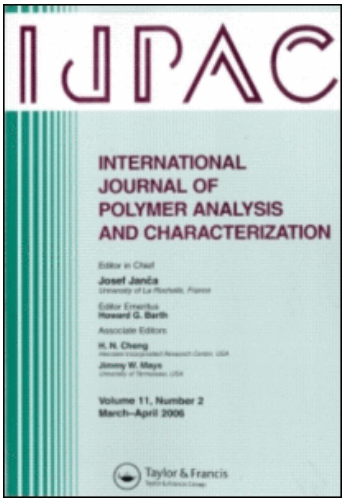

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

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To cite this Article Leidl, Manuela , Huber, Werner F. , Schwarzinger, Clemens and Endesfelder, Andreas(2007) 'Characterization of a Linear Melamine Formaldehyde Resin', International Journal of Polymer Analysis and Characterization, 12: 4, 301 — 314
To link to this Article: DOI: 10.1080/10236660701355337
URL: http://dx.doi.org/10.1080/10236660701355337

International Journal of Polymer Anal. Charact., 12: 301–314, 2007

ISSN: 1023-666X print
DOI: 10.1080/10236660701355337

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Characterization of a Linear Melamine Formaldehyde Resin

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Abstract: A novel linear melamine formaldehyde resin on the basis of the bifunctional tetramethylmelamine was created. It was found to posses several promising properties for industrial applications. Structural characterization of the material at its various production states was achieved with different mass spectrometric techniques. Liquid chromatography-ion trap mass spectrometry was used to completely separate the resins and identify the individual components. Detection with a diode array detector indicated a change of spectroscopic properties with the degree of polymerization. The material was also analyzed with analytical pyrolysis and a gel permeation chromatography system hyphenated to a mass spectrometer in order to unambiguously determine the molar masses.

Keywords: Linear melamine resin; Mass spectrometry; Structural characterization; Tetramethylmelamine

The authors wish to thank Prof. Günter Allmaier and Dr. Ernst Pittenauer from the Technical University Vienna for their help with the MALDI experiments.

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INTRODUCTION

An important commercial type of resinous material is obtained from the reaction of formaldehyde with melamine (2,4,6-triamino-1,3,5-triazine). The addition of formaldehyde to the amino groups results in the formation of so-called methylol groups, which then can undergo a polycondensation reaction, yielding products with a high degree of cross-linking. These materials possess good thermal stability, water resistance, and high surface brilliance, and have been adopted by industry to fit numerous applications, such as the manufacturing of plywood, laminates, and furniture, as cross-linkers in lacquers, or to improve wet strength of paper.

Recently, several applications of N-methylmelamines as substitutes for melamine in formaldehyde resins or cross-linking agents were published.[1–3] The use of 2,2,4,6-tetramethylmelamine (TMM) as a monomer results in the formation of a strictly linear melamine resin. Additionally, there are no more amino hydrogens left, which makes the final polymer rather hydrophobic. Considering different methylmelamines as building blocks for formaldehyde resins, TMM displays the very end of the chain and possesses the most different properties from melamine. The resins made thereof are no longer soluble in water and exhibit a melting point without etherification of the methylol groups. The purpose of this study was to identify all species within the resins and to find suitable methods for the characterization of these new materials at all processing stages. The methods of choice were mass spectrometry for the identification of individual species, as has been shown to work for conventional melamine resins,[4–9] gel permeation chromatography (GPC) for the characterization of the molar masses, and pyrolysis-gas chromatography/mass spectrometry (GC/MS) to investigate a fully cured resin.[10]

EXPERIMENTAL SECTION

Materials

2,2,4,6-Tetramethylmelamine (TMM) was synthesized by reacting cyanuric chloride with methylamine and dimethylamine according to the literature.[11,12] A 10 g amount of TMM was suspended in 30 mL of water and heated to 70°C. Formaldehyde was added as aqueous solution in a molar ratio of formaldehyde to melamine of 1.2, and the pH adjusted with 100 μL of acetic acid (pH ≈ 6). The reaction solution was stirred for about 10 min until the resin became insoluble. The solid was filtered, dried in a vacuum dessicator at 35°C, and pulverized with a centrifugal mill.

