ph			
	2.4	2.2	2.0	1.8	2.4	2.2	2.0	1.8
ortho-CH$_2$OH	57.4	62.2	60.7	57.6	57.3	56.2	56.8	55.5
para-CH$_2$OH	2.3	4.0	4.6	4.7	4.3	4.6	5.1	5.2
p,p'–CH$_2$	10.5	11.4	12.7	14.4	11.3	12.2	12.9	14.3
o,p'–CH$_2$	21.3	20.4	21.4	23.1	25.0	25.4	24.5	24.6
–CH$_2$–O–CH$_2$– (66–75 ppm)	–	–	–	–	1.6	1.2	–	–
CH$_3$–O–CH$_2$OH (91.5 ppm)	8.5	2.0	0.6	0.2	0.5	0.4	0.7	0.3
Occupied Ar positions:	2.96	2.86	2.67	2.47	3.26	3.02	2.73	2.49
• *para*	1.07	1.04	1.03	1.02	1.25	1.20	1.11	1.05
• *ortho*	1.89	1.82	1.64	1.45	2.01	1.82	1.62	1.44
Free Ar-*o*-positions, %	5.5	9.0	18.0	27.5	0	9.0	19.0	28.0
Free Ar-*o*-positions from C2–6, %	0	8.5	19.8	34.5	0.8	12.5	20.3	29.5
Bound FA, in moles	2.20	2.16	1.99	1.796	2.39	2.19	1.99	1.795
• o-CH$_2$OH	1.38	1.37	1.21	1.036	1.375	1.236	1.136	1.001
• p-CH$_2$OH	0.058	0.088	0.096	0.081	0.103	0.101	0.102	0.094
• p,p'–CH$_2$	0.252	0.252	0.254	0.259	0.271	0.268	0.258	0.257
• o,p'–CH$_2$	0.51	0.45	0.43	0.42	0.6	0.56	0.49	0.44
• –CH$_2$–O–CH$_2$–	–	–	–	–	0.038	0.026	–	–
$p,p'/o,p'$–CH$_2$	0.49	0.56	0.59	0.62	0.45	0.48	0.53	0.58
C1 (>158 ppm) from all C1 intensity, %	6.8	9.2	10.3	11.0	39.0	41.2	42.7	49.2
Oxidized F (by the 171 ppm), %	0.28	0.17	0.12	<0.1	0.98	0.90	0.42	0.39

in the condensation of p,p'-methylene containing a dimer with the *para*-HM group of 2,4-di-HM phenol or 2,4,6-tri-HM phenol. A small content of unreacted *para*-HM groups (65.5–66 ppm in Figs 1 and 2) indicates that some amount of oligomers contain only o,p'-methylenes. A large amount of *ortho*-HM groups is accumulated in polycondensates because of the exhaustion of *para* species (Table 2). Their content in methylene distribution is lower in case of larger amounts of alkali due to the increased polycondensation degree. This means also that increasingly more *ortho* positions remain unoccupied when the F excess decreases.

The presence of a higher content of alkali fosters the branching of oligomeric macromolecules. It can be pictured in the following way:
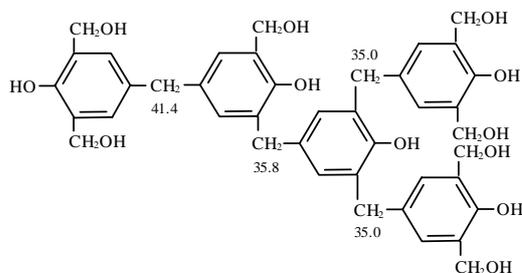
Owing to branching, in the broad signal of o,p'-methylene the relative intensity of resonances at 35.8 ppm diminishes as compared to that at 35.0 ppm. It was more thoroughly discussed in the previous study [11]. The very sharp signal at 41.4 ppm for p,p'-methylene (Figs 1 and 2) logically ensues from structural characteristics and is a good internal standard for the evaluation of changes with other chemical shifts.

It is clear that the chemical shift for the *ortho*-HM group depends on the alkali content (Figs 1 and 2). Obviously it is important whether the substituent of neighbouring C1 is the hydroxyl group or phenoxide ion. The difference of about 0.9 ppm is obtained assuming that the aromatic rings are substituted predominantly with two *ortho*-HM groups. In case of a higher content of alkali (7%), the intensity of the signal at 63.2 ppm increases as compared to that at 64.1 ppm about 1.5 times as the F amount decreases within the studied limits. This is probably connected with the decrease in the alkali/P ratio in this region. At the same time changes due to the partial substitution with *ortho*-HM groups or equilibrium between phenoxide ion and the quinone structure are also possible. An additional resonance at 63.4 ppm with an intensity of about 20% appears as a result of a smaller amount (4.5%) of alkali (Fig. 1). This means that the typical chemical shift for the *ortho*-HM group depends on the equilibrium content of the phenolic hydroxyl group and phenoxide ion. The chemical shift at 64.4 ppm (8% NaOH) supports the conclusion drawn [11].

