Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry of Synthetic Polymers. VI. Analysis of Phenol–Urea–Formaldehyde Cocondensates

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ABSTRACT: Phenolic resoles can be regarded as copolymers of phenol and formaldehyde that are distributed in the chain length and the number of methylol groups per molecule. While other spectroscopic methods like FTIR and NMR only give average structures, MALDI–TOF mass spectrometry is able to resolve the oligomer distribution of phenolic resoles. Using 2,5-dihydroxybenzoic acid or 2,4,6-trihydroxyacetophenone as matrices, MALDI–TOF spectra are obtained where each oligomer peak can be assigned to a particular chemical structure. Thus, the degree of polymerization and the number of reactive methylol groups can be determined. For urea-modified resoles, in addition to phenol–formaldehyde and urea–formaldehyde structures, for the first time, phenol–urea–formaldehyde cocondensate structures can be identified directly. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2540–2548, 2003

Key words: MALDI; mass spectrometry; structure; resins

INTRODUCTION

Condensation polymers, such as phenolic resins, are important technical products. Although they are rather low in molar mass, compared to polymerization products, they exhibit a complex polymer structure in many cases. In addition to the molar mass distribution, they may be distributed in chemical compositions, due to the formation of different monomer sequences along the polymer chain. From studies on polycondensation kinetics and the modeling of the individual steps of the synthesis, it is known that resin molecules with different numbers and types of functional groups may be formed. Accordingly, when describing the molecular heterogeneity of condensation polymers, their chemical composition and end-group functionality must be considered in addition to their molar mass distribution.

Using NMR spectroscopy, the average structure of phenolic resins may be determined.[1–3] The lower oligomers may be separated by HPLC.[4–9] A complete picture of the oligomer distribution, however, cannot be obtained by these methods.

For fine-tuning of application properties, phenolic resins are modified frequently with other monomers like urea or melamine. The resulting products can be copolymers of phenol–urea–formaldehyde (PUF) and phenol–melamine–formaldehyde (PMF), accordingly.[10] Up to now, the behavior of urea in such modified resins has not been fully described in the technical literature. There exists a number of investigations on the basis of model substances, which cannot be completely transferred to technical resins.[11–18] There is, however, clear ^{13}C-NMR proof that copolymerization occurs in technical resins[10] and ^{13}C-NMR shifts of different phenol-to-urea methylene bridges which are formed in industrial PUF resins were reported.[10]

The analysis of such complex resins by matrix-assisted laser desorption/ionization mass spectrometry (MALDI–MS) is described in this article. MALDI–MS, introduced by Karas et al.,[19] has greatly expanded the field of mass spectrometry toward large molecules. 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. Being primarily focused on biomolecule analysis,[20,21] this soft ionization technique has emerged as a powerful method for synthetic polymer characterization. For narrow-distributed polymers, fast and accurate determination of absolute molecular weights became possible.[22,23] In addition, information on the repeating units, end groups, polymer additives, and impurities can be obtained.[24,25]

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EXPERIMENTAL

Materials

The phenolic resol sample under investigation is a commercial product of Bakelite AG (Duisburg, Germany). The urea-modified resol sample was prepared according to a technical resin production procedure. One mole of phenol, 2.5 mol of formaldehyde, and 0.07 mol of sodium hydroxide were mixed and reacted at 70°C in a standard laboratory reactor equipped with a stirrer, condenser, and temperature control. After 90 min of precondensation, 0.75 mol of urea was added to the reaction mixture. The total reaction time was 120 min.

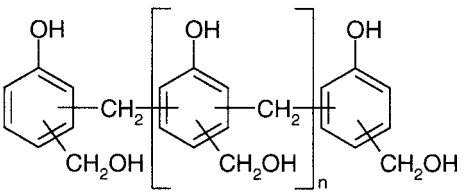
MALDI–MS

The samples were dissolved in acetone or THF (4 mg/mL). 2,5-Dihydroxybenzoic acid (DHB) or 2,4,6-trihydroxyacetophenone (THAP) were used as the matrices. They were dissolved in THF at a concentration of 10 mg/mL. Ten microliters of each solution was taken and mixed. Two microliters of the mixed solution was pipetted onto the sample slide and air-dried.