Further curing of the resins was done either in an oven at a temperature of 140°C for about 45 min (low molar mass) and to produce high molar mass resins, 5 g of this pre-cured resin was dissolved in 50 mL toluene, refluxed for 8 h at 110°C to remove the water formed in the condensation reaction.

Polystyrene (molar mass = 2430 g/mol, polydispersity index = 1.06) was obtained from Aldrich.

Methods

Electrospray Ionization-Mass Spectrometry (ESI-MS)

The samples were dissolved in a mixture of chloroform/methanol (50/50) at a concentration of about 10 μg/mL and injected into the ESI source of a Thermo LCQ Deca XP plus ion trap mass spectrometer via a syringe at a flow rate of 3–10 μL/min. Spectra were recorded in positive mode, with an acceleration voltage of 4.5 kV, transfer line at 250°C, and scan range of 150–2000 m/z for characterization of the low molar mass resins. The high molar mass resins were additionally recorded in the high mass range feature of the MS with a scan range of up to 4000 m/z.

Matrix-Assisted Laser Desorption Ionization-Time of Flight Mass Spectrometry (MALDI-ToF MS)

The sample was dissolved in chloroform/methanol (50/50), mixed with the trihydroxyacetophenone matrix, and an aliquot was placed on the target. The spectra were recorded on a Shimadzu Biotech Axima ToF^2 in reflectron mode with a scan range of 100 to 4000 m/z and of 900 to 4000 m/z to eliminate small fragments and optimize the range for the higher molar masses.

High-Performance Liquid Chromatography/Mass Spectrometry (HPLC/MS)

The samples were analyzed on an Agilent 1100 HPLC system consisting of an autosampler, quaternary gradient pump, degasser, and UV-diode array (UV-DA) detector hyphenated to a Thermo LCQ Deca XP plus ion trap mass spectrometer operated in ESI mode. The separation column was an ODS Hypersil (4.6 × 250 mm, 5 μm), 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 0.7 mL/min with the following linear gradient: from 40/10/50 within 50 min to 0/50/50, and kept constant for 10 min. Sample loading was

10 μL of a 0.1 mg/mL solution. The MS was set up to acquire full scan data as well as MS^2 spectra of the most abundant signals.

GPC and GPC/MS

Experiments were performed on an Agilent 1100 HPLC system with UV-DA detector. Separation was achieved on a series of three Phenomenex Phenogel 5 μ columns (50 A, 100 A, 500 A, each 4.6 × 300 mm and a 50 A pre-column) with 0.35 mL/min tetrahydrofuran as eluent. Sample loading was 100 μL of a 0.2 mg/mL solution in tetrahydrofuran. After the columns a flow of 0.35 mL/min methanol, supplied by a Jasco PU-980 pump, was added via a tee joint and the mixed eluent forwarded into the ESI source of a Thermo LCQ Deca XP plus ion trap mass spectrometer. The MS was programmed to record a scan range from 150 to 2000 m/z in normal mode and a second scan range from 1000 to 4000 m/z in high mass range to record the higher molar mass compounds.

Pyrolysis-GC/MS

About 50 μg of sample were 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 μm film) with helium 4.6 as carrier gas (1.5 mL/min) and identified by comparison of retention times and electrospray ionization (EI) mass spectra to authentic standards as well as comparison to NIST, Wiley, and NBS electronic libraries. Pyrolysis and GC/MS interfaces were both 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.