Evaluation of substitution in aromatic positions

Stereosensitivity of C2–6 aromatic carbon resonances in the region of 115–135 ppm to the chemical environment is evident (Figs 1 and 2) but not sufficient for quantitative characterization because of the overlapping of signals. For several reasons the signal intensity of aromatic carbon is about 70–80% of that for methylene carbon. More valuable information can be obtained from the carbon signals of free *ortho* and *para* positions at 116–119 and 120–122 ppm, respectively. Their quantitative estimation is not quite correct because of the higher intensity due to lower shielding effects as compared to substituted aromatic carbons. The resonances in the region of 116–119 ppm appear in a lower field due to the larger amount of alkali (7%).

Another approach on the basis of the methylene region was also used. It means that the amounts of occupied aromatic positions were calculated by the contents of methylene containing compounds (Table 2). An example is given here for P/F/NaOH 1/2.2/0.35:

Substituted *ortho* positions:
with CH_2OH: $2.2 \times 0.622 = 1.368$
with o,p'–CH_2: $2.2 \times 0.204 = 0.449$
   total   1.817

Substituted *para* positions:
with CH_2OH: $2.2 \times 0.04 = 0.088$
with p,p'–CH_2: $2.2 \times 0.114 \times 2 = 0.504$
with o,p'–CH_2: $2.2 \times 0.204 = 0.449$
   total   1.041

The accordance of the results by two approaches is not bad. Because of the high reactivity of *para* species all aromatic *para* positions were occupied in alkali promoted polycondensation. This is verified by the absence of a signal at 120–122 ppm (Figs 1 and 2). Despite the change in the ratio of F/P, a quite constant amount of F is bound to p,p'-methylene (Table 2). More than half of the *para* positions are occupied with p,p'-methylenes. Alkali promotes also the *ortho* substitution with o,p'-methylenes. A lower amount of F leaves a substantial amount of *ortho* positions unoccupied. Considering the shortcomings of quantitative evaluation, the similarity in the content of free *ortho* positions obtained by the two approaches is quite good (Table 2).

The excess of the occupied *para* positions as compared to theoretical functionality gives some trouble. In the case of a smaller amount of alkali (e.g. P/F/NaOH 1/2.4/0.37) it can be substantiated with different shielding effects of *ortho* and *para* groups in ^{13}C NMR
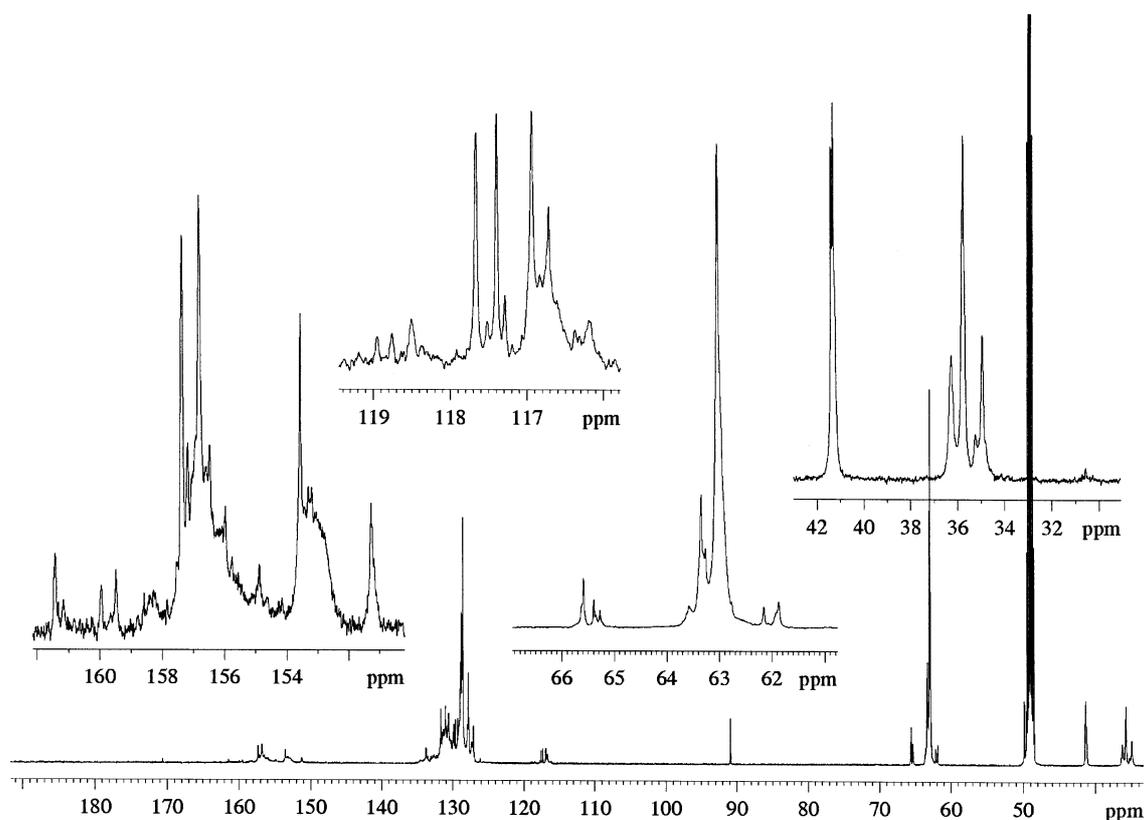

