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Fully quantitative carbon-13 NMR characterization of resol phenol–formaldehyde prepolymer resins

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Abstract

Different resol phenol–formaldehyde prepolymer resins have been synthesized with different Formaldehyde/Phenol (F/P) ratios or different catalysts and characterized by ^{13}C NMR spectroscopy in solution. A fast quantitative measuring protocol is proposed based on the use of chromium(III)acetylacetonate as a relaxation agent. APT (attached proton test) and DEPT (distortionless enhancement by polarisation transfer) spectra were acquired to enable proper resonance assignments, especially in the regions with severe signal overlap. Equations are presented in which the methylene bridges (MB), the methylol groups (MG) and the dimethylene ether bridges (DMEB) of resol resins are quantitatively taken into account. Important structural factors determined quantitatively for resol prepolymer resins are the F/P ratio after reaction, the degree of polymerization (n), the number average molecular weight (M_n) and the content of free *ortho* and *para* positions.
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1. Introduction

Phenol–formaldehyde resin, the first fully synthetic polymer, has a wide range of commercial applications in products such as molding compounds, coatings, wood binders and high-temperature polymers with ablative properties [1]. Since subtle variations in reaction conditions have been shown to have a profound effect on the final mechanical properties, the chemistry and molecular structure of phenol–formaldehyde resins have received much attention since their development by Baekeland in 1907 [1,2]. Of utmost importance is the Formaldehyde/Phenol (F/P) ratio as it determines the major classification into novolac and resol resins [1,3]. Resins produced with a molar excess of phenol (F/P < 1) are referred to as novolacs (Fig. 1) and consist of phenol rings connected solely by methylene bridges (MB). They are synthesized by using acidic catalysis in the condensation reaction. Resol resins (Fig. 1) on the other hand are synthesized with a molar excess of formaldehyde (F/P > 1), normally under alkaline conditions. They are characterized by additional dimethylene

ether bridges (DMEB) and remaining methylol groups (MG) in the *ortho* and *para* positions of the phenolic rings.

^{13}C NMR spectroscopy has proven to be the most successful and informative analytical tool to analyse resol resins. As a continuation of our research on novolac resins, for which a fast and fully quantitative measuring protocol was described a few years ago [4], we here present a ^{13}C NMR method to accurately analyse resol structures. Different resol prepolymer resins have been synthesized with different F/P ratios or different catalysts. Based on the use of chromium(III)acetylacetonate as a relaxation agent, fully quantitative ^{13}C NMR spectra were obtained. Equations are presented in which all chemical functionalities are taken into account. Important structural factors determined quantitatively for resol prepolymer resins are the F/P ratio after reaction, the degree of polymerization (n), the number average molecular weight (M_n) and the content of free *ortho* and *para* positions.

2. Experimental section

2.1. Resin synthesis

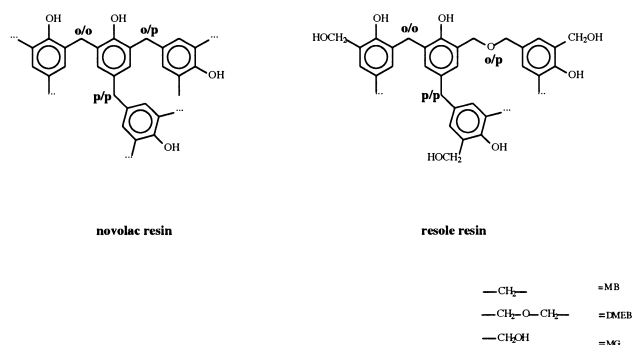Three resol prepolymer resins were prepared with the

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Fig. 1. Chemical structure of novolac and resol resins. Resol prepolymer resins differ from novolac resins in that they contain not only methylene bridges but also reactive methylol groups and dimethylene ether bridges.

same hexamethylenetetramine (HMTA) catalyst but with different F/P ratios: $R1$, $R2$ and $R3$ with F/P ratios of 1.254, 1.097 and 1.003, respectively. Two additional resols, $R4$ and $R5$, were prepared with a fixed F/P ratio of 1.097 but by using NEt_3 or NH_3 as a catalyst, respectively.

All resins were prepared by reacting 1000 g of commercial grade phenol with varying amounts of a 50% formaldehyde solution in addition of the catalyst. The temperature of the reaction mixtures was allowed to rise steadily to l00–102 °C followed by reflux for several hours until the mixture became cloudy. After removal of water under atmospheric pressure, the temperature was raised again to 85 °C. When the desired viscosity was reached the reaction was stopped by cooling and addition of MeOH as a solvent.

