

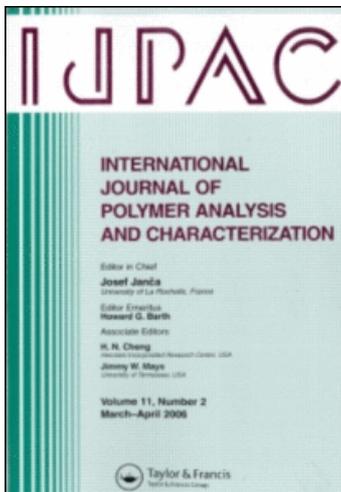
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## **Analysis of N-Methylmelamine Resins with Combined GPC, HPLC, Mass Spectrometric Techniques**

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**Abstract:** This article deals with the development of methods for characterization and structural elucidation of N-methylmelamine resins as well as the cured material and composites made with these products. Resin characterization was achieved by ESI-ion trap MS and HPLC/PDA/MS<sup>n</sup>, which made the assignment of each species in the mixture possible. GPC as well as MS were used to follow the curing of the resin. Completely cured resins and composites are no more soluble in any solvent, and, therefore, the characterization was carried out with analytical pyrolysis and thermally assisted hydrolysis and methylation (THM) hyphenated to a GC/MS system.

**Keywords:** Mass spectrometry; Melamine; Pyrolysis; THM

### **INTRODUCTION**

Melamine (2,4,6-triamino-1,3,5-triazine) is a well-known base material for the production of resins. It is condensed with formaldehyde to yield

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methylolmelamines with a varying degree of substitution. Because of the three amino groups, which display six potential reaction sites, the resins are rather polar and usually highly cross-linked thermosets. Typical applications for melamine resins are in the manufacturing of plywood, fiberboard, laminates, and furniture, as cross-linking agent in lacquers, and to improve the wet strength of paper.

Recently, several reports on applications of N-methylmelamines as substitutes for melamine in formaldehyde resins or cross-linking agents were published.<sup>[1-3]</sup> The benefits of N-methylmelamines are that with an increasing number of methyl groups the polarity decreases, which allows application with hydrophobic materials, and the degree of cross-linking can be reduced and therefore the material becomes less rigid and brittle. Because of the novelty of these materials, there are no analytical methods published; we have worked on developing means of characterization for all processing stages of these compounds, from resins to cured materials and composites.

Several studies have been published showing the possibilities of high-performance liquid chromatography-mass spectrometry (HPLC-MS) hyphenation for the characterization of classical melamine formaldehyde resins.<sup>[4-8]</sup> It is shown that mass spectrometry provides a valuable tool to assign structures to resin compounds and that by using ion trap mass spectrometers capable of performing MS<sup>n</sup> experiments it is also possible to differentiate between isomers that have the same molar mass.<sup>[9]</sup> For any material that cannot be dissolved or vaporized, pyrolysis-GC/MS and thermally assisted hydrolysis and methylation (THM) have become outstanding methods for characterization, as already shown in the analysis of classical melamine formaldehyde composites and copolymers.<sup>[10]</sup>

## EXPERIMENTAL SECTION

### Materials

The resins were prepared from 2,4,6-trimethylmelamine (TRM) and 2,2,4,6-tetramethylmelamine (TMM). These were synthesized by reacting cyanuric chloride with methylamine and dimethylamine according to the literature.<sup>[11-12]</sup> A 30 g amount of trimethylmelamine or a mixture of tri- and tetramethylmelamine (24 g TRM and 6 g TMM) were suspended in 90 mL water and heated to 70°C. Formaldehyde was added as aqueous solution in a molar ratio of formaldehyde to melamine of 1 to 1.5. The reaction solution was stirred for about 30 min until a viscous resin was formed. The remaining water was removed under reduced pressure to yield a solid methylmelamine resin.

Curing of the resins was done at a temperature of 140°C for several minutes using formic acid as catalyst. A particleboard was made from spruce wood chips with 8% of trimethylmelamine resin as binder.

