Structure of phenol-formaldehyde polycondensates

Jane Paju[a*], Tõnis Pehk[b], and Peep Christjanson[c]

[a] AS VKG Resins, Järveküla tee 14, 30325 Kohtla-Järve, Estonia
[b] National Institute of Chemical Physics and Biophysics, Akadeemia tee 27, 12618 Tallinn, Estonia; pehk@kbfi.ee
[c] Department of Polymer Materials, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia; peep.christjanson@ttu.ee

Abstract. Prepolymer resol resins with the molar ratio of phenol/formaldehyde 1/2.4 and different amounts of NaOH were synthesized and characterized using ^{13}C NMR spectra for samples in CD$_3$OD solution. Nearly the full substitution in *ortho* and *para* aromatic positions occurred, and quite constant ratios of hydroxymethyl/methylene or $o,p'/p,p'$-methylene groups were obtained. The content of free formaldehyde strongly depends on the NaOH content in synthesis. The prepolymeric chains end mainly with aromatic rings substituted with two *ortho*-hydroxymethyl groups. The alkali-dependent content of phenoxide ions causes the downfield shifts of ^{13}C signals for *ortho*-hydroxymethyl groups from 62.8 ppm to 64.4 ppm and for aromatic carbon bearing the hydroxyl group from 157 ppm to 163 ppm. A comparison with industrial resol resin for the manufacture of plywood is presented.

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

INTRODUCTION

Phenolic resins are the major adhesives in binding wood parts into various composite products, such as panels (plywood, oriented strandboard, fibreboard, waferboard, particleboard), gluelam, and laminated veneer lumber [1]. Their excellent properties include long-term mechanical, thermal, and weather stability. An extension of phenolic raw in the synthesis of adhesive resins partly with resorcinol [2] or oil shale alkylresorcinols [3] of high reactivity for manufacturing gluelam lumber at moderate temperature is also adequate. In the future the greatest attention should be paid to the resins from regenerable raw materials such as lignin and tannin, which have not given products of satisfactory quality up to now [2].

Quite different resin structures can be obtained depending on the molar ratio of phenol to formaldehyde (P/F) and catalyst [4]. The reason is the two-step mechanism where polycondensation in participation of hydroxymethylphenols (HMP) should be regarded as reaction with a new monomer different from initial F. The base-catalysed P/F reaction is more thoroughly studied because of practical importance. The model HMP can be synthesized and identified [5] but also the controlled branched prepolymer formation and final curing at a higher temperature can be used. It is clear that phenoxide ions both from P and HMP catalyse reactions [6]. Their quinoid transition states are shown as intermediate species for proton transfer but on ^{13}C NMR spectra only hydroxymethyl and methylene groups can be assigned [4].

It is generally accepted that direct C-alkylation by HM groups occurs in free *ortho* and *para* aromatic positions under strong alkaline conditions. In the synthesis of resol resins with a high F/P ratio these free aromatic positions can be predominantly in HMP, as well as the HM substituent has strong activating effect on the methylene formation reaction. In reality the F/P molar ratio predetermines the content of HM and methylene groups in resin as practically all aromatic positions are occupied, the amount of dimethylene ethers is very low, and the used F amount exceeds considerably the theoretical amount for full methylene

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formation (methylene/aromatic positions ratio 1.5). The higher reactivity of *para*-species and twofold amount of *ortho*-positions as well lead to a resin with the predominant content of *ortho* HM groups [7]. It has been shown in the condensation of 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 [8]. This reaction should be regarded as the main one in the curing of resol resins under strong alkaline conditions.

It seems at first approach that the mechanism of polycondensation in heat treatment of HMP without catalyst under mild acidic conditions is quite different as the HM group prefers as substrate another HM group despite the great prevalence of free aromatic positions. This phenomenon can be substantiated with the strong tendency of oxymethylene derivatives to exist in equilibrium with quinone methides [4]. For unsymmetrical dihydroxydibenzyl ethers one possibility is depicted in Scheme 1.