Fig. 1. The ^{13}C NMR spectrum of resin: phenol/formaldehyde/NaOH 1/2.2/0.35 (viscosity 2151 mPa · s; dry solids 50.6%) in CD_3OD solution.
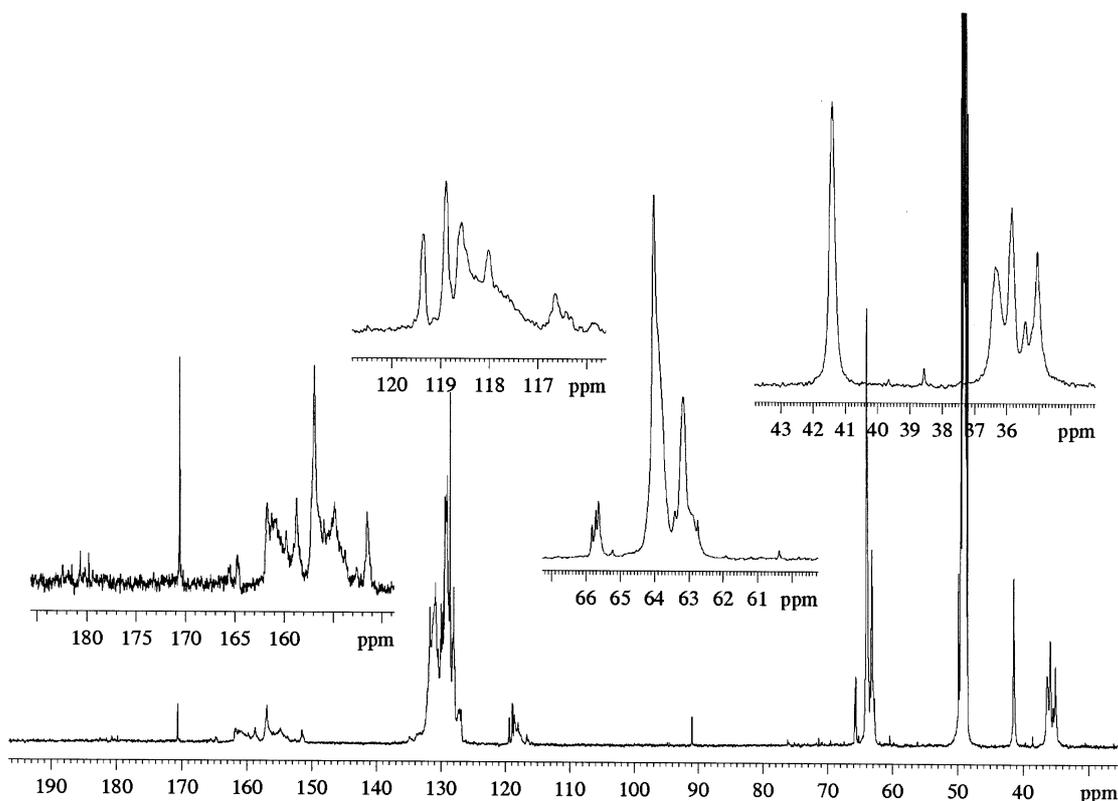
Fig. 2. The ^{13}C NMR spectrum of resin: phenol/formaldehyde/NaOH 1/2.2/0.59 (viscosity 2904 mPa · s; dry solids 47.9%) in CD$_3$OD solution.

analysis (Table 2). This means that the proportion of unoccupied *ortho* positions (about 5%) is an apparent value considering also the absence of resonances at 116–119 ppm. This is in good accordance with the content of free F estimated by a single signal at 91.5 ppm but supported by chemical analysis (Table 1). The value of 1.93% for free F in the resin corresponds to 8.9% of the used amount of F.