## Methods

### ESI-MS

The samples were dissolved in a mixture of chloroform/methanol (50/50) and injected into the electrospray ionization (ESI) source of a Thermo LCQ Deca XP plus ion trap mass spectrometer via a syringe at a flow rate of 3  $\mu\text{L}/\text{min}$ . Spectra were recorded in positive mode, with acceleration voltage 4.5 kV, transfer line 250°C, and scan range 150–2000  $m/z$ .

### HPLC/MS

The samples were analyzed on an Agilent 1100 HPLC system hyphenated to a Thermo LCQ Deca XP plus ion trap mass spectrometer operated in ESI mode. The separation column was an ODS Hypersil ( $2.1 \times 250$  mm, 5  $\mu\text{m}$ ), and the solvents were 0.044 M ammonium acetate in water (A), 0.044 M ammonium acetate in acetonitrile/water (4/1) (B), and isopropanol (C). The flow rate was 0.2 mL/min with the following gradient: isocratic with 70A/0B/30C for 10 min, within 20 min to 25A/25B/50C, back to 70A/0B/30C in 1 min, and held for a further 19 min. Sample loading was 25  $\mu\text{L}$  of a 0.1 mg/mL solution. The MS was set up to acquire full scan data as well as  $\text{MS}^2$  and  $\text{MS}^3$  spectra of the most abundant signals.

### GPC

Experiments were performed on a gel permeation chromatography (GPC) system consisting of a Bischoff 728 autosampler, a Jasco PU-980 pump, a Bischoff LAMBDA 1000 UV detector, a Bischoff 8110 RI detector, and a Wyatt Technology Mini Dawn light scattering detector. Separation was achieved on a Phenomenex Phenogel 5  $\mu$  50 A column ( $4.6 \times 300$  mm) with 0.35 mL/min tetrahydrofuran as eluent at room temperature. Sample loading was 100  $\mu\text{L}$  of a 0.1 mg/mL solution in tetrahydrofuran.

### Pyrolysis-GC/MS and THM-GC/MS

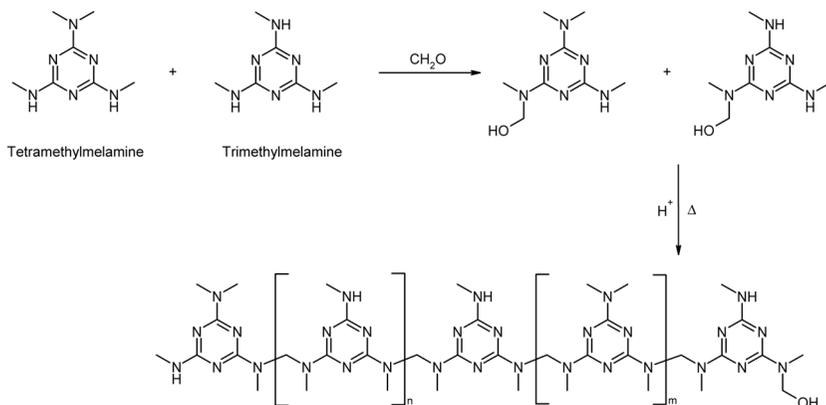
A sample of about 50  $\mu\text{g}$  of a fiberboard made with a TRM resin was pyrolyzed at 500°C for 10 s with a CDS pyroprobe 2000 attached

to a Thermo Trace GC/Polaris Q GC/MS system. The volatile products were separated on a Varian CP Wax 52CB column (60 m, ID 0.25 mm, 0.25  $\mu\text{m}$  film) with helium 4.6 as carrier gas (1.5 mL/min) and identified by interpretation of their electron impact (EI) mass spectra and comparison to NIST, Wiley, and NBS electronic libraries and reference compounds. The pyrolysis and GC/MS interfaces were kept at 250°C, and the GC was programmed from 50° to 90°C at a rate of 10°C/min and to 260°C at a rate of 4°C/min, where it was kept for 35 min. The mass spectrometer was operated in EI mode (70 eV) at a source temperature of 200°C.