Under the conditions described above the quinoidal forms for *para*- and *ortho*-species can be assigned by characteristic chemical shifts in ^{13}C NMR spectra [7]. This stabilizing equilibrium is disturbed by the involvement of free aromatic positions in continuing the heat treatment by the formation of thermally more stable dihydroxydiphenylmethanes. Considering that quinone methides are the resonance hybrids between the quinoid and benzenoid structures, and their high reactivity to electrophiles and nucleophiles, it is evident that the polycondensation mechanism in all catalytic conditions can be explained by their participation. Strong base or acid catalysts promote the formation of active intermediate species and the formation of dihydroxydibenzyl ethers retards subsequent reactions.

Although both wood and resol resin are hydrophilic materials, a permanent wood/adhesive joint is obtained with the support of strong alkaline catalyst (pH over 10). The technological details in the manufacture of e.g. plywood predetermine the content of alkaline catalyst (usually NaOH) in resin but the higher content (7–8%) is usually preferred although it leads to a higher pressing time. Alongside the desired technological para-

meters or properties of products, the reactivity is useful for characterization of the chemical structure of resin. The ^{13}C NMR method suits best for determination of different functional groups derived from F [9,10]. It is more difficult to determine the content of aromatic carbons in different substitution patterns, as the multiple substitution with HM and methylene groups in *ortho*- and *para*-positions prevails [7]. The solid-state ^{13}C NMR analysis has not been very effective for differentiating between *ortho*- and *para*-substituted derivatives in the curing of resins [11,12]. In this study resol resins with different NaOH contents and polycondensation steps were characterized by ^{13}C NMR spectra. The main purpose was to show how NaOH content influences the typical signals in ^{13}C NMR spectra, mostly for HM groups and aromatic C1 carbon bearing the hydroxyl group.

EXPERIMENTAL

Synthesis

Industrial grade P, 45% F aqueous solution, and 47% NaOH aqueous solution were used for the synthesis of resol resins. The same molar ratio of P/F (1/2.4) was used at different P/NaOH ratios: 1/0.3, 1/0.55, 1/0.8. Melted P (5.2 kg), NaOH solution, and additional water were loaded into the stirred glass reactor (30 L) and cooled to 35–40 °C. Formaldehyde solution (8.84 kg) was added slowly, maintaining the temperature under 50 °C. After that, the reaction mixture was stirred at the temperature of 50–60 °C for 1.5 h, then the temperature was raised to boiling, and the mixture was refluxed for various times (about 0.5–1.5 h) depending on NaOH content and desired viscosity. After cooling the resins were characterized by standard methods.

Analysis

Viscosity was measured by a Höppler-type viscometer at 25 °C and reported in mPa · s. Dry solids content was determined with 1.0 g of resin on a metal plate as residue after heating at 105 °C for 3 h. The content of
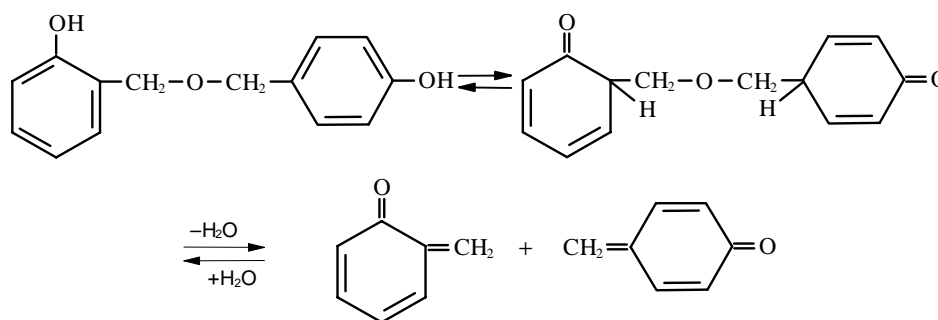
Scheme 1.

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_3OD solutions by 5 mm [13]C–[1]H dual probehead. The spectra were accumulated into 32 K data points and processed using exponential multiplication with a 2 Hz line broadening into 128 K spectra. A total of 10 000–15 000 scans were accumulated for the resulting spectra. All spectra were received in identical conditions, using power gated Waltz decoupling with a 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

General reaction route

The resins were synthesized with three contents of NaOH in the limits which are actually used in the manufacture of resol resins for the production of wood panels [1]. For better comparison the dry solids content of resins was kept quite constant (Table 1). The polycondensation step was changed, so that resins of different viscosity were obtained. The resin of the high content of NaOH (NaOH/P molar ratio 0.8) was similar to industrial resin, only the viscosity was enhanced considerably (Table 1). The polycondensation time depends strongly on alkali content. It is in good accordance with the synthesis of pure HM compounds where alkali is used for restricting their further polycondensation. In the studied limits of alkali the polycondensation time at reflux prolongs about three times. The resin of a higher content of alkali has a lower curing rate, evaluated in technical analysis by a gel time

of resin (Table 1). Logically, the gel time increases in the case of too slight precondensation in resin synthesis. A lower polycondensation rate strengthens the effect. When both factors are joined the rate of curing industrial resins can be excessively low (Table 1).

