Structure of Resorcinol, Phenol, and Furan Resins by MALDI-TOF Mass Spectrometry and ^{13}C NMR

A. Pizzi,[1] H. Pasch,[2] C. Simon,[1] K. Rode[2]

[1]*ENSTIB, University of Nancy 1, 27 Rue du Merle Blanc, F-88000 Epinal, France*
[2]*Deutsche Kunststoff-Institut, Schlossgartenstr. 6, D-64289 Darmstadt, Germany*

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ABSTRACT: The structure of traditional, linear phenol–resorcinol–formaldehyde (PRF) resins, urea-branched PRF resins, and phenol–resorcinol–furfural (PRFuran) resins has been investigated in depth by both matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectroscopy and ^{13}C NMR. The structure of a variety of oligomers has been obtained, and the structures present in each of the three types of resins related to the very different percentages of resorcinol needed for their equal performance as adhesives. The oligomers type and species distribution appeared very different for each case. PRF resins performance is improved by maximizing either the proportion of resorcinol-containing oligomers or methylol-groups containing oligomers, even without any resorcinol, or both. It is equally obtained by the minimization of the relative proportion of the low reactivity Phenol (CH_2 Phenol) species in which resorcinol is not present, this being the most important parameter. This can be obtained by more effective use of the resorcinol by just modifying the resin manufacturing procedure. This parameter instead does not appear to be determinant in PRFuran resins. In these, it is the higher molecular weight of furfural in relation to formaldehyde that engenders for the same manufacturing procedure a correspondingly lower proportion of resorcinol in the resin.
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Key words: adhesives; structure; NMR, MALDI; phenolic resins; furanic resins; resorcinol resins

INTRODUCTION

Phenol–resorcinol–formaldehyde (PRF) resin have been used as cold-set, exterior-grade structural wood adhesives for almost half a century.[1] Phenol–furan and resorcinol–furan resins have been used for equally as long as thermosetting and cold-setting binders for foundry core sand.[1] PRF resins are prepared with a deficiency of formaldehyde and the stable, indefinite shelf-life liquid resin stored. Additional formaldehyde, generally paraformaldehyde powder, is added as hardener only in the glue-mix just before application of the resin as an adhesive. To decrease the dependence of PRF resins on formaldehyde, and hence decrease their potential formaldehyde emission during application, phenol–resorcinol–furan cold-set resins have also been developed.[2] These use furfural, instead of formaldehyde, a slower reacting aldehyde obtained in many parts of the world from abundant agricultural and forestry waste products. In these resins furfural is used as the aldehyde for preparing the polycondensation resin. Formaldehyde is still used later, in the glue mix, as the hardener. These PRFurfural resins have the advantage of (1) a much lower formaldehyde content, hence of lower emission during application; and (2) of a lower resorcinol proportion by weight on resin solids content due to the higher molecular weight of furfural in relation to formaldehyde. Equally, PRF resins, based on prebranching of the resin by small amounts of urea, have been prepared to markedly decrease the content of the expensive resorcinol in the resin while maintaining parity of performance.[1,3] The procedure of preparation of both PRF and PRFuran resins is, in general, very similar, and often is the same.[1–3] Equally, the concept of the decrease of resorcinol content by the use of aldehydes of higher molecular weight than formaldehyde has also been pursued by using other types of aldehyde, for instance, benzaldehyde.

Since its introduction by Karas and Hillenkamp in 1987,[4] Matrix-Assisted Laser Desorption/Ionization (MALDI) mass spectrometry has greatly expanded the use of mass spectrometry towards large molecules, and has revealed itself to be a powerful method for the characterization of both synthetic and natural polymers.[5–12] Fragmentation of analyte molecules upon laser irradiation can be substantially reduced by embedding them in a light absorbing matrix. As a result, intact analyte molecules are desorbed and ionized along with the matrix and can be analyzed in a mass spectrometer. This soft ionization technique is mostly combined with time-of-flight (TOF) mass analysers. TOF-MS has the advantage of being capable to provide a complete mass spectrum per event, for its vir-

Correspondence to: A. Pizzi (pizzi@enstib.uhp-nancy.fr).

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tually unlimited mass range, for the small amount of analyte necessary and the relatively low cost of the equipment.

This article deals with the investigation of the structure of these resins by MALDI-TOF and to the correspondence found between the structures found by this technique with that found by ^{13}C NMR.

EXPERIMENTAL

Resins manufacture

The manufacturing procedure and reagents proportions for the three resins have already been reported, for the commercial PRF resin[1,3] (18% resorcinol on total liquid resin), for the urea-branched PRF resin[3] (11% resorcinol on total liquid resin) and for the PR-Furan resin[2] (13.5% resorcinol on total liquid resin).

MALDI-TOF-MS

The spectra were recorded on a KRATOS Kompact MALDI 4 instrument. The irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm. The length of one laser pulse was 3 ns. The measurements were carried out using the following conditions: polarity-positive, flight path-linear, mass-high (20 kV acceleration voltage), 100–150 pulses per spectrum. The delayed extraction technique was used applying delay times of 200–800 ns.

MALDI-TOF sample preparation

The samples were dissolved in acetone (4 mg/mL). The sample solutions were mixed with an acetone solution (10 mg/mL acetone) of the matrix, as the matrix 2,5-dihydroxy benzoic acid was used. For the enhancement of ion formation LiCl was added to the matrix. The solutions of the sample and the matrix were mixed in equal amounts and 0.5 to 1 μL of the resulting solution were placed on the MALDI target. After evaporation of the solvent the MALDI target was introduced into the spectrometer.