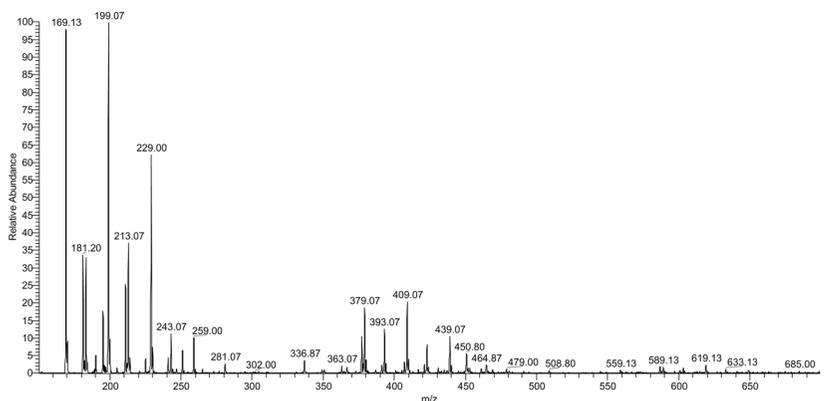
THM conditions were identical to pyrolysis conditions except that the sample was covered with 5  $\mu\text{L}$  of an aqueous solution of tetramethylammonium hydroxide (25%) prior to pyrolysis.

## RESULTS AND DISCUSSION

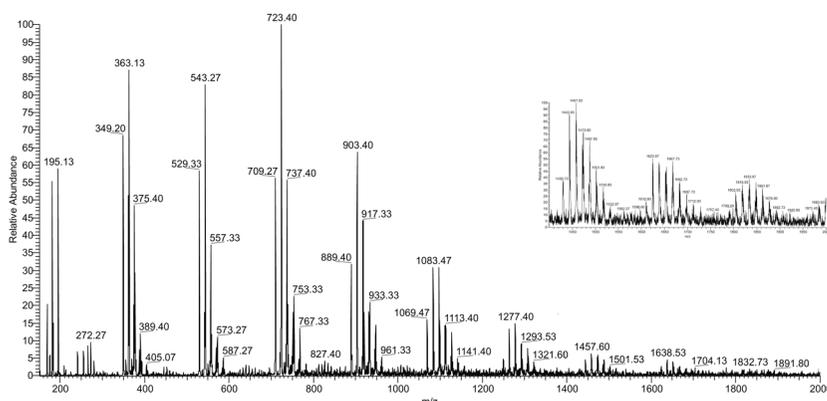
Methylmelamine resins, as are shown in Scheme 1, can readily be characterized by mass spectrometry because for each degree of methylation, methylation, and polymerization (or exactly condensation) one obtains different molar masses. The only structures that cannot be distinguished by molar mass are isomers (e.g., position of the methylol groups). Figure 1(a) shows the ESI mass spectrum of a methylmelamine resin made of TRM and TMM. In the monomer region between 169 and 259 g/mol one can easily see that both melamine species have reacted with formaldehyde to give methylolmelamines with an average degree of substitution of about 1. The relative intensity ratio of



**Scheme 1.** Synthesis of methylolated 2,4,6-trimethyl- and 2,2,4,6-tetramethylmelamine and structure of a precured resin.



(a)



(b)

**Figure 1.** (a) ESI-MS of a methylmelamine resin (80% TRM, 20% TMM); (b) after curing with formic acid at 140°C.

tetramethylmelamine to trimethylmelamine of 0.23 shows a good approximation of the starting composition of 21 mol% tetramethylmelamine; therefore, it is concluded that neither melamine species shows a preference for the reaction with formaldehyde. The region from 349 to 469 g/mol comprises three different types of dimers: the hexamethyl (349), the heptamethyl (363), and the octamethyl (377) species together with their methylolated forms. The most abundant species are the hexamethyldimers, bearing one (379) and two (409) methylol groups.