Quite an interesting change occurs due to the higher content of alkali (Table 2). The resin with a great F excess (P/F/NaOH 1/2.4/0.64) is most expressive. The substitution over the theoretical value (3) occurs because of the increased substitution in the *para* position. In another case (P/F/NaOH 1/2.2/0.59) the whole substitution is close to theoretical, but an over-substitution in the *para* position (about 20%) is compensated by the presence of free *ortho* positions (12.5% in Fig. 2). The main difference is that the resin contains an essentially lower amount of free F. It is not probable that F is consumed by side reactions as the content of *para*-substituted compounds is unexpectedly high. Usually the signals in the region of 66–75 ppm are interpreted as belonging to dimethylene ethers, but as their content is small it is not very probable (Table 2). It is not purposeful to attach to hemiformal structures as the over-substitution of *para* positions mainly occurs by *o,p′*-methylenes. The

quantity of oxidized F increases in case of a larger amount of F and alkali but if the signal is at 171 ppm, remains under 1% (Table 2). Very often [3] it is supposed that quinoid transition forms are important in P/F polycondensation. An intramolecular stabilization due to H-bonds strengthens the negative charge on the *para* position. It can be presented in the following way:
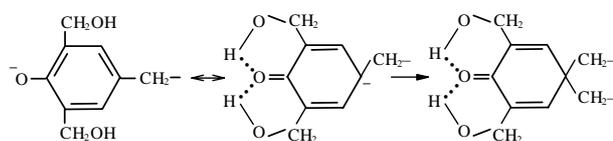
The change of intensities in *o,p′*-methylene resonances due to a higher content of alkali supports this speculation [11]. The intensity at 36.3 ppm (Fig. 2) increases about 30–40% as well. No evidence can be found for the abstraction of hydrogen from *o,p′*-methylene (=CH−) in the formation of quinone. A well-known catalysis mechanism includes the formation of a quinone methide intermediate and subsequent Michael type addition with the formation of a methylene group between aromatic rings [3]. In this case the next substitution in the *para* position with the methylene group substantiates the enhanced functionality in synthesis. The symmetrical substitution with two *o,p′*-methylenes

is the preferred pattern. The structure fragments with p,p'-methylene are left untouched due to stereochemical restrictions. A small content of unreacted *para*-HM groups is consistent with the presence of quinone rings substituted with two o,p'-methylenes. This can happen when the repeated substitution occurs with 2,4- or 2,4,6-substituted HM derivatives. At the same time their low reactivity in polycondensates with the great excess of free *ortho* positions is not fully understandable. The very low tendency to the formation of o,o'-methylenes is verified by their lack in polycondensates consisting of great amounts of *ortho*-HM groups and free *ortho* positions (e.g. P/F 1/1.8) but continuing the polycondensation by the o,p'-methylenes (Table 2).

The appearance of resonances at 180–183 ppm can be evaluated as an additional evidence of the presence of the quinone structure $C1 = 0$ [18]. The resins with increased *para* functionality (1.2–1.25) obtained with a larger amount of alkali contain up to 3% of C1 in the quinone structure (Fig. 2). This content is quite probable considering also the lower intensity of resonances due to the restricted mobility of the group.

Some additional information can be obtained from the region of 150–165 ppm where the resonances of aromatic carbon (C1) bearing the hydroxyl group are found (Figs 1 and 2). The total intensity of the resonances of C1 is about 49–55% of that for methylene carbon. Stereosensitivity of C1 resonances is clear but its interpretation is not very successful due to the complicated patterns of substitution in aromatic rings. The most shielded C1 of in-chain trisubstituted aromatic rings gives the signals in the higher field (151–155 ppm). It can be supposed that the sharp signal at 157 ppm belongs to C1 of end aromatic rings substituted with two *ortho*-HM groups. No change was observed in the decrease of the F amount in synthesis due to the presence of unoccupied aromatic positions. At the same time the C1 region was strongly dependent on the alkali content. Enhanced intensity of resonances downfield from 158 ppm in the case of higher amounts of alkali was most characteristic (Table 2). The different signals mainly in the region of 158–162 ppm (Fig. 2) appeared due to C1 bearing the phenoxide ion.