A high molar ratio of F/P guarantees that resins contain a very low amount of free P, which does not depend on alkali content. As shown below, a common feature of all synthesized resins is that due to the high amount of F, they do not contain any free aromatic positions. The lower content of alkali does not favour the binding of F. This phenomenon is connected with the change in relative rates of hydroxymethylation and polycondensation. It means that all aromatic positions are occupied in binding a lower amount of F. Further polycondensation does not improve remarkably the binding of F. It is not probable that free F combines to resin structure also in curing. Apparently better F binding to polycondensate structure occurs at a higher content of alkali.

The content and assignment of methylene containing functional groups

The well-known assignment of signals allows us to get the molar distribution of functional groups obtained from F (Table 2). Some structural characteristics facilitate the interpretation of results. All synthesized resins do not contain notable contents of free aromatic positions and *o,o'*-methylene groups (30–31 ppm). The structure of resins in the studied limits of alkali content is quite similar and is determined mostly by the same amount of F reacted. Considering also the very low content of other functional groups, the obtained methylene/hydroxymethyl ratio shows that about 7% of F is consumed to side reactions. It means that the resins contain about 2.25 moles of methylene containing functional groups to three aromatic positions. This is not surprising as there are many different reaction possibilities for the very active F and HM groups [4]. The role of side reactions (e.g. Cannizarro reaction) is

Table 1. Technical analysis of resol resins, synthesized with the phenol/formaldehyde molar ratio of 1/2.4 in the presence of different amounts of NaOH

Characteristics	NaOH content, % in resin					
	Low content		Medium content		High content	
	3.6	3.6	6.2	6.2	8.4	8.4–8.7*
Dry solids, 105 °C, 3 h/%	47.6–48.2	47.0–47.5	46.9–47.8	47.6–48.5	45.9–46.2	47.3–48.0
pH, 25 °C	10.1–10.2	10.1–10.2	11.0–11.1	10.9–11.0	12.3–12.5	12.1–12.5
Viscosity 25 °C, mPa · s	664–911	3439–4052	2338–2937	6806–7117	1329–1580	375–426
Gel time 100 °C, min	18–22	13–14	18–19	15–18	24–28	36–42
Free formaldehyde, %	1.48–1.54	2.02–2.11	0.04–0.05	0.04–0.05	0–0.01	0–0.03
Free phenol, %	0.06–0.08	0.08–0.09	0.05–0.07	0.02–0.07	0.04–0.08	0.04–0.06

* Industrial resin for the manufacture of plywood (limits of characteristics of ten batches).

Table 2. Molar distribution (%) of methylene containing functional groups in resol resins with the phenol/formaldehyde molar ratio of 1/2.4 in the presence of different amounts of NaOH

Assignment	Typical signal, ppm	NaOH content, %					
		3.6		6.2		8.4	8.4–8.7
		Low η	High η	Low η	High η		
ortho-CH$_2$OH	62–65	59.4–59.8	56.0–56.2	59.7–60.6	59.0–60.0	56.8–57.2	60.5–61.1
para-CH$_2$OH	65–66	2.5–2.7	2.1–2.3	3.5–3.9	3.7–4.0	3.6–3.9	3.2–3.6
p,p′–CH$_2$	41–41.5	10.0–10.2	9.9–10.0	11.0–11.1	11.0–11.2	11.2–11.8	11.1–11.3
o,p′–CH$_2$	34.5–36.5	17.3–17.6	21.2–21.4	23.3–23.5	23.8–24.1	25.6–26.1	22.2–24.0
–CH$_2$–O–CH$_2$–	69–73	–	1.2	0.7–0.8	0.8–1.0	1.3–2.0	0.7–0.8
–CH$_2$O–CH$_2$OH	79–91	10.1–10.3	9.1–9.4	0.9–1.2	1.2–1.6	0.3	0.3–0.7

η – viscosity.

insignificant at low amounts of NaOH and nearly the full substitution of aromatic positions is obtained at a higher content of free F.