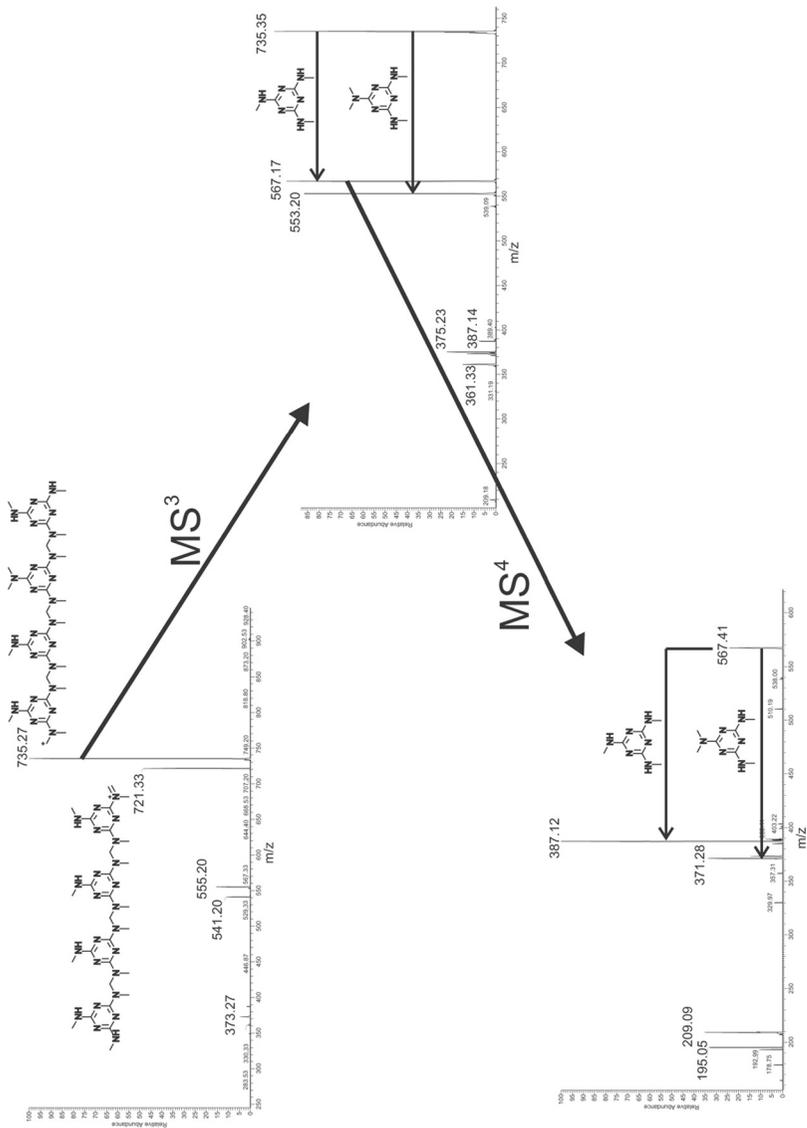
Upon curing, the methylol groups react with free amino functionalities under elimination of water, or with other methylol groups under elimination of water and formaldehyde, to form methylene linkages, as shown in Scheme 1. These reactions can be accelerated using an acidic catalyst and elevated temperatures. Figure 1(b) shows the mass spectrum

of the described resin after curing with formic acid at 140°C. Besides the obvious increase of molar mass, the spectrum shows the distribution of oligomers. With an increasing degree of condensation ( $dc$ ) the number of TMM molecules that can be incorporated into the oligomer increases accordingly. An oligomer with a  $dc$  of  $n$  therefore consists of  $n$  species with different numbers of methyl groups attached. In addition to these nonfunctional oligomers, there are still species with remaining methylol groups left, which increase the number of signals within a given  $dc$ , but still the oligomers with a different  $dc$  are clearly separated in the spectrum. In the monomer region the masses 181 and 195 are found, which are due to fragmentation of larger oligomers. The most abundant species are now the tetramers with masses from 709 to about 800 g/mol. The highest masses detected with the ion trap MS were over 2000 g/mol, corresponding to 10 condensed melamine rings.