Curing of resol resins

Polycondensation with the formation of o,p'-methylenes can be regarded as the main reaction in heat curing of resol resins promoted also by high temperature at a lower content of alkali. Despite the analytical problems the solid state NMR study [18] supports this conclusion. In the absence of free aromatic positions analogically to the polycondensation of o,p'-substituted *ortho*-HM phenols alkali can favour the self-condensation of *ortho*-HM derivatives with the formation of o,o'-dimethylene ethers group and subsequent F release from

Table 3. Characterization of resol resins of different degree of polycondensation (8.4% NaOH; pH 12.3; F/P 2.4)

Characteristic	Viscosity, mPa · s		
	410	2240	~20 000
Formaldehyde molar distribution			
• *ortho*-CH$_2$OH	61.1	58.0	56.2
• *para*-CH$_2$OH	3.6	3.7	3.2
• p,p'–CH$_2$	11.3	11.3	11.4
• o,p'–CH$_2$	22.6	25.5	27.4
• –CH$_2$–O–CH$_2$–	0.7	0.9	1.5
• CH$_3$–O–CH$_2$OH	0.7	0.6	0.3
Occupied aromatic positions			
• *ortho*	2.01	2.00	2.02
• *para*	1.11	1.23	1.28
Free aromatic positions from C2–6, %	1.2	0.9	0.5
$p,p'/o,p'$–methylene	0.5	0.44	0.42
Oxidized CH$_2$O (by 171 ppm), %	0.75	0.9	1.0
$C1 = 0$ (by 180–183 ppm), from C1, %	3.5–4	4–4.5	5–5.5

these ethers [20]. This mechanism was not very important in the studied case as a very small amount of F was emitted during resin cure. The amount of F scavenged by oxidation in strong alkaline conditions was also low. The absence of o,o'-methylenes (30–31 ppm) in the presence of a high content of *ortho*-HM groups and free *ortho* positions is an additional verification. The conclusions drawn are supported by changes in the structure of industrial resins [11] in ageing. These resins of quite low viscosity (Table 3) contain usually 61–62% of F preferably in di-*ortho*-HM groups. In thermal ageing to the moment just before gelling the decrease of *ortho*-HM groups approximately corresponds to the increase of o,p'-methylenes. As the *para* positions are occupied, the only possibility is the inclusion of the second o,p'-methylene to the *para* position. The contents of *para*-substituted positions and quinone $C1 = 0$ support the proposed curing mechanism (Table 3). The formation of dimethylene ether and oxidation of F were not very remarkable. If the final *ortho* and *para* functionality were equal, the amount of first-formed p,p'-methylenes would determine the excess of unreacted *ortho*-HM groups. Actually the thermosetting curing process never reaches that level.

CONCLUSIONS

A higher amount of alkali promotes more thorough binding of formaldehyde to the structure of resol resins at a great excess over phenol (2.2–2.4). This phenomenon is substantiated by the enhanced functionality of the *para* position because of the accumulation of the additional negative charge due to the formation of the

quinone structure. Heat curing of resol resin involves mainly the *o,p′*-methylene formation in polycondensation between the *ortho*-hydroxymethyl group and the *para* position substituted previously with one *o,p′*-methylene. The assignment of quinone C1 and a small amount of oxidizied formaldehyde supports the proposed curing mechanism. The proposed curing mechanism is important for understanding the processes in the manufacture of adhesively bonded wood panels.

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Resoolsete fenoolformaldehüüdvaikude analüüs

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On hinnatud resoolitüüpi prepolümeersete vaikude omadusi standardsete määramismeetoditega ja struktuuri ^{13}C NMR spektroskoopia abil. Vaigud on sünteesitud erineva fenooli/formaldehüüdi/NaOH suhtega. Viimase suurem sisaldus soosib formaldehüüdi täielikumat sidumist sünteesil. Iseloomulik on bensokinoonse struktuuriga ringide teke, mis on asendatud paraasendis kahe *o,p′*-metüleenrühmaga. Topeltasendus paraasendis jätkub termoreaktiivse kõvenemisprotsessina vaikude kuumtöötlemisel. Väheoluline on ortohüdroksümetüülrühmade omakondensatsioon, formaldehüüdi eraldumine ja oksüdatsioon ning hemiformaalide teke. ^{13}C keemiliste nihete interpretatsioonil on määrav fenoolsete hüdroksüülrühmade, fenolaatioonide ja asendatud kinoonide esinemine vaikude keemilises struktuuris.