2.2. ^{13}C NMR spectroscopy

All solutions were prepared by dissolving 800 mg of prepolymer resin in 800 µl CD$_3$OD (lock and internal chemical shift reference at 49.2 ppm). ^{13}C spectra were recorded at 25 °C on a Varian Unity 400 spectrometer. Spectral parameters used were a spectral width of 21,200 Hz, a 90° pulse width of 7.2 µs, a filter bandwidth of 21,000 Hz, an acquisition time of 0.9 s and 2500 repetitions. To eliminate NOE effects, the decoupler was gated on only during acquisition (inverse gated decoupling), In order to improve the signal-to-noise ratio and simultaneously reduce the analysis time as much as possible, chromium(III)acetylacetonate (20 mM) was added as a paramagnetic relaxation agent to shorten the carbon T_1 decay times. A pulse preparation delay of at least 5 times the longest T_1 was respected.

While Attached Proton Test (APT) spectra were used to discriminate between the protonated and the nonprotonated aromatic carbon resonances, DEPT spectra were acquired to look for the presence of low intensity [5] methine carbons in the region between 50–75 ppm.

3. Results and discussion

3.1. Chemical shift assignment of resol resins

The carbon resonance assignments presented in Table 1 are based on the former study on novolacs [4] and literature [3,6–11]. As shown in Fig. 2, the main difference between ^{13}C NMR spectra of resol and novolac resins are the signals due to the methylol groups (MG, **h**: 58–63 ppm) and dimethylene ether bridges (DMEB, **g**: 65–75 ppm). The spectrum can be divided in four main regions: the highfield regions between 29 and 42 ppm (**m**, **l** and **k**) and between 58 and 75 ppm (**h** and **g**) from the aliphatic methylene carbons, the complex region between 111 and 137 ppm (**e**, **d**, **c** and **b**) due to the aromatic non-phenoxy carbons and the region 148–160 ppm (**a**) from the phenoxy carbons. To achieve more clarity in the region of the substituted (s) and unsubstituted (u) aromatic non-phenoxy carbons (between 111 and 137 ppm), APT spectra were acquired. APT spectra discriminate between protonated and nonprotonated aromatic carbon resonances and enables to define four spectral subregions between 111 and 137 ppm as shown in Table 1 and Fig. 3. The region between 132.2 and 137 ppm can be assigned to the substituted *para* carbons (P$_s$, **b**) while this between 123 and 132.2 ppm to the *meta* and the substituted *ortho* carbons (M + O$_s$, **c**). We were not able to further discriminate between the *meta* carbons (M) and the substituted *ortho* carbons (O$_s$). The region between 118 and 122 ppm contains the unsubstituted *para* carbons (P$_u$, **d**) while the unsubstituted *ortho* carbons (O$_u$, **e**) are situated between 111 and 118 ppm. The resonances at 53–58 ppm (**i**) and 91 ppm (**f**) could be assigned by means of DEPT and in agreement with literature [6] to hemiacetal carbons (Table 1) formed by the addition reaction of formaldehyde and the solvent MeOH. DEPT spectra discriminate between all carbon multiplicities and, as expected, show no aliphatic methine carbons [5] for these resol prepolymer resins. Hemiformals [7] were, as expected, neither found in these

Table 1
Chemical shift assignment of phenol–formaldehyde resol resins in CD$_3$OD