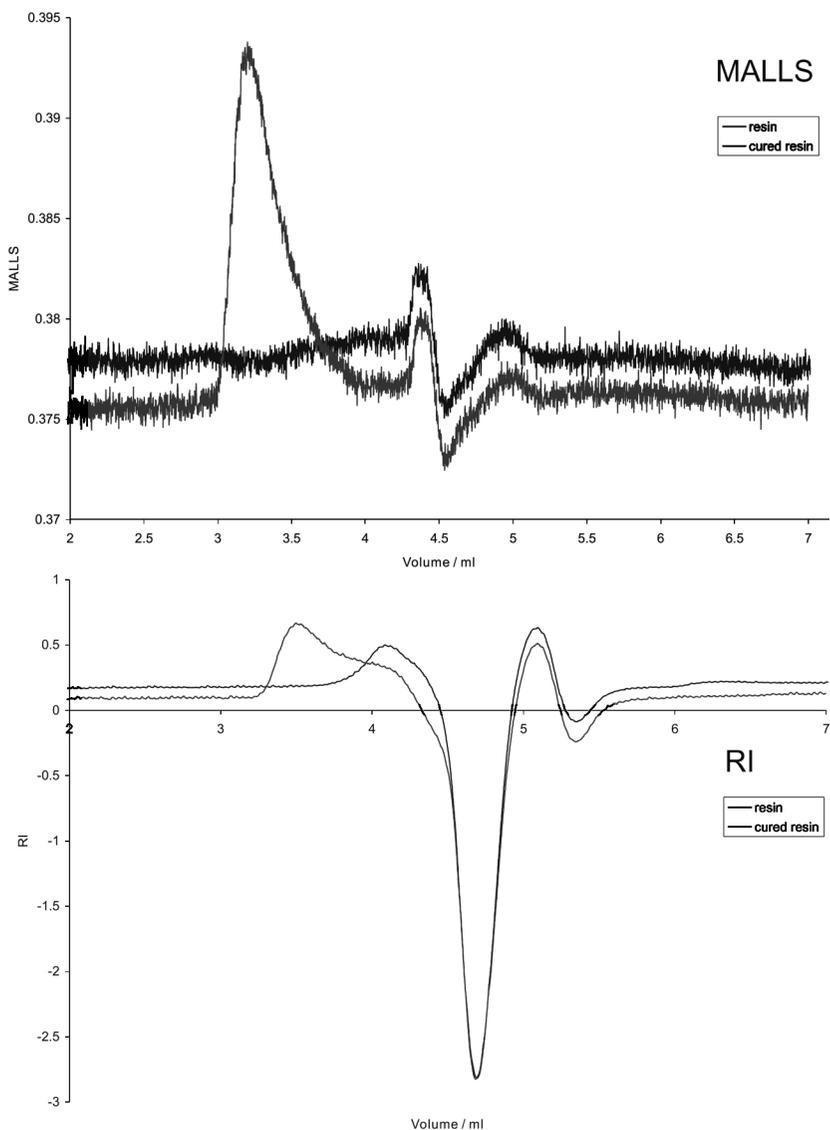
MS/MS fragmentation of a selected ion gives deeper insight into the molecule structure (Figure 2). The ion with 903 g/mol represents a pentamer with four TRM and one TMM units. The  $MS^2$  spectrum shows loss of a tri- and a tetramethylmelamine radical in the first step, which indicates that there are molecules having the tetramethylmelamine in the first position (721 g/mol) and others having it in the middle (735). The latter ions produce a  $MS^3$  spectrum that again shows the loss of a tri- (567 g/mol) as well as a tetramethylmelamine (553 g/mol) radical, and the  $MS^4$  spectra of 567 gives the same result. The  $MS^n$  spectra can therefore be used to perform a sequence analysis of each polymer species, and it could be shown for the selected pentamer that the tetramethylmelamine unit is randomly distributed within the oligomer.

Further characterization of the resin was achieved by the hyphenation of separation techniques such as HPLC or GPC to mass spectrometry to optimize the resolution of the analysis. GPC can readily be used to follow the curing process of the resin, as shown in Figure 3. The low molar mass resin gives a peak at a retention time of 3.8–4.5 min and no light scattering signal. The cured material shows a shift in retention time to 3.2–4.4 min as well as a signal in the light scattering detector. This is rather uncommon because molar masses of below 2000 g/mol (determined with MS) should not result in light scattering. A determination of the molar mass with polystyrene standards is impossible because the selected column has a range of 100 to 3000 g/mol and even the lowest molar mass PS standards (2400 and 4000 g/mol) elute with the dead volume of the column of 3.2 mL. Assuming a linear separation behavior of the column, the average molar mass of the sample would be between 1000 and 2000 g/mol, which is far above the data determined with mass spectrometry.