RESULTS AND DISCUSSION

In Figure 1, the synthesis route from cyanuric chloride (1) over TMM (2) and monomeric methylol compounds (3) to a resin (4) and finally to the polymer (5) is displayed. Unfortunately, the solubilities at different degrees of polymerization are not equivalent. Whereas monomers and resins with a low degree of polymerization (dp) possessing free methylol groups are somewhat soluble in acetonitrile/water, the addition of isopropanol is essential for a higher dp. Once the material is cured and therefore has only a low percentage of methylol groups left, it becomes soluble in toluene. The only solvent that is capable of dissolving the resin

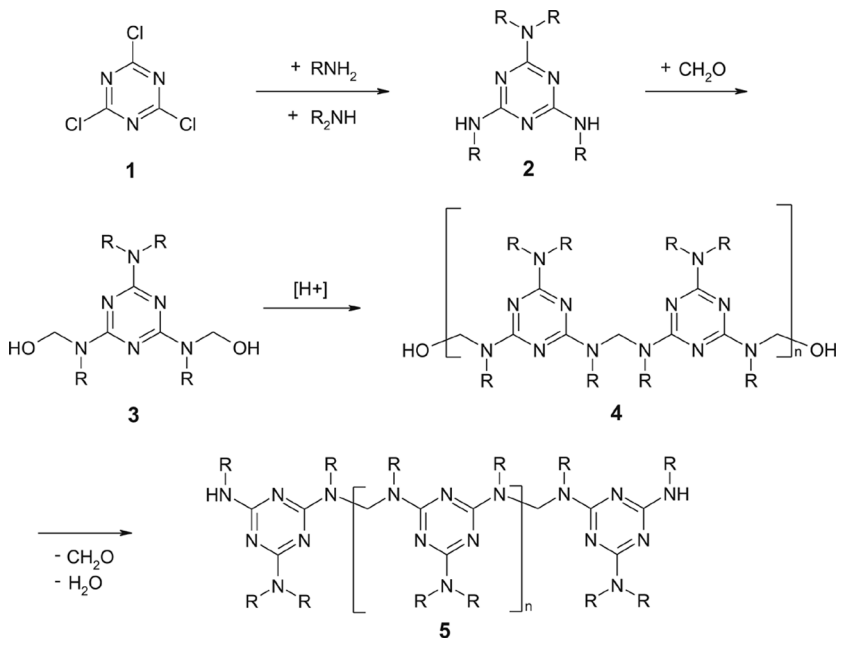

Figure 1. Synthesis of 2,2,4,6-tetraalkylmelamine (**2**) from cyanuric chloride (**1**), formation of a resin (**3, 4**), and structure of a cured resin (**5**).

at all stages of manufacture and is suitable to perform mass spectrometry is a 50/50 mixture of chloroform/methanol.

Mass Spectrometry

First, all samples were dissolved in chloroform/methanol and directly injected into the ESI source of the ion trap mass spectrometer. The resins can be written according to the following formula:

$$(C_7H_{12}N_6)_x(CH_2)_{x-1}(CH_2OH)_nH_{2-n}$$

where x represents the degree of polymerization and n the number of reactive methylol groups, which usually can be 0, 1, or 2. For singly charged ions, the masses are unique and therefore a structure can be directly derived from the mass spectrum. Table I shows important m/z values of the species found in the resins.

During the first minutes of the reaction, the resin is still mostly monomeric or dimeric (Figure 2(a)) and has already a high amount of formaldehyde attached to it. After the precipitation of the resin, a shift

Table I. Calculated m/z values for ions observed in the mass spectra of tetramethylmelamine resins

	Degree of polymerization (x)						
	1	2	3	5	7	10	16
$M_x \cdot H^+$	183.1	377.2	571.4	959.6	1347.9	1930.3	3095.0
$M_x(CH_2OH) \cdot H^+$	213.1	407.3	601.4	989.6	1377.9	1960.3	3125.0
$M_x \cdot Na^+$	205.1	399.2	593.4	981.6	1369.9	1952.3	3117.0
$M_x \cdot 2H^{2+}$	92.1	189.1	286.2	480.3	674.4	965.6	1548.0
$M_x \cdot 3H^{3+}$	61.7	126.4	191.1	320.5	450.0	644.1	1032.3