| ^{13}C NMR δ (ppm)	Assignment	Symbol
148–160	Phenoxy carbons	**a**
132.2–137	Substituted *para* carbons (P$_s$)	**b**
123–132.2	*meta* Carbons (M) and substituted *ortho* carbons (O$_s$)	**c**
118–122	Unsubstituted *para* carbons (P$_u$)	**d**
111–118	Unsubstituted *ortho* carbons (O$_u$)	**e**
91	CH$_3$O–**CH$_2$**–OH	**f**
65–75	Dimethylene ether bridges (DMEB)	**g**
58–63	Methylol groups (MG)	**h**
53–58	**CH$_3$**O–CH$_2$–OH	**i**
49.2 and 49.3	Singlet and heptet of MeOH (solvent) and CD$_3$OD	**j**
39–42	*para*/*para* Methylene bridges (MB$_{p/p}$)	**k**
34–36	*para*/*ortho* Methylene bridges (MB$_{p/o}$)	**l**
29–31	*ortho*/*ortho* Methylene bridges (MB$_{o/o}$)	**m**
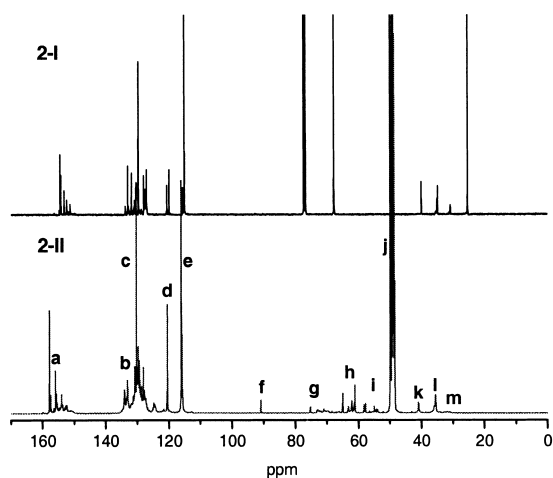
Fig. 2. (a) and (b) Quantitative ^{13}C NMR spectra of (I) a high *ortho* novolac in a mixture of CDCl$_3$ and THF and (II) resol resin R1 in CD$_3$OD. The main difference between the ^{13}C NMR spectra of resol and novolac resins are the signals due to the methylol groups (**h**) and the dimethylene ether bridges (**g**).

resols [12] which is confirmed by the absence of significant resonances in the region between 80 and 90 ppm. So, the described resol prepolymer resins consist solely of phenol rings, methylene bridges (MB), methylol groups (MG) and dimethylene ether bridges (DMEB). An overview of the ^{13}C NMR chemical shift assignments of resol resins is shown in Table 1 and is completely in agreement with literature [3,6–11].

3.2. Optimisation of quantitative NMR characteristics

To obtain fully quantitative ^{13}C NMR spectra, several NMR-factors should be taken into account: the NOE-effect, the signal/noise (S/N) ratio and the long T_1 relaxation times.

Despite several precautions with respect to T_1 relaxation, pulse length, signal-to-noise ratio etc., ^{13}C NMR spectra
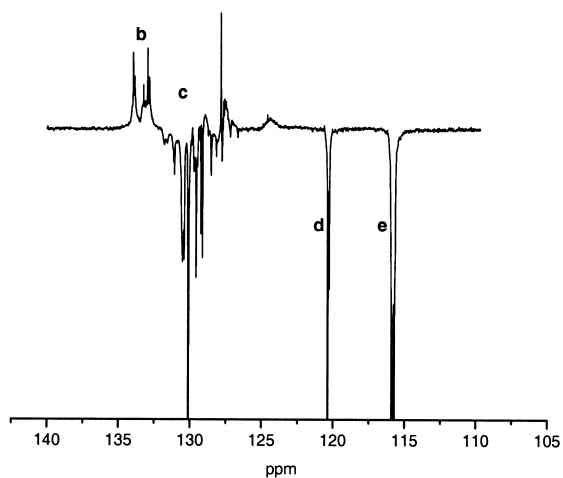

Fig. 3. APT spectrum of the resol prepolymer resin R1 showing the four subregions between 111 and 137 ppm: the substituted *para* carbons (**b**), the *meta* and substituted *ortho* carbons (**c**), the unsubstituted *para* carbons (**d**) and unsubstituted *ortho* carbons (**e**).

acquired under full broad-band proton decoupling are often not quantitative due to unequal NOE's [13]. Even if care is taken to ensure that pulse repetition times are much longer than relaxation decay times, there remains the problem of carbons that receive less than the maximum NOE because they not solely relax by the intramolecular dipole–dipole mechanism [14]. One way to avoid NOE [14] is using the inverse gated decoupling technique in which the decoupler is on during the detection pulse and FID acquisition, but off during the long preparation delay [15]. This however, results in a dramatic loss of sensitivity due to the loss of NOE enhancement and explains why most ^{13}C NMR studies despite make use of the NOE enhancement. Without NOE, quantitative ^{13}C NMR spectroscopy, for which a pulse preparation delay of five times the longest T_1 decay time has to be respected, becomes almost impossible due to the long carbon T_1 decay times. More specific for resols, the longest T_1 decay times are those of the non-protonated aromatic carbons (in the order of 15 s) and result in preparation delays of at least 75 s.