The HPLC method was specially developed for the use with methylmelamine resins; the use of a ternary gradient with isopropanol

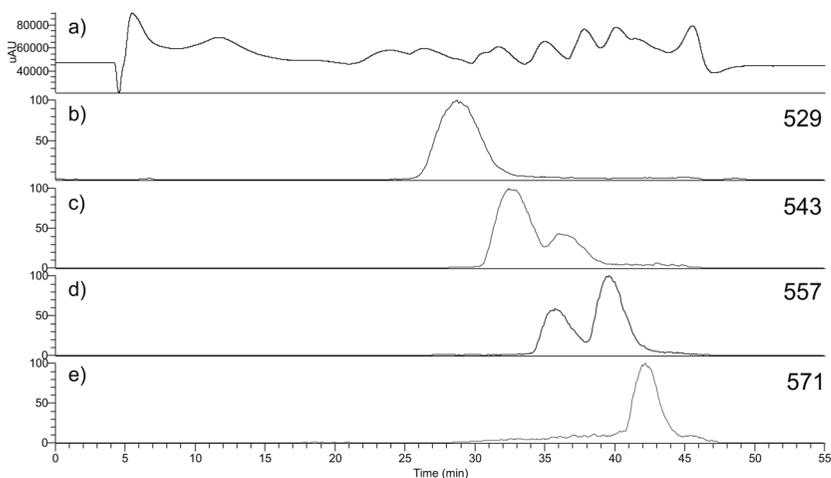


**149** **Figure 2.** MS<sup>2</sup>, MS<sup>3</sup>, and MS<sup>4</sup> fragmentation analysis of a pentamer containing one tetramethyl- and four trimethylmelamine units (903 g/mol).



**Figure 3.** GPC analysis of a methylmelamine resin (80% TRM, 20% TMM) before and after curing; light scattering (above) and refractive index (below) detection.

was necessary to overcome the weak solubility of the material while maintaining the applicability of the solvent system for MS analysis. Figure 4 shows the chromatogram obtained from the tri- and tetra-methylmelamine copolymerizate after curing (see also Figure 1(b)).

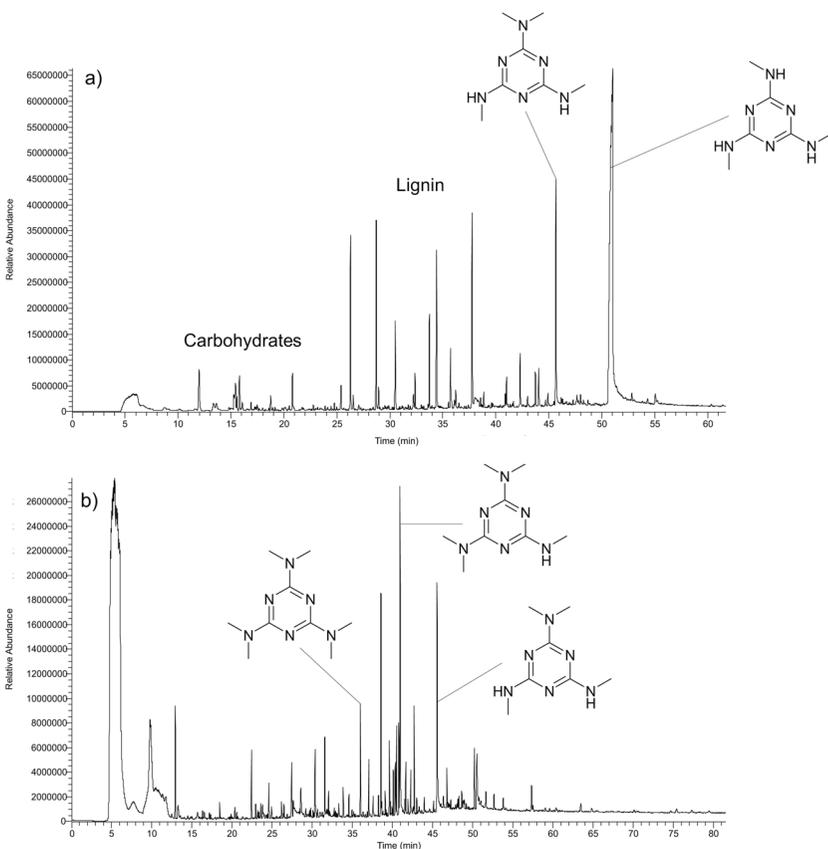


**Figure 4.** HPLC analysis of a cured methylmelamine resin (80% TRM, 20% TMM); (a) UV detection, (b)–(e) MS detection with extracted ions of the different trimers with 529, 543, 557, and 571 g/mol.