The liquid ^{13}C NMR spectrum of the resins used were obtained on a Brüker MSL 300 FT-NMR spectrometer after addition of a few drops of methanol-d4 for the PRF resin and of D_2O for the PRFuran resin. Chemical shifts were calculated relative to $(CH_3)_3Si(CH_2)_3SO_3Na$ dissolved in D_2O for NMR shifts control.[13] The spectra were done at 62.90 MHz for a number of transients of approximately 1000. All the spectra were run with a relaxation delay of 5 s and chemical shifts were accurate to 1 ppm.

RESULTS AND DISCUSSION

In Table I and Figure 1 are reported the MALDI-TOF fragmentation patterns for a commercial phenol–resorcinol–formaldehyde resin, the parameters of manufacture of which are well known.[1,3] The peak masses were calculated according to the expression $[M^+Li^+]$ = 7(Li) + 94/110 (Phenol/Resorcinol) + 106/122 (P+F/R+F). Table I and Figure 1 indicate the presence of several types of different oligomers, only few of them being of the schematic type R CH_2 (P $CH_2)_n$ R, which is generally used to represent PRF resins. It is interesting to note that only the 345-Da trimer and the pentamer and hexamer at 556 and 669 Da, respectively; hence, only 5% of the resin fall in this cathegory. However, some of the other oligomers containing resorcinol appear to derive from fragmentation of these, such as the dimers at 237 and 249 Da, bringing the relative abundance of these species to 15.1% of the total. Stable, noncharged molecules containing just one resorcinol group are also present such as the 223-Da dimer, the 329-Da trimer, and and the 541-Da pentamer; these type of oligomers total 24% of the resin. These would be expected in this resin and their likely existence already foreseen by calculation.

A considerable number of the resin oligomers is composed of just PF condensates, methylolated or not, without any resorcinol. This is interesting, because the methylolated PF oligomers present can still react with resorcinol during hardening, and hence, partecipate actively to the formation of the hardened network. These oligomers constitute 21.1% of the resin. The nonmethylolated PF oligomers instead are not likely to take part to any great extent in network formation, due to their low reactivity. The latter is the case for the 207, 313, 419, and 525 Da oligomers. They constitute 23.7% of the resin oligomers. Finally, free, unreacted resorcinol and pure RF oligomers (362 Da) constitute, respectively, 11.4 and 4.7 % of the total.

It is easy to see that any improvement in resin effectiveness could come from decreasing the proportion of nonmethylolated pure PF oligomers. This could be achieved either by increasing the proportion of resorcinol in the resin or by lengthening the length of the PF chains to which resorcinol is attached. The first approach is uneconomical, as the trend in the last 50 years has been to maintain these resins performance while markedly decreasing the relative proportion of expensive resorcinol. The second approach will unduly lengthen resin manufacturing times. It has been taken, however, by using the "molecular doubling" or "rapid branching" principle of using a small amount of urea as a brancher for PF and PRF oligomers. This principle has allowed the preparation of PRF resins (called "blue glues" for their characteristic color) of much lower resorcinol content and equal performance.[1,3]

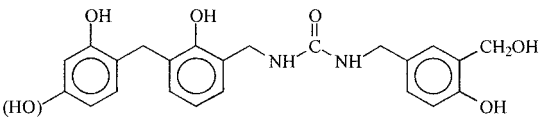
Figure 2 and Table II show the MALDI-TOF results of just this type of urea-branced PRF blue-glue resin.

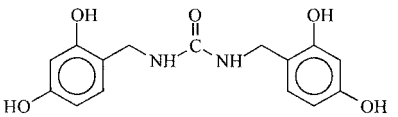
TABLE I
MALDI Fragmentation Peaks for a Commercial Phenol–Resorcinol–Formaldehyde Resin

$M + Li^+$ (exp)	Relative proportion	Unit type			Oligomer type
		Phenol	Resorcinol	Formaldehyde	
Monomers					
117	75	—	1	—	**R**
131	33	1	—	1	P CH_2OH
Dimers					
207	87	2	—	1	P CH_2 P
223	100	1	1	1	P CH_2 **R**
237	37	1	1	2	**R** CH_2 P CH_2^+
249	28	2	—	3	**R** CH_2 P $(CH_2^+)_2$ and $^+CH_2$ **R** CH_2 P CH_2
263	72				$HOCH_2$ P CH_2 P $(CH_2^+)_2$
Trimers					
313	42	3	—	2	P CH_2 P CH_2 P
329	48	2	1	2	P CH_2 P CH_2 **R** and P CH_2 **R** CH_2 P
345	22	1	2	2	**R** CH_2 P CH_2 **R**
362	31	—	3	2	**R** CH_2 R CH_2 **R**
Tetramers					
419	21	4	—	3	P CH_2 P CH_2 P CH_2 P
435	23	4	—	4	P CH_2 P CH_2 P CH_2 P CH_2 OH
450	11	4	—	5	$HOCH_2$ P CH_2 P CH_2 P CH_2 P CH_2 OH
Pentamers					
525	6	5	—	4	P CH_2 P CH_2 P CH_2 P CH_2 P
541	10				P CH_2 P CH_2 P CH_2 P CH_2^+ and P CH_2 P CH_2 P CH_2 P CH_2 **R**
556	6				P CH_2 P CH_2 P CH_2 P CH_2 P CH_2OH and **R** CH_2 P CH_2 P CH_2 P CH_2 **R**
Hexamers					
669	6				**R** CH_2 P CH_2 P CH_2 P CH_2 P CH_2 **R***

The resin has very different molecular characteristics than the standard-type PRF described above (Table III). Comparing the two resins (Table III) the relative proportion of nonmethylolated PF oligomers has been markedly decreased by the different preparation approach in the branched PRF resin. It must be noted that the branched resin contains only 60% of the resorcinol used for the standard PRF,[1,3] and the performance is the same.[1,3] The decrease of the nonmethylolated PF oligomers and the improved effectiveness of the resin has been achieved by (1) the increase of the methylolated PF oligomers; (2) the elimination of pure RF oligomers that partially waste resorcinol, as shown for other type of resins;[14] and (3) the presence of an increased amount of free resorcinol still capable to combine with methylolated PF oligomers during curing. The marked increase of unreacted resorcinol monomer is a necesarry measure to shift total resin DP to lower values. If the free resorcinol was lower, the viscosity of the resin would be too high for use. This principle is already used to good effect in very high molecular weight PF resin "drowned" in urea monomer at the end of their preparation.[15,16]

Table II show other interesting facts. The first the existence of methylolated urea branched PF and PRF oligomers, i.e., the 417- and 431-Da oligomer, and of urea-resorcinol oligomers, i.e., the 313-Da oligomer.