A way to decrease the long T_1 decay times and to avoid NOE (by inverse gated decoupling) is to add a shiftless paramagnetic relaxation reagent like chromium(III)acetyla-cetonate. Because the gyromagnetic ratio of an unpaired electron is 1000 times larger than this of protons, the carbon T_1 relaxation will be rapid, being dominated by the unpaired electron. The addition of chromium(III)acetylacetonate however has to be made cautiously as it also results in line-broadening (decrease of the carbon T_2 decay time). An optimal compromise between spectral characteristics and T_1 relaxation was obtained by adding 20 mM chromium(III)a-cetylacetonate which reduces the longest T_1 decay time to 0.8 s. The proposed procedure allows to obtain fully quantitative spectra by using a preparation delay time of only 4 s and reduces the total acquisition time from 53 h to 3.5 h for 2500 scans. Last but not least, a filter bandwidth equal to the spectral width has to be used in contrast to the standard setting of about half the spectral width.

3.3. Quantitative structural analysis of resol resins

3.3.1. Measure of the degree of quantitativeness

All integration values are expressed per phenolic unit (p.p.u. or/P) by dividing them by 1/6 of the total aromatic intensity. Only for the dimethylene ether bridges, the integration value is further divided by 2 since such a bridge contains two methylene carbons. So, in the following equations, all the different chemical functionalities are expressed per phenolic unit (/P).

The number of unreacted phenolic carbon positions [U], being the sum of the unsubstituted *para* [P$_u$] and unsubstituted *ortho* [O$_u$] positions, can be obtained directly from the quantitative ^{13}C NMR spectra. The number of substituted phenolic positions [S] is the sum of substituted *para* [P$_s$] and substituted *ortho* [O$_s$]. As mentioned before [O$_s$] cannot be obtained directly from the quantitative ^{13}C

NMR spectra because of peak overlap with *meta* (M) carbons. However, [O_s] can be derived from the following Eq. (3), since the number of *meta* carbons per phenolic ring is 2:

$$[U] = [P_u] + [O_u] \qquad (1)$$

$$[S] = [P_s] + [O_s] \qquad (2)$$

$$[O_s] = [M + O_s] - 2 \qquad (3)$$

As reported earlier [4], the accuracy reflecting the quantitative character of the NMR data can be expressed by calculating the deviation of the phenol functionality, d and d' by means of the following equation:

$$d = (3 - 2k - MG/P - [U]) \qquad (4)$$

$$d' = (3 - [U] - [S]) \qquad (5)$$

The functionality of phenol is 3 since only the *para* (P) and *ortho* (O) positions can be substituted. The parameter k is a measure for the amount of bridges per phenolic ring, according to the relation:

$$k = MB/P + DMEB/P \qquad (6)$$

The factor 2 in front of k in equation (4) is needed since k is a measure for the amount of bridges per phenolic ring but each bridge connects two different phenolic rings. So Eq. (4), d, represents a measure of the deviation from quantitativeness when aliphatic and aromatic signal intensities are used from the NMR spectra: the amount of bridges per phenolic ring (multiplied by 2), the amount of methylol groups per phenolic ring and the amount of unreacted phenolic carbon positions are substracted from the ideal functionality, 3, of phenol. Eq. (5), d', on the other hand is based on aromatic signal intensities only. In all equations presented in this paper, cyclic derivates are not taken into account because intramolecular reactions are rather unlikely in bulk polymerizations. Moreover, the molecular size of resol prepolymers in general is rather small. This means that, for non-cyclic prepolymers, k is always smaller than 1 since a bridge always connects two phenolic rings. It can easily be calculated that only for cyclic derivates k can become 1 or even approach the theoretical value of 1.5 bridges per phenolic ring.

Table 2 presents the values of d and d' obtained by applying the proposed carbon-13 NMR measuring protocol. The obtained deviations are smaller than those mentioned in the literature [16,17] and confirm the quantitative character of the NMR method. Included in Table 2 is the the ratio of l/6 of the total aromatic intensity to the intensity of the phenoxy carbons, 1/6[Ar]/[arCON], which also confirms the quantitative character of the NMR spectra.

From Table 2 it is also clear that smaller deviations are obtained by using Eq. (5), indicating that the use of the aromatic region is favoured over the aliphatic region due to the relatively larger intensities of the aromatic resonances.