In contrast to the analysis of systems with only one melamine species where a separation of the oligomers is easily possible,<sup>[13]</sup> a separation of the copolymer cannot be achieved completely. With an increasing number of melamine rings the number of possible isomers increases dramatically. Whereas the dimers can consist of either two trimethylmelamine units, one tri-, and one tetramethylmelamine unit, or two tetramethylmelamine units, there is the possibility of isobaric structures for higher degrees of polymerization as well. For example a trimer with one tetramethylmelamine unit has two possible isomers, one with the tetramethylmelamine at the beginning and one with the tetramethylmelamine in the middle of the molecule. This results in a total number of 3 different dimers, 6 trimers, 10 tetramers, 18 pentamers, and so on, with several isobaric structures and very little difference in polarity. Nevertheless, the use of a MS as detector enables interpretation when looking at selected ions, e.g., the separation of the 6 trimers can be achieved by extracting the ions with 529, 543, 557, and 571 g/mol (Figure 4, curves b–e). Another possibility is the use of a neutral loss scan, where only the compounds that lose a certain fragment are registered. This technique can be used, for example, to detect all compounds with a tetramethylmelamine end group, since these eliminate a tetramethylmelamine radical in MS/MS mode as already described above, or all methylol groups containing molecules, which eliminates water and formaldehyde.

After complete curing the polymers are no longer soluble in non-degrading solvents and in most cases are part of composites with wood or other types of fibers, which also cannot be dissolved. In this case none of the methods described above can be used any longer. Pyrolytic techniques have therefore been selected for the characterization of a wood TRM resin particleboard (Figure 5).

In Figure 5(a) the chromatogram obtained from pyrolysis at 500°C shows two major peaks, which are trimethylmelamine and tetramethylmelamine. The formation of the latter one can be explained by the cleavage of the C–N bond of a methylene linkage, thus producing methylmelamines with a higher degree of methylation. The wooden part of the composite can be identified as soft wood due to its lignin composition, as extensively shown in the literature.<sup>[14]</sup>



**Figure 5.** (a) Pyrolysis-GC/MS of a wood particleboard with a trimethylmelamine resin; (b) THM-GC/MS of the same sample.

When using thermally assisted hydrolysis and methylation, the melamine resin is detected as hexa-, penta-, and tetramethylmelamine (Figure 5(b)). These higher methylated species are less indicative for the original state of the resin but are more amenable to gas chromatography. Also, the lignin and carbohydrate fractions are methylated and give more abundant and sharper peaks than conventional pyrolysis.<sup>[15,16]</sup>

## CONCLUSIONS

Several techniques for the characterization of different processing stages of methylmelamine resins have been presented. GPC can be used to indicate a molar mass distribution but the molar masses found seem to be too high. A possible reason might be that separation is not only based on size exclusion but also on polarity of the molecules, which is strongly influenced by the end groups of the melamine resin. A better and faster method is direct injection ESI-MS, which shows the different methylmelamines used, the degree of condensation, and the amount of methylol groups. HPLC/MS<sup>n</sup> is a rather time-consuming method but combines the valuable results of mass spectrometry with good separation for low molar mass resins. For higher molar mass resins the separation cannot be achieved completely, but with the possibilities of sequential MS/MS spectra a very strong technique is available. Once the polymers are completely cured none of the above-mentioned techniques is suitable any more. Pyrolysis as well as thermally assisted hydrolysis and methylation are very sensitive methods for the identification of melamine composites, even though only a little information on the original structure of the resin is maintained. Additionally, any organic reinforcements, fillers, and additives can be identified.

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