Of note is also the presence in the urea-branched resin of a relatively high proportion of **R** $(CH_2\ P)_n$ CH_2^+ species, 22.5% against 9.5% for a standard PRF resin. This is an indication that MALDI-TOF has broken down part of the urea-branched molecules, as the urea—CH_2— bond is well known to be particularly sensitive and easily cleaved.[1] That this is the case is supported by the total absence of **R** $(CH_2\ P)_n$ CH_2 **urea** CH_2 $(P\ CH_2)_n$ **R** species. This is unusual if it is considered that the equivalent **R** $(CH_2\ P)_n$ CH_2 **R** in the standard PRF resin constitute 15.1% of the total. MALDI-TOF might then be useful as a powerful analytical support technique, but it must be kept in mind that for easily cleaved bonds such as in aminoplastic resins it might also lead to misinterpretation of the result.

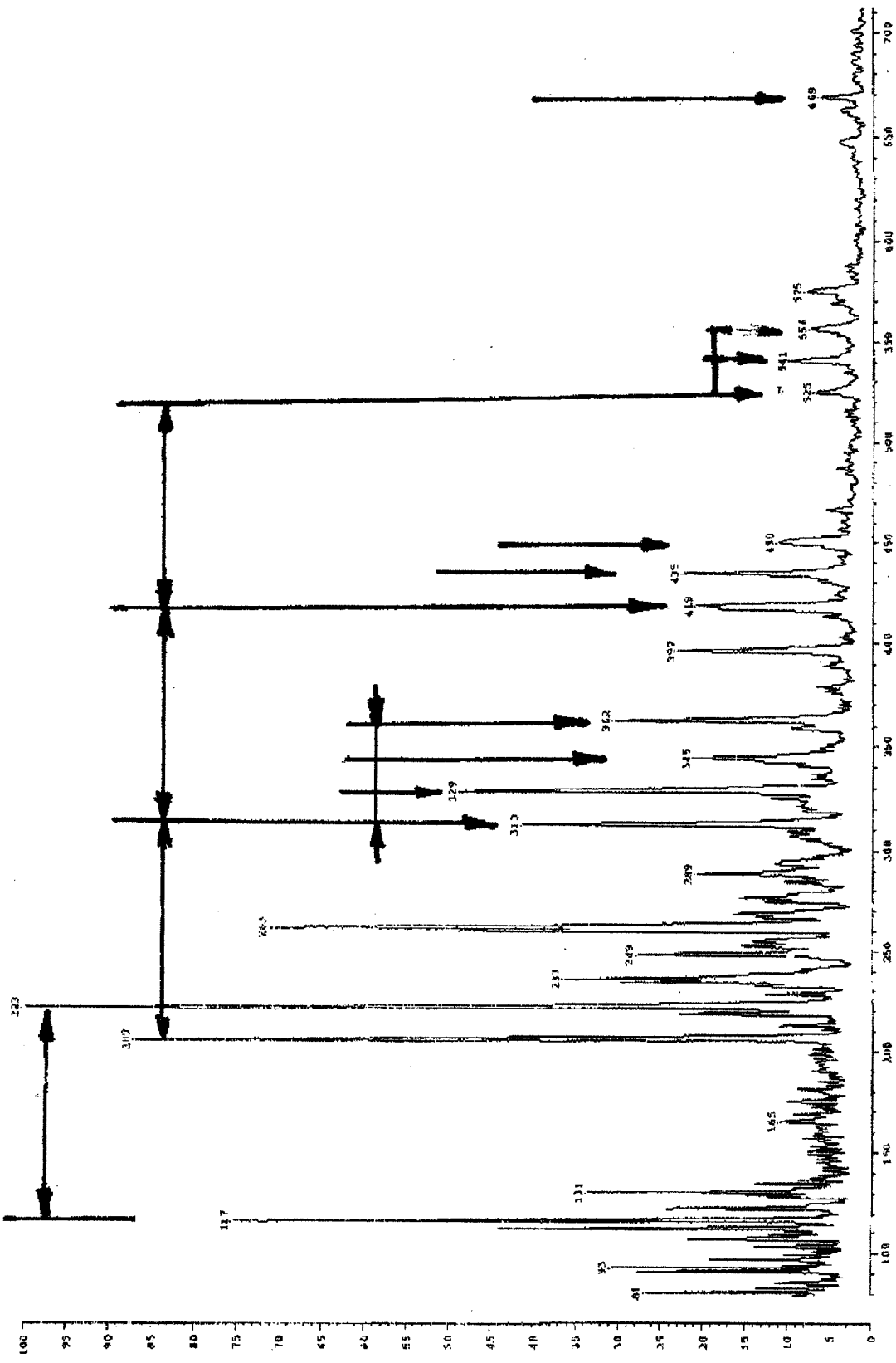


Figure 1 MALDI-TOF mass spectrum of a traditional, linear phenol–resorcinol–formaldehyde (PRF) resin for cold set adhesives. Note the number of 106 Da and 16 Da mass increment steps indicated on the spectrum.