Table 2
Amount of unsubstituted and substituted ortbo and *para* positions and illustration of the degree of quantitativeness

	[O_U]	[P_U]	[O_S]	[P_S]	d	d'	l/6[Ar]/[Ar$_{COH}$]
$R1$	1.02	0.38	0.97	0.62	0.31	0.01	1.00
$R2$	1.07	0.39	0.92	0.62	0.28	−0.01	1.00
$R3$	1.11	0.40	0.80	0.60	0.28	0.01	1.00
$R4$	0.98	0.24	1.03	0.75	0.23	0.01	1.00
$R5$	1.12	0.44	0.84	0.59	0.44	0.01	0.99

The content of unsubstituted *ortho* [O_U], unsubstituted *para* [P_U] and substituted *para* [P_S] positions per phenolic ring can be obtained directly from the ^{13}C NMR spectra; [O_S] is defined by Eq. (3); d and d' are defined by Eqs. (4) and (5) and l/6 [Ar]/[arCON] is the ratio of one-sixth of the total aromatic carbons intensity to the phenolic carbon intensity.

3.3.2. Formaldehyde/phenol (F/P) ratio after reaction

The F/P ratio is a measure of the amount of formaldehyde units per phenolic unit (p.p.u. or/P) build into the chemical structure of phenol formaldehyde resins. For novolac resins in which only methylene bridges (MB) appear between the phenol rings, the F/P ratio is indicative of the number of MB per phenolic unit which of course is a direct measure of the number of linkages p.p.u. In resol resins, not only methylene bridges (MB) but also dimethylene ether bridges (DMEB) and methylol groups (MG) are present (Fig. 1). Therefore, the F/P ratio for resol resins is considered as the total amount of aliphatic methylene carbons/phenol ring which can further be split into the DMEB/P, MG/P and the MB/P ratios, all expressed p.p.u.:

$$F/P = MB/P + 2DMEB/P + MG/P \qquad (7)$$

In this formula, the amount of dimethylene ether bridges per phenolic ring is multiplied by 2, since, each ether bridge contains two methylene units. The F/P ratios are reported in Table 3 for the different resol resins. As expected [1,12], increased initial F_0/P_0 ratios result in increased F/P ratios after reaction, Note that the MG/P and DMEB/P ratios increase, but the MB/P ratio decreases, for increasing F_0/P_0 in the HMTA catalysed reactions ($R1-R3$). Comparison of the different catalysts reveals that the use of NEt$_3$ ($R4$) and

Table 3
The formaldehyde/phenol ratio before and after reaction and the number of methylene bridges, methylol groups and dimethylene ether bridges per phenolic ring

	F_0/P_0	MBP	MGP	DMEB/P	F/P
$R1$ (HMTA)	1.254	0.36	0.34	0.115	0.93
$R2$ (HMTA)	1.097	0.39	0.31	0.08	0.86
$R3$ (HMTA)	1.003	0.40	0.28	0.06	0.80
$R4$ (NEt$_3$)	1.097	0.56	0.37	0.025	0.93
$R5$ (NH$_3$)	1.097	0.33	0.28	0.03	0.66

F_0/P_0 is the formaldehyde/phenol ratio before reaction; F/P is the formaldehyde/phenol ratio after reaction and is defined in Eq. (7); the quantitative amount of the methylene bridges MB/P, the methylol groups MG/P and the dimethylene bridges DMEB/P per phenolic ring are obtained by dividing the respective intensities by one-sixth of the total aromatic intensity.

NH$_3$ (R5) results in a drastic drop in the dimethylene ether bridge (DMEB) content. Also striking are the very high MB/P and MG/P ratios and so high F/P ratio when NEt$_3$ is used as a catalyst. The opposite result is obtained by applying the NH$_3$ catalyst.

3.3.3. Degree of polymerization, n

The degree of polymerization (n) of resol prepolymer resins can be determined by means of the following equations:

$$k = MB/P + DMEB/P \tag{8}$$

$$n = 1/(1 - k) \tag{9}$$

As mentioned before, k is a measure for the number of linkages p.p.u. and has a value between 0 and 1. In contrast to the novolac prepolymer resins, for which the degree of polymerisation can also be determined indirectly from the substituted *ortho* and *para* aromatic resonances [4], Eq. (6) is the only way to obtain k for resol resins. This is because for resol resins remaining free methylol groups (MG) are also substituted on these positions. In earlier literature reports [18] the dimethylene ether bridges (DMEB) were not taken into account. In this work, the MB/P and the DMEB/P are taken into account quantitatively.

Table 4 presents the degree of polymerisation for the different resol resins. It should be noted from Eq. (9), that the error on the degree of polymerisation (n) increases when k approaches unity, causing a decreasing reliability with increasing molecular weight. However, this phenomenon is inherent to all molecular weight determination methods based on end group determination.