The samples were measured on a Kratos MALDI Kompact 4 instrument. The spectrometer was equipped with a nitrogen laser (337 nm, 3 ns pulse width) and a time-of-flight (TOF) analyzer. Mass spectra were obtained in the positive reflectron mode with an accelerating voltage of 20 kV. One hundred scans were summed to produce a full spectrum.

RESULTS AND DISCUSSION

Phenolic resols are usually prepared by base-catalyzed polycondensation of phenol and formaldehyde in a molar ratio of 1:1 to 1:3. As a result, polynuclear compounds are formed, where the phenolic units are bound in the polymer chain via methylene bridges (**1**). Every free *ortho*- or *para*-position of the phenolic nuclei can be substituted by formaldehyde, forming hydroxymethyl groups. The different amounts of substitution lead to relatively complex structures:

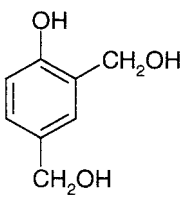


1

Depending on the molar ratio of phenol to formaldehyde, mixtures of species with one, two, three, or more methylol groups are obtained, making the analysis of phenolic resols a difficult task.

The MALDI–MS spectrum of a phenolic resol is presented in Figure 1. Using THAP as the matrix and THF as the solvent, well-resolved mass peaks are obtained, corresponding to the intact $[M + Na]^+$ molecular ions of the respective oligomers.

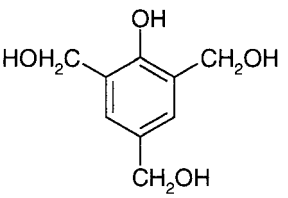
As the primary reaction products, dimethylolphenol (**2**) and trimethylolphenol (**3**) are formed, which produce mass peaks at 177 and 207 Da, respectively. Peaks at 237 and 267 Da indicate that further formaldehyde is added to **4**, yielding hemiformal structures:



2

M = 154 Da

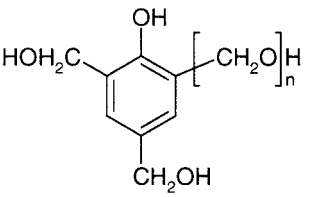
$M + Na^+$ = 177 Da



3

M = 184 Da

$M + Na^+$ = 207 Da



4

M = 214 Da (n=2)

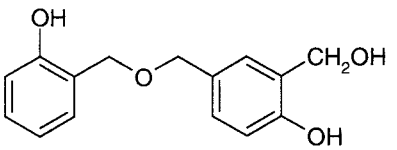
M + Na^+ = 237 Da (n=2)

M = 244 Da (n=3)

M + Na^+ = 267 Da (n=3)

Via condensation, the methylol phenols react with each other or with phenol, forming dinuclear compounds or higher oligomers. The phenolic nuclei can be linked to each other via methylene or dimethylene ether bridges.

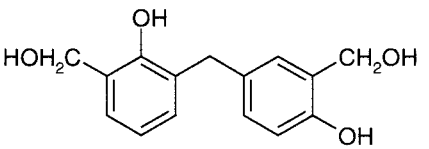
Frequently, oligomers with isobar masses are obtained. These oligomers cannot be unequivocally identified in the MALDI–TOF spectrum. For example, the mass of compound **5a** with a dimethylene ether bridge between the phenols is equal to the mass of compound **5b** with a methylol group. Therefore, it is not possible to assign one single chemical structure to, for example, a peak at 283 Da in the mass spectrum:



5a

M = 260 Da

M + Na^+ = 283 Da



5b

M = 260 Da

M + Na^+ = 283 Da

In general, a phenolic resol can be regarded as a copolymer of the average structure P_XF_Z, X being the number of phenolic nuclei P and Z being the number of incorporated formaldehyde molecules F. Therefore, each peak in the MALDI–TOF spectrum can be assigned to a certain P_XF_Z. The complete assignment of all oligomer peaks in the spectrum is given in Table I.