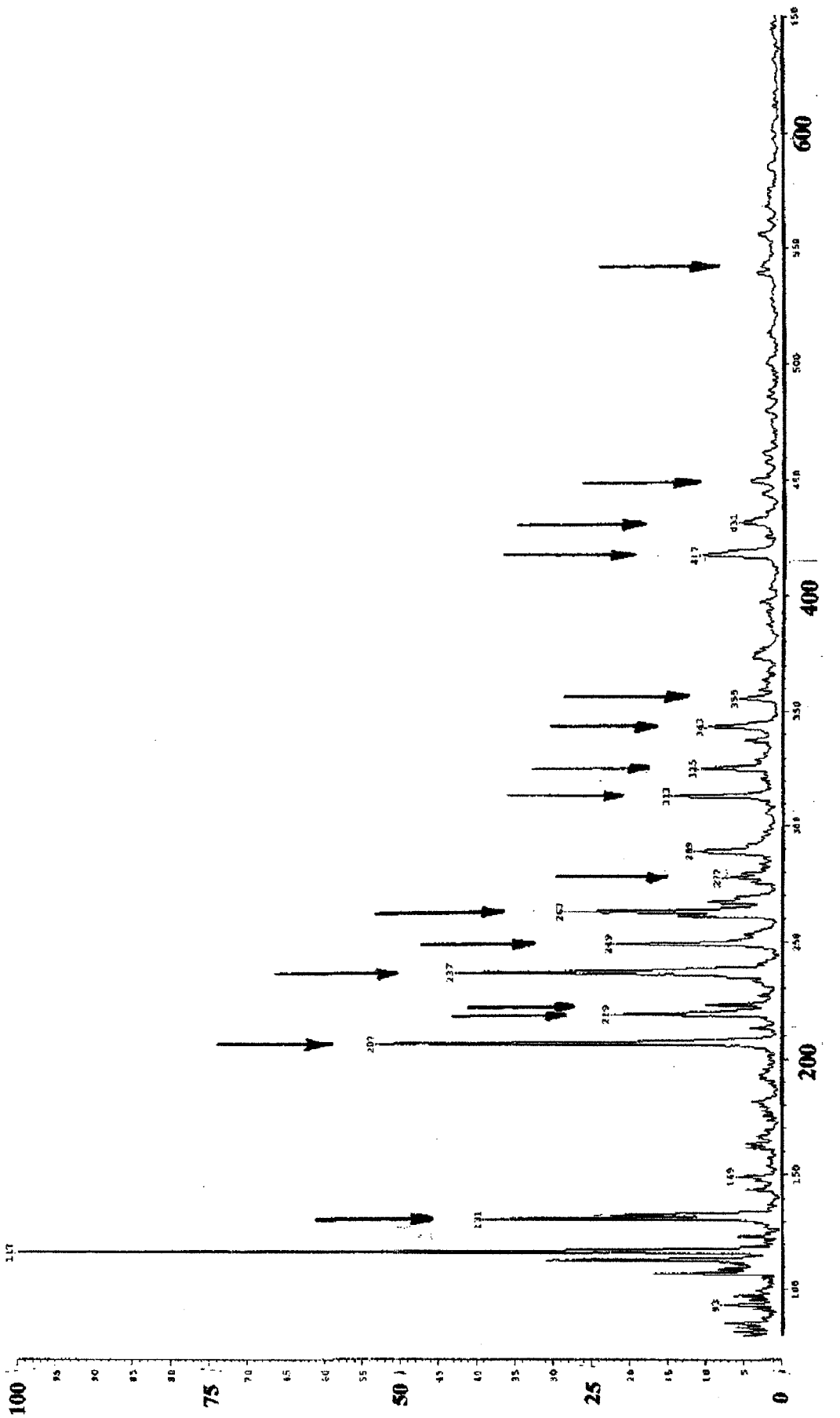


Figure 2 MALDI-TOF mass spectrum of a urea-branched, low resorcinol phenol–resorcinol–formaldehyde (PRF) resin for cold set adhesives. The peaks pattern is indicated by arrows corresponding to what is reported in Table II.

TABLE II
MALDI Fragmentation Peaks for a Urea-Branched "Blue-Glue"-Type Phenol–Resorcinol–Formaldehyde Resin

$M + Li^+$ (exp)	Relative proportion	Unit type: Urea	Phenol	Resorcinol	Formaldehyde	Oligomer type
Monomers						
117	100	—	—	1	—	**R**
131	40	—	1	—	1	P CH_2OH
Dimers						
207	54	—	2	—	1	P CH_2 P
219	23	—	2	—	2	P CH_2 P CH_2^+
223	11	—	1	1	1	P CH_2 **R**
237	43	—	1	1	2	**R** CH_2 P CH_2^+
249	23	—	2	—	3	$HOCH_2$ P CH_2 P CH_2^+ and $^+CH_2$ **R** CH_2 P CH_2^+
		—	1	1	3	
263	30	—	2	—	4	$HOCH_2$ P CH_2 P $(CH_2^+)_2$
Trimers						
277	8	1	2	—	2	P CH_2 **urea** CH_2 P
313	16		3	—	2	P CH_2 P CH_2 P and **R** CH_2 **urea** CH_2 **R**
		1	—	2	2	
325	12	—	3	—	3	P CH_2 P CH_2 P CH_2^+
343	11	—	2	1	3	P CH_2 **R** CH_2 P CH_2^+
355	6	—	2	1	4	$^+CH_2$ P CH_2 **R** CH_2 P CH_2^+
Tetramers						
417	11	1	3	—	4	P CH_2 P CH_2 P CH_2 **urea** CH_2OH and/or P CH_2 P CH_2 **urea** CH_2 P CH_2OH and/or P CH_2 P CH_2 **urea** $(-CH_2OH)$ CH_2 P and/or P $(-CH_2OH)$ CH_2 P CH_2 **urea** CH_2 P
431	6	1	2	1	4	(as 417 but one P substituted by a R) i.e., **R** CH_2 P CH_2 **urea** CH_2 P CH_2OH
450	4	—	4	—	5	$HOCH_2$ P CH_2 P CH_2 P CH_2 P CH_2 OH
Pentamers						
541	2	—	5	—	5	P CH_2 P CH_2 P CH_2 P CH_2 P CH_2^+ and/or P CH_2 P CH_2 P CH_2 P CH_2 **R**
		—	4	1	4	