3.3.4. Determination of the molecular weight, M$_n$

The number average molecular weight can be calculated by means of the degree of polymerisation according to Eq. (10):

$$M_n = 106(n - 2) + 200 + (MG/P)n30$$
$$+ (DMEB/P)n30 \tag{10}$$

In this equation, additional terms account for the contribution of methylol groups and the dimethylene ether bridges

Table 4
The initial formaldehyde/phenol ratio F$_0$/P$_0$ and NMR-based results for the different resol resins

	F$_0$/P$_0$	k	n	M$_n$
R1 (HMTA)	1.254	0.48	1.92	218
R2 (HMTA)	1.097	0.47	1.89	210
R3 (HMTA)	1.003	0.46	1.85	203
R4 (NEt$_3$)	1.097	0.59	2.44	276
R5 (NH$_3$)	1.097	0.36	1.56	168

The quantitative value of k (measure for the amount of bridges p.p.u.), defined by Eq. (6); the degree of polymerisation n, defined by Eq. (9) and the number average molecular weight M$_n$, defined by Eq. (10).

on the molecular weight. This is in contrast to earlier literature reports [18] in which the contribution of the dimethylene ether bridges was neglected. Our quantitative measuring protocol makes it possible to take into account the methylene bridges, as well as the methylol groups and dimethylene ether bridges.

The number average molecular weights are reported in Table 4. As expected from the degree of polymerisation (the prepolymer resins consist of about 2 phenolic units), the number average molecular weights are rather small. Since polystyrene-standards definitely lead to an overestimation of the low molecular weights of resol prepolymer resins, it can be considered to use these calculated M$_n$ values for the calibration of GPC experiments on these type of resins. It however, has to be stressed that the proposed method is only absolute if no cyclic structures appear in the formulation.

Table 4 shows that increased initial F$_0$/P$_0$ ratios lead to higher molecular weights. Table 3 shows that the higher molecular weights are due to an increased amount of MG/P and DMEZB/P. Comparison of the different catalysts reveals that higher or lower molecular weights are obtained by using NEt$_3$ (R4) or NH$_3$ (R5), respectively, as compared to HMTA (R2). The large difference in molecular weight between the prepolymer resins synthesized under NEt$_3$ and NH$_3$ catalysis is mainly due to the higher MG/P and MB/P ratios for the NEt$_3$ catalysed reactions. The higher MB/P ratio results in a higher degree of polymerisation n and so in a higher molecular weight.

3.3.5. Determination of the number of unreacted ortho and para positions

Higher amounts of free *para* positions will result in an increase of the reaction rate in the thermal cure reaction of the prepolymers since crosslinks in the *para* position are favoured over *ortho* positions [1]. The number of unreacted *para* [P$_u$] and *ortho* [O$_u$] positions per phenolic ring can easily be obtained by dividing the signal intensity of the unsubstituted *ortho* and *para* aromatic carbons by 1/6 of the signal intensity of the total aromatic region.

The values of [P$_u$] and [O$_u$] were already presented in Table 2 for the different resol prepolymers. For the HMTA catalysed resols (R1–R3), the number of unreacted positions decreases with increasing F$_0$/P$_0$, as a consequence of the higher possibility of hydroxymethyl addition when more formaldehyde is available [19]. Comparison of the different catalysts reveals that the lowest amount of free positions is observed for NEt$_3$ (R4). This can easily be explained by the high MG/P and MB/P ratios. The opposite result is obtained by applying the NH$_3$ (R5) catalyst.

4. Conclusion

A fast and more sensitive ^{13}C NMR quantification protocol is proposed to study the structural characteristics of resol prepolymer resins. The protocol was successfully

tested on resols prepared with different F_0/P_0 ratios and catalysts. Only minor deviations in the quantitative character of the resulting ^{13}C NMR spectra were observed.

Based on such high signal-to-noise, quantitative spectra it becomes possible to analyse the structure of resol resins in more detail and with higher reliability. Equations are presented in which all chemical functionalities are taken into account. Small differences in important structural features, such as the F/P ratio after reaction, the degree of polymerisation (n), the number average molecular weight (M_n) and the content of free *ortho* and *para* positions, can be determined with a high degree of precision.

As a further application, it can be considered to use the number average molecular weight for the calibration of GPC experiments on resole prepolymers. This is of major importance since calibration of GPC with styrene-standards leads to an overestimation of the molecular weights for low molecular weight novolac and resol prepolymer resins.

Acknowledgements

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