As was pointed out earlier, for specific applications, phenolic resols are modified with urea or melamine. When a resin is produced from phenol, urea, and formaldehyde, different reaction products can be formed, including phenol–formaldehyde, urea–formaldehyde and PUF oligomers. These oligomers have different chemical compositions and different degrees of polymerization.

The MALDI–MS spectrum of such a resin is presented in Figure 2. In this case, DHB is used as the matrix. As can be seen, the spectrum is very complex and it is complicated, at first glance, to make a proper peak assignment. However, careful inspection of the spectrum reveals a peak order that is characteristic for PUF resins. Peak-to-peak mass increments of 106 and 72 Da are obtained, which are typical for the repeating units of phenol–formaldehyde and urea–formaldehyde resins, respectively. A mass increment of 30 Da indicates the additional attachment of a methylol group.

The mass peaks at 207, 237, and 267 Da and at 253, 283, and 313 Da are typical for phenol–formaldehyde oligomers, while the mass peaks at 83 Da (**6**), 113 Da (**7**), 143 Da (**8**), 155 Da (**9**), 185 Da (**10**), and 215 Da (**11**) indicate urea–formaldehyde oligomers:

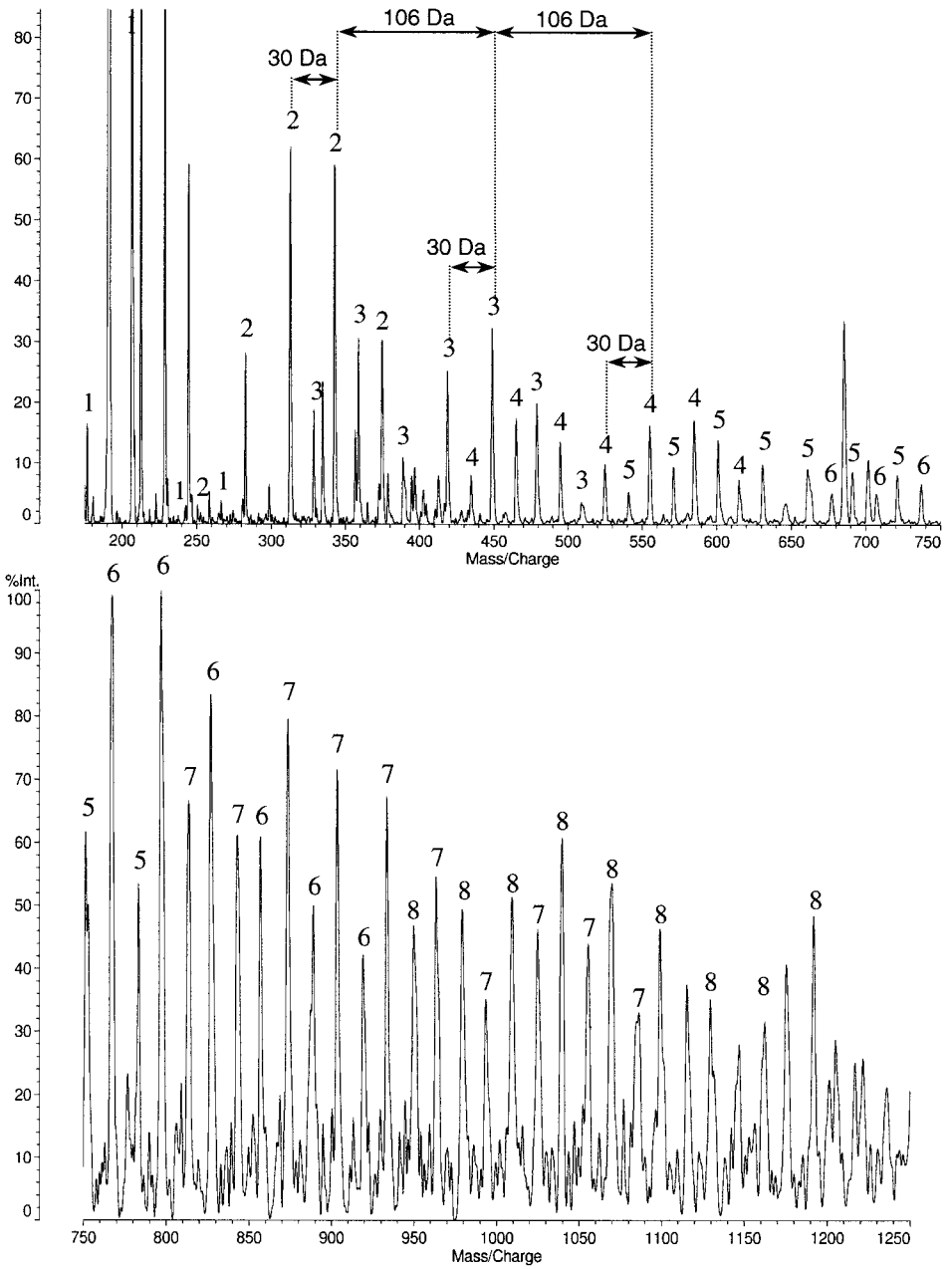
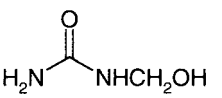