Figures 3 and Table IV refer instead to the MALDI-TOF analysis of a PRFuran resin. The peak masses were calculated according to the expression $[M^+Li^+]$ = 7(Li) + 94/110 (Phenol/Resorcinol) + 172/188 (P+Furfural/R+Furfural). The absence of Furan–CH_2OH, Furan–CHOH, Furan–CH_2^+, and Furan–CH^+ groups is noticeable in Figure 3 and Tables III and IV.

TABLE III
Relative Proportions by Weight in the Three Different Resorcinol Resins of the Relevant, Different Oligomer Classes Determining Resin Performance

	PRF standard	PRF branched	PRFuran
P unreacted	—	—	2.8
R unreacted	11.4	25.0	6.4
—**R** CF **R** —	4.7	4.0	17.7
R CF (P CF)$_n$**R**	15.1	—	3.8
R CF (P CF)$_n$—	24.0	25.5	10.5
(P CF)$_n$P CH_2^+ and (P CF)$_n$ P CH_2OH	21.1	30.0	—
P (CF P)$_n$	23.7	15.5	58.8

* F = H_2 for formaldehyde resins; F = furan ring for furfural resins.

This is shown by the relative proportions of furanic moieties always being less than those of phenol + resorcinol. This could be due to several factors. First, the furfural can react with itself. This reaction is not very favored under alkaline reaction conditions. Furthermore, there is no trace in Figure 3 of any peaks of furfural polycondensation with itself. Second, it could be that steric hindrance could limit the existence of these groups in phenol–furanic resins. This might be the case of the very ractive resorcinol, but it is definetely not the case for phenol. Finally, and the only acceptable explanation is that the bridges connecting phenols and furan rings are particularly stable: this is know to be the case. This means that the Furan–CH_2OH, Furan–CHOH, Furan–CH_2^+, and Furan–CH^+ species are absent simply because the PRFuran resin cannot be cleaved by MALDI-TOF. This implies that the P—CH_2OH and P—CH_2^+ species present for the two formaldehyde-based PRF resins must originate in part by cleavege during MALDI analysis; otherwise, these groups would not be be present. Again, this supports the fact that MALDI-TOF might lead to some misinterpretation of the results for resins presenting easily cleaved bonds, unless the reactions