Different NaOH amounts influence the succession of reactions. In case of a lower content of alkali the first-formed monohydroxymethylphenols have a greater tendency to further condensation to diphenylmethane derivatives. The higher content of alkali promotes the formation of dihydroxymethylphenols mainly from *o*-hydroxymethylphenol (*o*-HMP) as *p*-hydroxymethylphenol (*p*-HMP) has a low tendency to further hydroxymethylation in *ortho*-positions [4]. Both further reactions, the hydroxymethylation of dihydroxydiphenylmethanes and polycondensation of dihydroxymethylphenols proceed at a higher rate than that of first-formed compounds [13–15]. This verifies the dependence of the polycondensation rate on alkali content, as well as the similar final structure of synthesized resins (Table 2).

An alkaline catalyst has a strong activating effect on *p,p′*-methylene formation. The presence of a free *para*-position in P or of higher activity of that in *o*-HMP [13] predetermines that this reaction is the most favoured one among all condensation variants. Another preferred condensation occurs between the *para* HM group and free *ortho*-position with the formation of *o,p′*-methylenes. The *ortho*-position in *o*-HMP or dihydroxydiphenylmethanes is more active than *p*-HMP. So, further selfcondensation of *p*-HMP is retarded because

there is also no necessity for the formation of *p,p′*-dimethylene ether groups as supposed in polycondensation of *p*-HMP alone [13,16,17].

Despite high *para*-activating influence of alkali, a quite constant amount (about 4%) of *para* HM groups remains unreacted. This amount is very low in comparison with the accumulation of *ortho* HM groups (about 60%). It supports the conclusion that the presence of *o,o′*-methylenes in alkali-catalysed polycondensation is not probable. It also means that every prepolymer molecule can contain only one *p,p′*-methylene group. The molar distribution of functional groups (Table 2) allows us to calculate that statistically more frequently in the mixture of prepolymers there can be met the tetramer with the determined ratio of *o,p′*- to *p,p′*-methylenes (2/1) and with the predominant substitution with *ortho* HM groups. This structure is depicted in Scheme 2.

This prepolymer molecule contains only *ortho* HM groups. The best way is to suppose that the first-formed dimeric molecules contain mainly *p,p′*-methylenes. Their *ortho*-positions are hydroxymethylated before or after dimerization or there proceeds the reaction with compounds containing *para* HM groups or free *para*-positions. Some amount of *para* HM containing oligomers can form in polycondensation of *para* HM groups with a free *ortho*-position of compounds with a *para* HM group but this reaction is not much favoured [17].
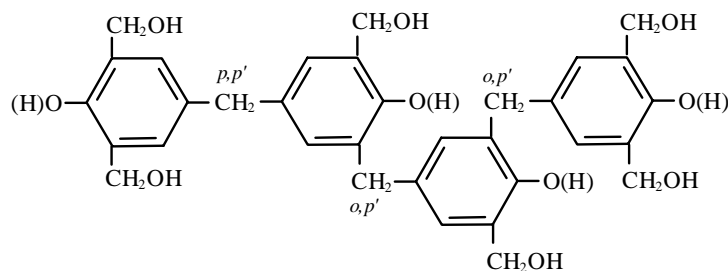
Scheme 2.

It is evident that at a low content of NaOH further polycondensation does not increase the binding of F as all aromatic positions are already occupied. The low content of dimethylene ether groups in resins of a higher polycondensation step may be the result of the beginning of polycondensation between HM groups. The addition of large molecules causes a steep viscosity increase at a small change in the content of functional groups. Some increase in the content of *o,p′*-methylenes can be seen as the result of polycondensation in participation of *ortho* HM groups.