Figure 1 MALDI–MS spectrum of a phenolic resol; for assignments, see Table I.

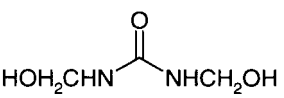
6

M = 60 Da
M + Na^+ = 83 Da



7

M = 90 Da
M + Na^+ = 113 Da



8

M = 120 Da
M + Na^+ = 143 Da

TABLE I
Assignment of the Peaks $[M + Na]^+$ in the MALDI–TOF Spectrum of a Phenolic Resol (P_xF_z) (Fig. 1)

Series	Peak (Da)	*X*	*Z*
1	177	1	2
1	207	1	3
1	237	1	4
1	267	1	5
2	253	2	2
2	283	2	3
2	313	2	4
2	343	2	5
2	373	2	6
3	329	3	2
3	359	3	3
3	389	3	4
3	419	3	5
3	449	3	6
3	479	3	7
3	509	3	8
4	435	4	3
4	465	4	4
4	495	4	5
4	525	4	6
4	555	4	7
4	585	4	8
4	615	4	9
5	541	5	4
5	571	5	5
5	601	5	6
5	631	5	7
5	661	5	8
5	691	5	9
5	721	5	10
5	751	5	11
5	781	5	12
6	677	6	6
6	707	6	7
6	737	6	8
6	767	6	9
6	797	6	10
6	827	6	11
6	857	6	12
6	887	6	13
6	917	6	14
7	814	7	8
7	844	7	9
7	874	7	10
7	904	7	11
7	934	7	12
7	964	7	13
7	994	7	14
7	1024	7	15
7	1054	7	16
7	1084	7	17
8	919	8	9
8	949	8	10
8	979	8	11
8	1009	8	12
8	1039	8	13
8	1069	8	14
8	1099	8	15
8	1129	8	16
8	1159	8	17
8	1189	8	18