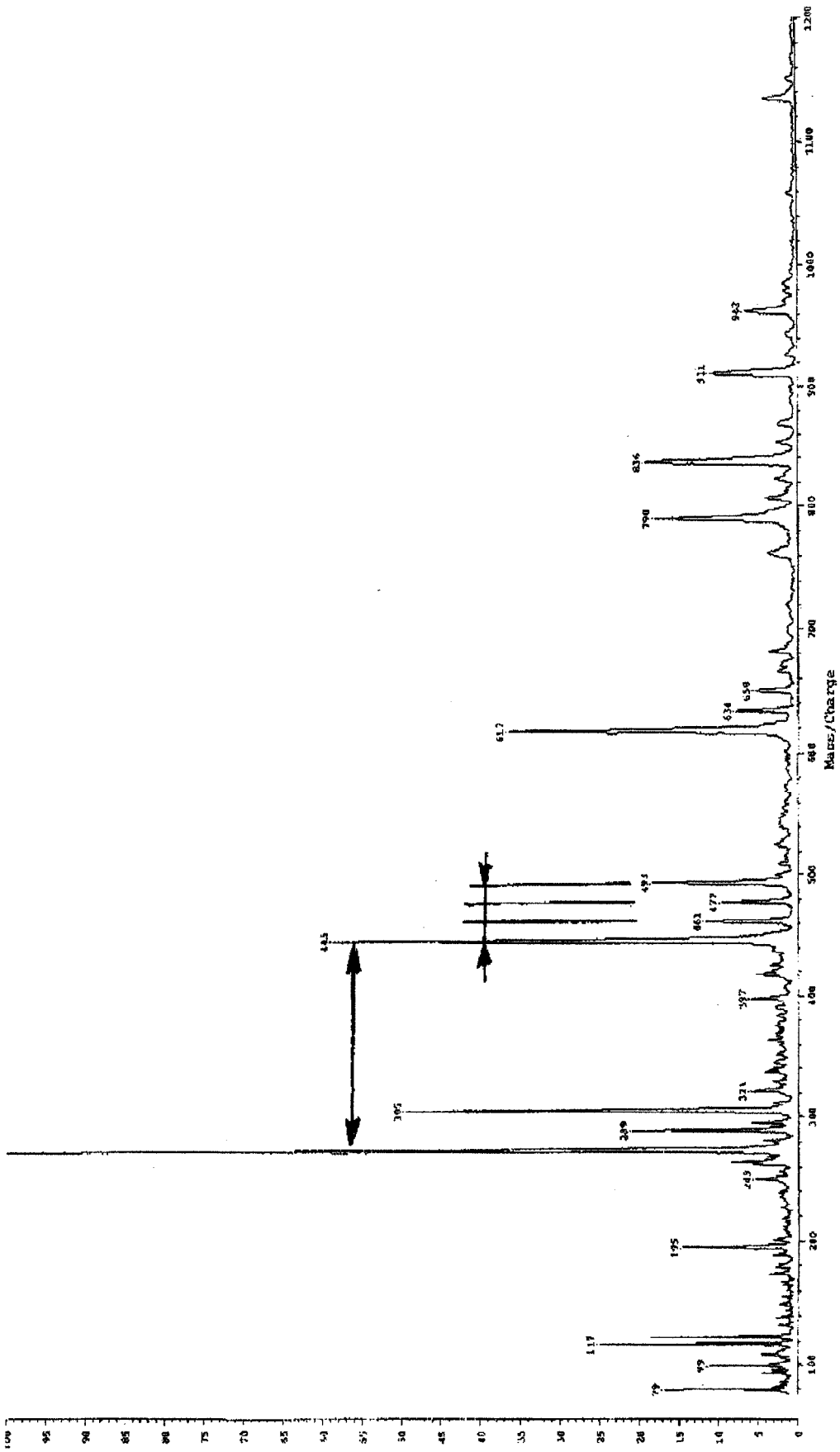


Figure 3 MALDI-TOF mass spectrum of a linear phenol–resorcinol–furfural (PRFuran) resin for cold set adhesives. Note the repeating 172 Da and 16 Da mass increment steps indicated on the spectrum.

TABLE IV
MALDI Fragmentation Peaks a Phenol–Resorcinol–Furan Resin

$M + Li^+$ (exp)	Relative proportion	Unit type			Oligomer type
		Phenol	Resorcinol	Furfural	
Monomers					
99	11	1	—	—	
117	25	—	1	—	
Dimers					
273	100	2	—	1	P F P
289	21	1	1	1	P F **R**
305	50	—	2	1	**R** F **R**
Trimers					
445	60	3	—	2	P F P F P
461	12	2	1	2	P F P F **R** and P F **R** F P
477	10	1	2	2	**R** F P F **R**
493	19	—	3	2	**R** F **R** F **R**
Tetramers					
617	37	4	—	3	P F P F P F P
634	8	3	1	3	P F P F P F **R**
650	5	2	2	3	**R** F P F P F **R**
Pentamers					
790	18	5	—	4	P F P F P F P F P
Hexamers					
962	11	6	—	5	P F P F P F P F P F P
Heptamers					
1134	4	7	—	6	P F P F P F P F P F P F P

P = phenol; F = Furfural; R = Resorcinol.

and their products are already known. This is, of course, not the case, or not completely the case, because P—CH_2OH species are observed also by ^{13}C NMR (62.6, 62.1, and 61.4 ppm, Fig. 4), and thus they are not obtained by cleavage. It must however be the case for the P—CH_2^+.

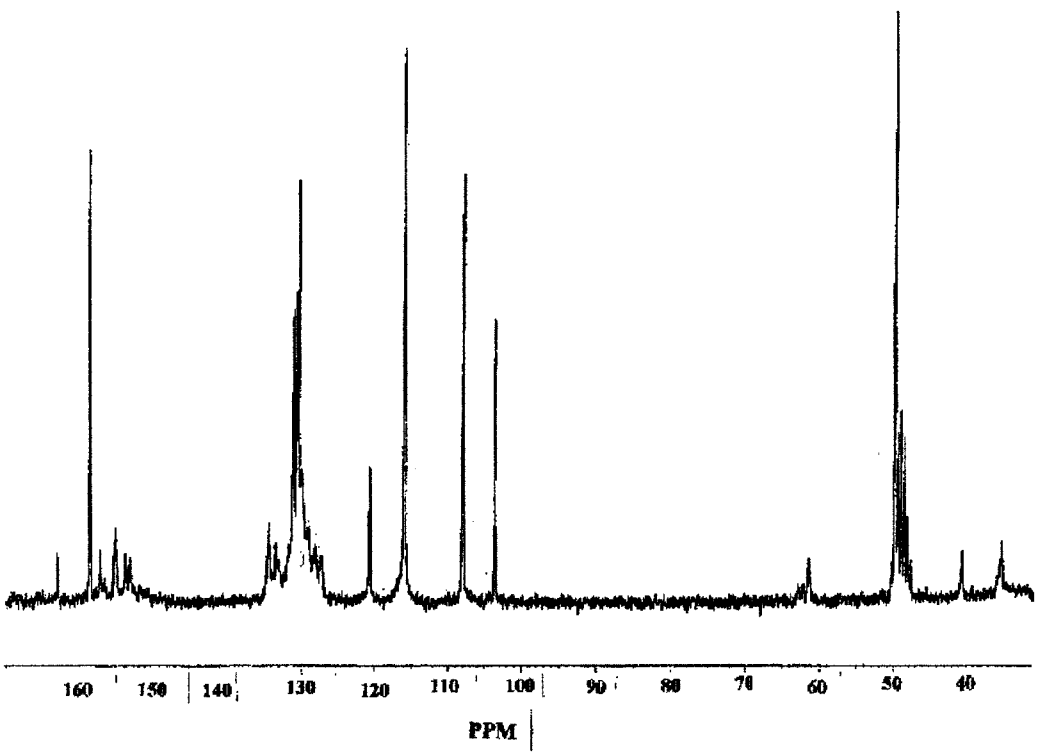
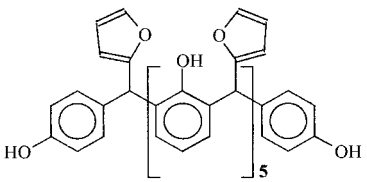
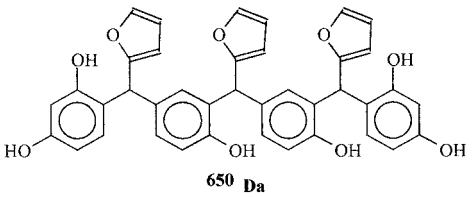