The structure of ^{13}C signals of methylene containing functional groups

The sharpest peak with a quite constant chemical shift at 41.3–41.4 ppm is obtained for *p,p′*-methylene (Figs 1 and 2). Due to symmetrical substitution in diphenyl-methanes and neighbouring free *meta*-positions the chemical shift does not depend essentially on the size of oligomers and other structural characteristics. This signal can be regarded as an internal standard for the evaluation of changes in other signals. The signal for the *para* HM group at 65–66 ppm is surely the multiplet but because of low intensity cannot be used for further assignment.
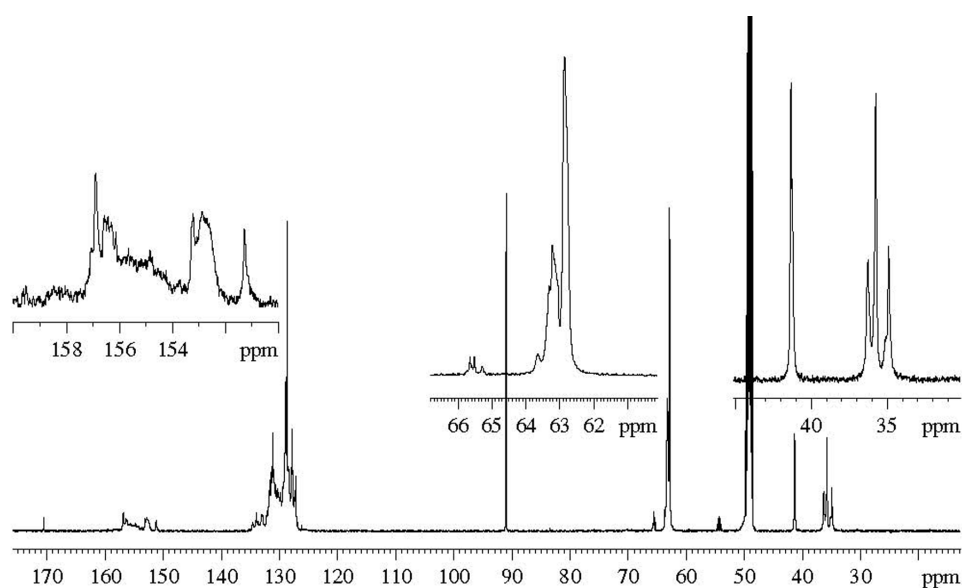

Fig. 1. The ^{13}C NMR spectrum of resin: phenol/formaldehyde/NaOH 1/2.4/0.3 (viscosity 4052 mPa · s; dry solids 47.3%) in CD$_3$OD solution.
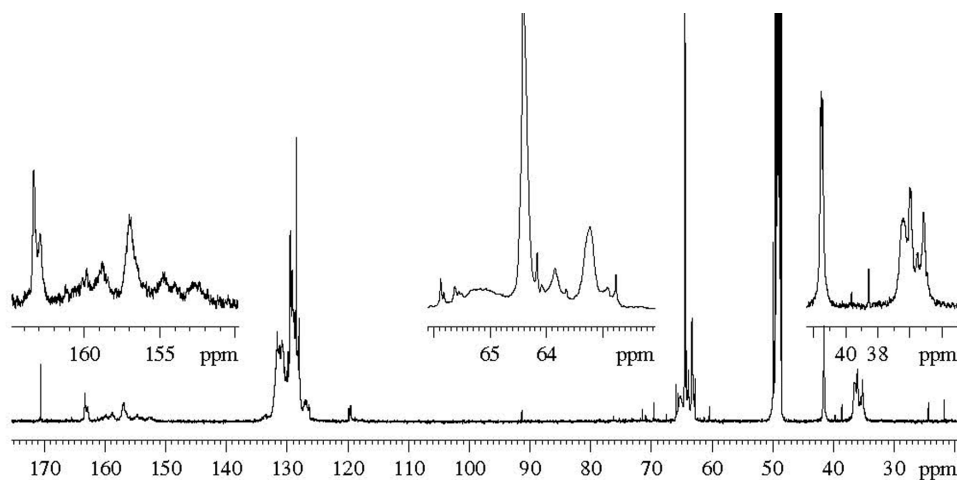

Fig. 2. The ^{13}C NMR spectrum of resin: phenol/formaldehyde/NaOH 1/2.4/0.8 (viscosity 1330 mPa · s; dry solids 45.9%) in CD$_3$OD solution.