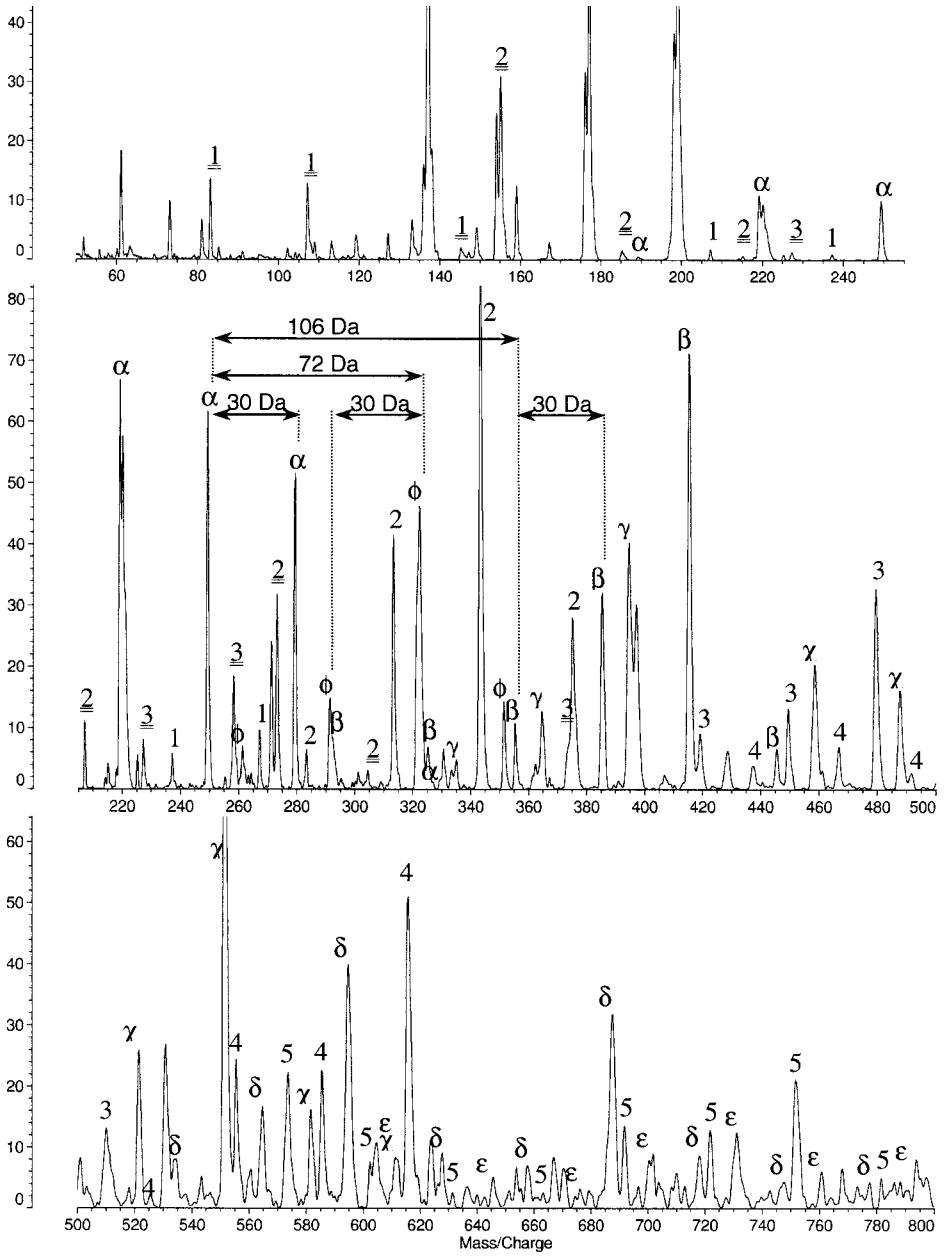
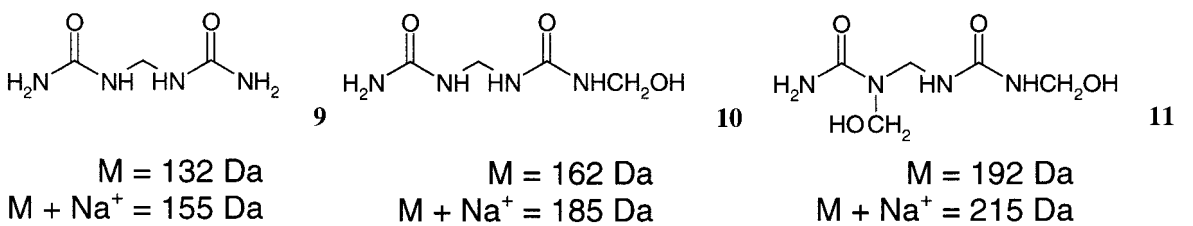
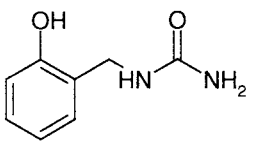