of molar mass can be noticed (Figure 2(b)), and the average dp is now between 2 and 3. When looking at a material after refluxing in toluene (Figure 2(c)) one can see that there are only a few methylol groups left and molar masses exceed the conventional range of the mass spectrometer (2000 m/z). When looking closer at the mass spectrum, it can be seen that the most intense ion is due to the tetramer with no methylol groups attached. In the lower m/z range the spectrum is dominated by fragments such as 195, 389, and 777 g/mol, which are due to cleavage of higher oligomers, according to Figure 3. The ions in the pentamer region of 950 to 1060 (Figure 4) can be assigned in the following way: 959, 989, and 1019 are the pentamers with 0, 1, and 2 methylol groups; 971 and 1001 are fragments according to Figure 3; and 1003 and 1033 are methoxymethyl species, which are due to the reaction of the methylol groups with the methanol used for the stabilization of formaldehyde. In between this series is another series of ions with a charge state of 2: 965, 980, and 995. These are the doubly protonated decamers, which can also be found as their singly protonated form with m/z 1929, 1959, and 1989, respectively. The maximum abundance of the doubly charged series can be found between m/z 850 and 1000, which lets us conclude that a proton is likely to be attached to approximately every fifth melamine ring in the oligomers. Due to this observation, it is obvious that ESI-MS underestimates the amount of higher molar mass oligomers when only looking at the singly protonated species. A series of triple-charged ions can also be found with m/z 1032, 1042, and 1052 (hexadecamers), which also supports the conclusion stated above.

The MALDI spectrum (Figure 5) shows almost exclusively fragmentation below 1000 m/z, but from there on up to about 4000 m/z the sodium adducts can readily be seen. In contrast to the ESI experiment, only singly charged molecules are found, but the resolution and signal-to-noise level seem to be worse. Nevertheless, both techniques