More interesting changes occur with the *ortho*-substituted groups. The broad signal in the region of 34.5–37 ppm for *o,p′*-methylene has three well-resolved peaks with quite constant chemical shifts but with different intensities dependent on the substitution pattern and hydroxyl group or phenoxide ion in C1 position (Table 3). The pattern shown in Scheme 2 (35.7–35.9 ppm) is met more frequently. It is well known that alkali promotes multiple hydroxymethyla-tion and branching in oligomers. It means that an inside ring has methylene in the place of the HM group. This influence is quite great because after that two *ortho*-methylenes are in an equal situation (34.9–35.1 ppm) without the effect of the hydrogen bond between hydroxyl and HM groups. The higher role of phenoxide ion causes the shift of the signal to the lower field (36.2–36.3 ppm). To some extent the same phenomenon is in force in the increase in the polycondensation step.

The predominant content of *ortho*-dihydroxymethyl groups causes the high intensity of one peak in the broad signal at 62.5–65 ppm. Disubstitution and oligomeriza-tion shift the signal obtained for *o*-HMP at 61.2 ppm [7] to 62.8 ppm (Table 3, Fig. 1). The influence of the phenoxide ion makes this chemical shift alkali-dependent, extending to 64.4 ppm at a high content of alkali (Fig. 2). It means that HM groups occur mostly in phenoxide ions (molar ratio of NaOH/P up to 0.8). It can be supposed that the signal at 63.2 ppm is typical of the inside HM group of oligomer influenced as well by the neighbouring phenoxide ion.

Assignment of ^{13}C signals of aromatic carbons

Stereosensitivity of C2–6 aromatic carbons in the region of 115–135 ppm depending on the amount, position, and structure of substituents is obvious. This region cannot be used for quantitative characterization because of the

overlapping of the signals and various shielding effects. The carbon signals for free *ortho*- and *para*-positions, respectively at 115–116 and 120–122 ppm, are more valuable. The very low intensity of these signals or even their absence in this case shows that nearly all aromatic *ortho*- and *para*-positions are occupied. It is clear that when moving in the region of 126–135 ppm to a lower field, there appear first the signals for substituted *ortho*-carbons, then those for unsubstituted *meta*-carbons, and finally the signals for substituted *para*-carbons. Theoretically their ratio should be 2/2/1 but in reality this is strongly distorted by various effects.

In case of a low amount of alkali the signals at 127–128 ppm can be assigned to *ortho*-carbons substituted with HM groups (Fig. 1). This is in accordance with the results obtained in the polycondensation of *o*-HMP [7]. Probably the signals of *ortho*-carbons linked to methylenes are shifted to a lower field and are overlapped by signals of *meta*-carbons. Three different substitution patterns influence preferably the signals of *meta*-carbons in the region of 128–132 ppm. The signals of *para*-carbons adjacent mostly to *p,p′*- and *o,p′*-methylenes appear upfield from 135 ppm but their intensity shows that they partly reach the region covered by signals of *meta*-carbons. The high amount of alkali causes greater overlapping of signals due to downfield and upfield shifts of signals, respectively, of *ortho*- and *para*-substituted carbons (Fig 2).

The region of 150–165 ppm where the signals for quaternary aromatic carbon directly bonded to the hydroxyl group are found is more useful (Table 4). As synthesized resol resins have no free *ortho*- and *para*-positions, their hydroxyl-bearing carbons (C1) are strongly shielded by substituents. Of all variants C1 of the chain inside trisubstituted aromatic rings, preferably with three methylene groups in branched chains, should be the most shielded. The signals of that kind of C1 lie

Table 3. Relative intensities of ^{13}C NMR signals of methylene containing functional groups in resol resins with the phenol/formaldehyde molar ratio of 1/2.4

Assignment	Typical signal, ppm	NaOH content, %					
		3.6		6.2		8.4	8.4–8.7
		Low η	High η	Low η	High η		
o,p′–CH$_2$	34.9–35.1	23.6–26.7	27.8–28.8	33.1–33.4	33.6–34.2	35.0–37.9	33.3–34.9
	35.7–35.9	50.8–52.1	44.6–45.1	35.2–35.3	34.4–35.4	23.1–29.1	32.8–33.8
	36.2–36.3	22.5–24.4	26.7–27.1	31.2–31.5	31.1–31.3	34.4–39.0	32.2–33.9
o-CH$_2$OH	62.5–63.0(62.8)[1]	61.7–63.3	58.9–59.1	6.5–7.3	6.7–7.3	5.4–5.6	3.6–4.3
	63.0–63.5(63.2)	37.0–38.3	36.3–37.0	18.0–18.9	18.4–19.2	20.0–20.6	15.5–16.0
	63.5–65.0(64.4)		3.9–4.8	74.6–74.7	74.1–74.3	73.8–74.7	80.2–80.4

[1] In brackets the chemical shift of the main peak; η – viscosity.