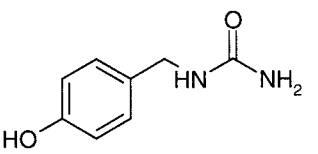
Figure 2 MALDI–MS spectrum of a urea-modified phenolic resol; for assignments, see Tables II and III.



In addition to these types of structures, phenol–urea cocondensates (e.g., **12a,b** and **13a–e**) are formed which can be observed in the spectrum:

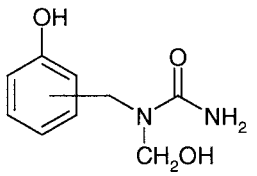


12a

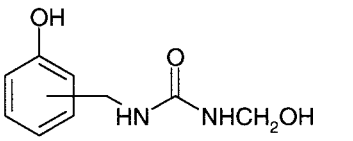


12b

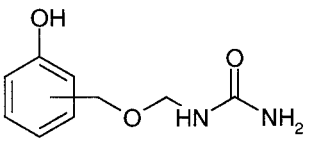
M = 166 Da
M + Na^+ = 189 Da



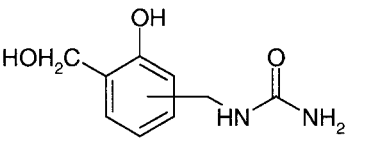
13a



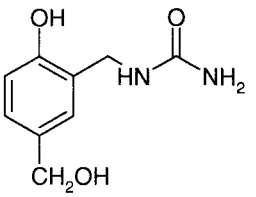
13b



13c



13d

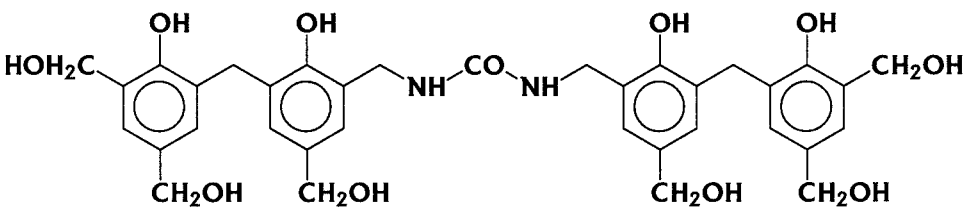


13e

M = 196 Da
M + Na^+ = 219 Da

The assignments of the phenol–urea cocondensate mass peaks in Figure 2 are summarized in Tables II and III. For these oligomers, the code $P_X U_y F_z$ is used, where X, Y, and Z indicate molecules of phenol, urea, and formaldehyde in the respective oligomers.

As can be seen in Figure 2, PUF cocondensates are formed up to high molar masses. For example, the mass peaks at 687 and 793 Da correspond to linear urea-linked PF oligomers containing one molecule of urea. Such oligomers are directly detected for the first time. They could have been formed by the condensation of PF dimers and trimers with urea:



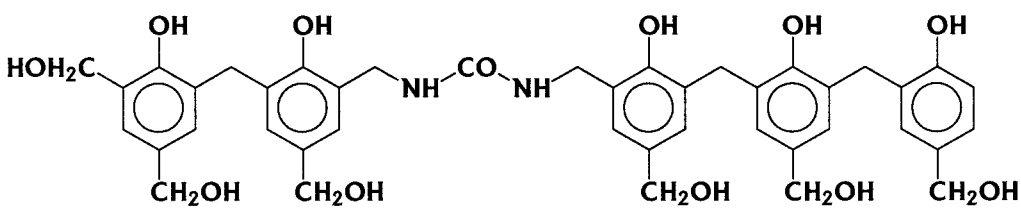


TABLE II
Assignment of the Peaks $[M + Na]^+$ for Phenol–Formaldehyde and Urea–Formaldehyde Condensates in the MALDI–TOF Spectrum of a PUF Resol ($P_xU_yF_z$) (Fig. 2)

Series	Peak (Da)	X	Y	Z
1 =	83	—	1	—
1 =	113	—	1	1
1 =	143	—	1	2
2 =	155	—	2	1
2 =	185	—	2	2
2 =	215	—	2	3
2 =	245	—	2	4
2 =	275	—	2	5
2 =	305	—	2	6
3 =	227	—	3	2
3 =	257	—	3	3
3 =	377	—	3	7
3 =	407	—	3	8
1	207	1	—	3
1	237	1	—	4
1	267	1	—	5
2	283	2	—	3
2	313	2	—	4
2	343	2	—	5
2	373	2	—	6
3	419	3	—	5
3	449	3	—	6
3	479	3	—	7
3	509	3	—	8
4	435	4	—	3
4	465	4	—	4
4	495	4	—	5
4	525	4	—	6
4	555	4	—	7
4	585	4	—	8
4	615	4	—	9
5	571	5	—	6
5	601	5	—	6
5	631	5	—	7
5	661	5	—	8
5	691	5	—	9
5	721	5	—	10
5	751	5	—	11
5	781	5	—	12

CONCLUSIONS

Phenolic resins can be analyzed by MALDI–MS when DHB or THAP are used as matrices. In the case of a commercial phenolic resol, the MALDI–MS spectrum shows the oligomer distribution. The oligomer peaks appear as $[M + Na]^+$ molecular ions. From the oligomer masses, the degree of polymerization and the number of reactive methylol groups per phenolic nucleus can be determined.

Much more complex is the MALDI–MS spectrum of a urea-modified phenolic resole. In addition to phenol–formaldehyde structures, the spectrum exhibits mass peaks for urea–formaldehyde oligomers. For the first time, mass peaks were identified, which can directly be assigned to PUF cocondensates. The composition of these structures as $P_XU_YF_Z$ can be determined from the MALDI mass peaks.

TABLE III
Assignment of the Peaks $[M + Na]^+$ for PUF Cocondensates in the MALDI–TOF Spectrum of a PUF Resol ($P_xU_yF_z$) (Fig. 2)

Series	Peak (Da)	X	Y	Z
α	189	1	1	1
α	219	1	1	2
α	249	1	1	3
α	279	1	1	4
α	309	1	1	5
β	295	2	1	
β	325	2	1	2
β	355	2	1	3
β	385	2	1	4
β	415	2	1	5
β	445	2	1	6
χ	461	3	1	5
χ	491	3	1	6
χ	521	3	1	7
χ	551	3	1	8
χ	581	3	1	9
χ	611	3	1	10
ϕ	261	1	2	2
ϕ	291	1	2	3
ϕ	321	1	2	4
ϕ	351	1	2	5
δ	537	4	1	5
δ	567	4	1	6
δ	597	4	1	7
δ	627	4	1	8
δ	657	4	1	9
δ	687	4	1	10
δ	717	4	1	11
δ	747	4	1	12
δ	777	4	1	13
ε	613	5	1	5
ε	643	5	1	6
ε	673	5	1	7
ε	703	5	1	8
ε	733	5	1	9
ε	763	5	1	10
ε	793	5	1	11
γ	333	1	3	3
γ	363	1	3	4
γ	393	1	3	5

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