Figure 4 ^{13}C NMR of the urea-branched, low resorcinol phenol–resorcinol–formaldehyde (PRF) resin for cold set adhesives. Same resin shown in Figure 2



The type of PFuran (1134 Da) and PRFuran (650 Da) species present are:

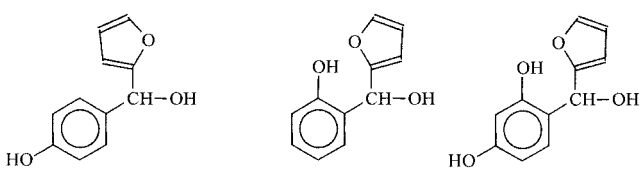


650 Da

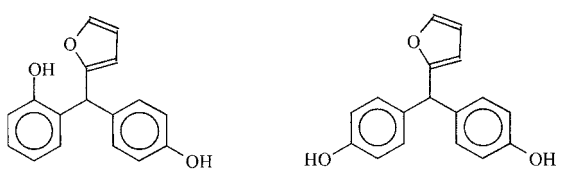
The distribution of oligomers for PRFuran resins shown in Table III is very different to what shown for the two PRF resins. First of all, the relative proportion of all the resorcinol-containing species is lower at 38.4% than the total against the 55.2% and the 54.5% of the two PRF resins. The relative lower proportion of resorcinol on resin solids is due mainly to the higher molecular weight of furfural in relation to formaldehyde. Just this factor would account for 1/3 of resorcinol less by weight on the resin, and hence, 1/3 less by weight of resorcinol containing species in an equivalent PRFuran resin. The decrease observed in Table III is, in fact, of this order of magnitude.

Regarding the same two resins examined by ^{13}C NMR, similar and different information can be gathered. Thus, Figure 4 shows the ^{13}C NMR spectrum of the urea-branched PRF resin, the spectra of the standard PRF being the same except for the signals characteristic of the urea. Thus, only the NMR of the branched PRF is reported. The carbonyl peak of the urea is at 163 ppm, indicating that the urea is all disubstituted. No other urea peak is present. This confirms (1) the urea is present as —CH_2—urea—CH_2— corresponding in Table II to oligomers 313 and 417 Da obtained by MALDI-TOF. The NMR signal, being a single carbonyl one, clearly indicates that the third structure proposed in Table II for the MALDI peak at 417 Da is not correct, as the NMR clearly shows that only disubstituted urea is present. The exclusion of this structure is supported by the absence in the NMR spectrum of the signal (usually at ±67 ppm) for a urea-linked methylol (—CH_2OH) group. The series of peaks between 153 and 158.7 ppm belong to the C1 and C3 of resorcinol. The 158.7 to unsubstituted, unreacted resorcinol and the other to reacted mono- and disubstituted resorcinols confirming the existence of the MALDI identified oligomers presenting peaks at 223, 237, 249, 313, 431, and 541 Da. The two peaks at 131 and 130 ppm correspond to the C5 of resorcinol with and without a substituent on another site of the aromatic ring. The rest of the peaks in the 127.4 to 134.4 ppm range belong to free meta sites and reacted *ortho* and *para* sites of both phenol and resorcinol. The peaks at 120 and 116 ppm belong, respectively, to the unsubstituted *para* and *ortho* sites of phenol. The peak at 106.8 ppm and at 103.6 ppm belong, respectively, the former to unreacted resorcinol C4 and C6 and the latter to the unreacted resorcinol C2 site. The three signals at 62.6, 62.1, and 61.4 ppm are the carbons of the hydroxybenzyl alcohol group (—CH_2OH), the methylol group of the phenol. The signal dominating the solvent at 49.4 ppm is that exactly reported to describe the carbon of the methylene bridge linking a phenolic para site with the amide group of urea.[15,17] The equivalent *ortho* link might also exists, but its signal, if at all present, is drowned in the multitude peaks from the solvent. The signals at 40 and 35 ppm represent the methylene bridges between phenolic nuclei, the former for a o,p —CH_2— link, and the second for a p,p —CH_2— link.

Figure 5 shows the ^{13}C NMR spectrum of the PRFuran resin. The spectrum is more complex than that of the PRF resins. The peak at 184 ppm is either a phenolic quinone or the aldehyde group of some unreacted furfural. The pattern presented is similar to that in Figure 4, but with added the signals at 145.2, 144, and 112.9 ppm, representing, respectively, the furfural unreacted *ortho* site, a furfural *ortho* site linked through a —CH_2— bridge to a phenol, and a second aromatic site on the furfural ring. More interesting are the signals at 74.8 and 65.4 ppm, representing, respectively, the methylenol (—CHF—OH) carbons of the following three structures:



The signals at 58.6, 51.9, and 26.3 ppm belong to sterically crowded —CHF— carbons, the last one belonging to self-polymerized furfural. The peaks at 45 and 40 ppm belong to —CHF— bridges linking two phenols o,p and p,p.



When comparing the results of MALDI and of the NMR analysis it appears that the two techniques are