Table 4. Assignment of ^{13}C NMR signals of hydroxyl-bearing aromatic carbon in resol resins with the phenol/formaldehyde molar ratio of 1/2.4

Assignment	Typical signal, ppm	Molar distribution, %			
		NaOH content, %			
		3.6	6.2	8.4	8.7
Trisubstituted in-chain rings	151–155	42.3	23.1	21.5	15.3
Trisubstituted end rings	155–158	50.5	31.2	29.3	25.6
Trisubstituted in-chain rings with phenoxide ions	158–162	7.2	24.2	26.0	29.6
Trisubstituted end rings with phenoxide ions	162–164 *		21.5	23.2	29.5

* The main peak at 163.3 ppm.
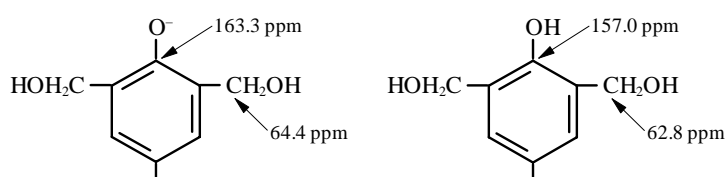
Scheme 3.

in the region of 151–155 ppm. The aromatic end rings of chains are preferably substituted with two *ortho* HM groups and give quite sharp C1 signals at 157 ppm (e.g. Fig. 2). The C1 region is strongly dependent on the alkali content in resins. In any case the signals downfield from the most deshielded C1 signal of P (158.5 ppm) are influenced by phenoxide ions in oligomers. Their amount can reach 60% of all C1 at a high content of alkali (Table 4). Probably most of aromatic end rings of chains are disubstituted with *ortho* HM groups of phenoxide ions. This structure element as compared to unionized form can be identified by two typical signals depicted in Scheme 3.

Certainly, the quantitative constitution (Table 4) is a great approximation. At the same time, a clear coincidence is seen when comparing the results on methylene and C1 regions of spectra. The most essential in the use of alkali is the change of the hydrogen bond in *ortho* HM compounds with the highly nucleophilic phenoxide ion.

CONCLUSIONS

The used molar ratio of phenol/formaldehyde (P/F) gives resins with a very low content of monomers and a similar ratio of hydroxymethyl/methylene groups. On the background of other equal characteristics the advised NaOH content in resin should be in the limits of 6.5–7%. This amount guarantees the optimum curing rate of resin and consumption of F not bound in polycondensate to side reactions.

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Fenooli ja formaldehüüdi reaktsioonil saadud polükondensaatide struktuurist

Jane Paju, Tõnis Pehk ja Peep Christjanson

On uuritud resooli tüüpi prepolümeersete vaikude struktuuri lahustatuna CD_3OD-s ^{13}C NMR-spektroskoopia abil. Vaigud on sünteesitud fenooli ja formaldehüüdi reaktsioonil moolivahekorras 1/2,4, kasutades erinevat hulka NaOH-d (0,3, 0,55 ning 0,8 mooli). On toimunud aromaatsete tuumade täielik orto- ja paraasendus ning saadud sarnane (~2/1) hüdroksümetüül- ning metüleenrühmade moolivahekord eri vaikudes. Vaikude vaba formaldehüüdi sisaldus oleneb leelise kogusest sünteesil. Prepolümeersed ahelad lõpevad peamiselt fenooli tuumadega asendatuna kahe ortohüdroksümetüülrühmaga. Viimaste ja aromaatse tuuma hüdroksüülrühmaga seotud süsiniku ^{13}C-signaalid nihkuvad tingituna fenolaatioonide mõjust madalamasse magnetvälja.