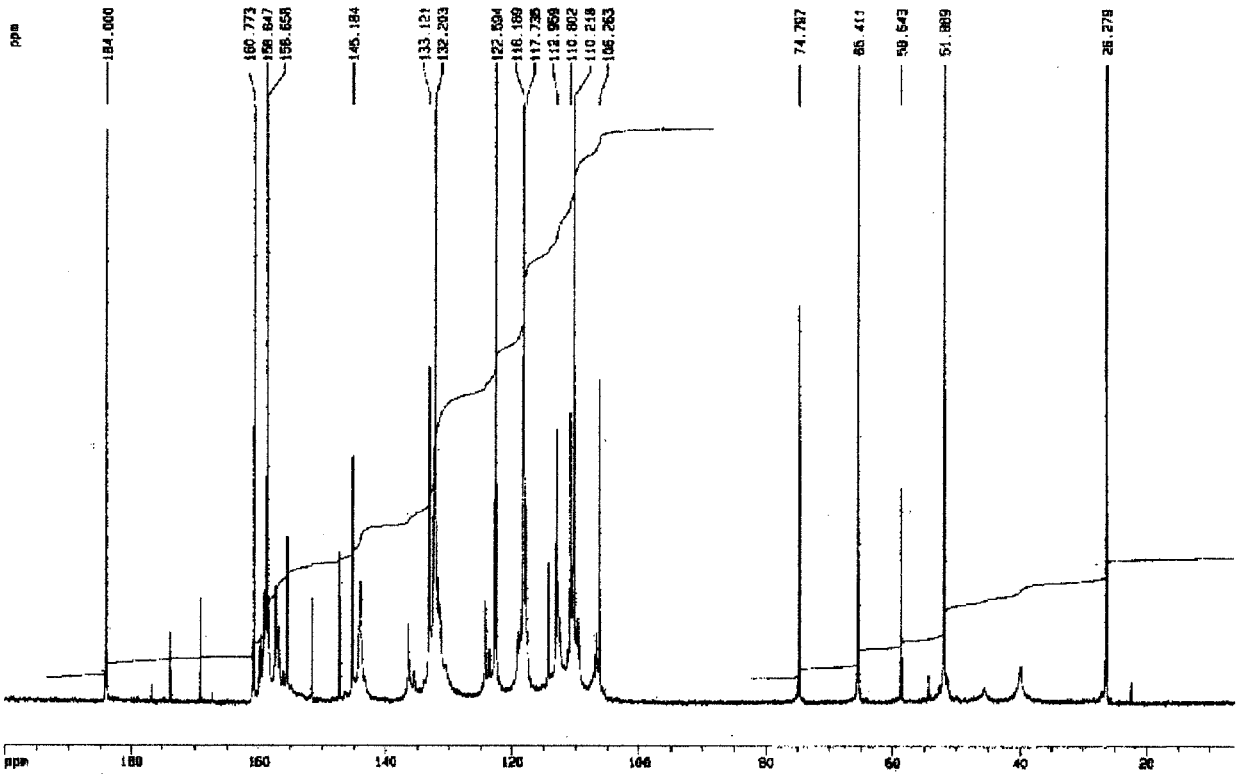


Figure 5 ^{13}C NMR of the urea-branched, low resorcinol phenol–resorcinol–furfural (PRFuran) resin for cold set adhesives. Same resin shown in Figure 3

strongly complementary. MALDI gives the relative distribution of different oligomers, which is not possible to obtain by NMR. The NMR clearly indicates chemical structure features, such as the methylene bridges linking o,p or p,p, or even p,urea, structural information that MALDI cannot yield. There is sometime information given by MALDI that may not be straightforward to interpret. One example is the presence of **R** CH_2 P CH_2^+, and P CH_2 P CH_2^+ species in MALDI, indicating that in branched PRF resins these species appear to be equipment- or conditions-induced decomposition species of —CH_2 P CH_2 **urea** CH_2 P CH_2— species. The NMR analysis appears then to indicate that —CH_2 P CH_2 **urea** CH_2 P CH_2— species are more common than what would appear from MALDI. This is only so because of the very well-known lability of the **urea**—CH_2— link.

In general, however, the two techniques strongly reinforce one another.

CONCLUSIONS

MALDI-TOF mass spectrometry and ^{13}C NMR are complementary rather than mutually exclusive techniques that applied to the determination of the structure of resins yield different information on resin structure. Their combination yields more in-depth information than each technique used alone. In the study of three different types of PRF and PRFuran resins the structural information obtained by combining the two techniques has yielded novel insights on resin structure and why some resins are able to present high performance while the relative proportion of resorcinol is much lower than others.

References

1. Pizzi, A. Advanced Wood Adhesives Technology; Dekker: New York, 1994.
2. Pizzi, A.; Orovan, E.; Cameron, F. A. Holz Roh Werkstoff 1984, 42, 12.
3. Scopelitis, E.; Pizzi, A. J Appl Polym Sci 1993, 47, 351.
4. Karas, M.; Bachmann, D.; Bahr, U.; Hillenkamp, F. Int J Mass Spectrom Ion Proc 1987, 78, 53.
5. Bahr, U.; Deppe, A.; Karas, M.; Hillenkamp, F.; Giessmann, U. Anal Chem 1992, 64, 2866.
6. Ehring, H.; Karas, M.; Hillenkamp, F. Org Mass Spectrom 1992, 27, 472.
7. Danis, P. O.; Karr, D. E.; Mayer, F.; Holle, A.; Watson, C. H. Org Mass Spectrom 1992, 27, 843.
8. Danis, P. O.; Karr, D. E. Org Mass Spectrom 1993, 28, 923.
9. Pasch, H.; Resch, M. GIT Fachz Lab 1996, 40, 90.
10. Pasch, H.; Gores, F. Polymer 1995, 36, 1999.
11. Pasch, H.; Pizzi, A.; Rode, K. Polymer 2001, 42, 7531.
12. Pasch, H.; Pizzi, A. J Appl Polym Sci 2002, 85, 429.
13. Breitmaier, E.; Voelter, W. Carbon-13 NMR Spectroscopy; VCH: Weinheim, 1987, 3rd ed.
14. Prestifilippo, M.; Pizzi, A.; Norback, H.; Lavisci, P. Holz Roh Werkstoff 1996, 54, 393.
15. Zhao, C.; Pizzi, A.; Garnier, S. J Appl Polym Sci 1999, 74, 359.
16. Oldörp, K.; Marutzky, R. Holz Roh Werkstoff 1998, 56, 75.
17. Tomita, B.; Hse, C.-Y. Mokuzai Gakkaishi 1993, 39, 1276.