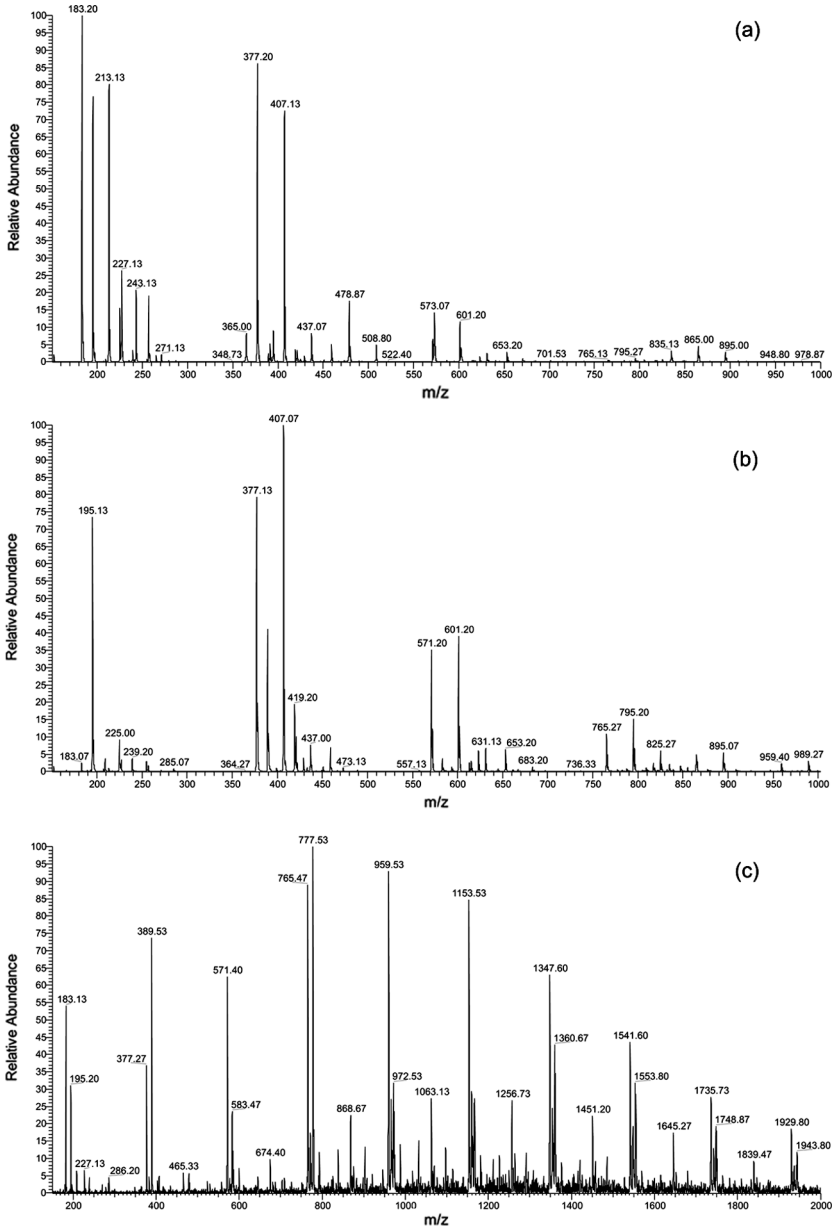

Figure 2. ESI mass spectra of (a) a low molecular weight resin; (b) a resin after precipitation; and (c) a high molecular weight sample.

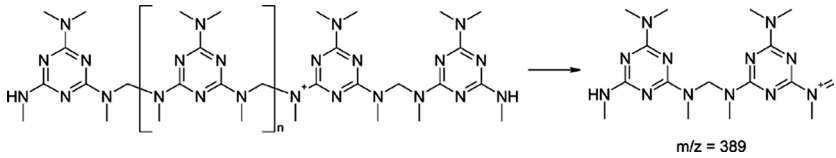

Figure 3. Fragmentation pathway of higher molecular weight oligomers.

give the same overall results. The highest masses observed in both cases are above 5000 g/mol, corresponding to about 27 condensed melamine rings.

Chromatography

A resin sample cured in an oven was subjected to reversed-phase HPLC. Peak identification was done by combined UV scan and ESI-MS. As can be seen in Figure 6, the lower molar mass oligomers could be separated very well, and it was observed that the UV absorption maxima for the different oligomers are not the same. Whereas TMM has a maximum at 218 nm, the maxima are shifted to higher wavelength with increasing dp until they become constant at around 235 nm from the dp of 5 and higher. This might be essential when trying to quantify individual species with a UV detector because different wavelengths will lead to different results.

GPC shows a strong shift in retention time from monomeric resin to cured materials, but calibration with authentic standards is not possible,

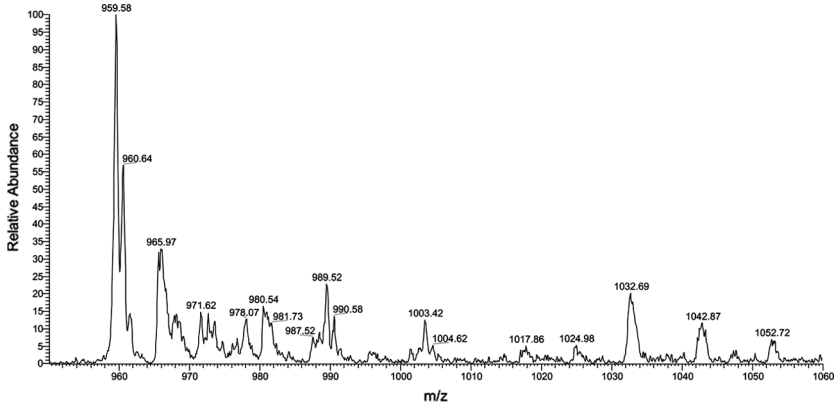

Figure 4. Enlargement of the ESI mass spectrum of high molecular weight material showing the region assigned to pentamers.

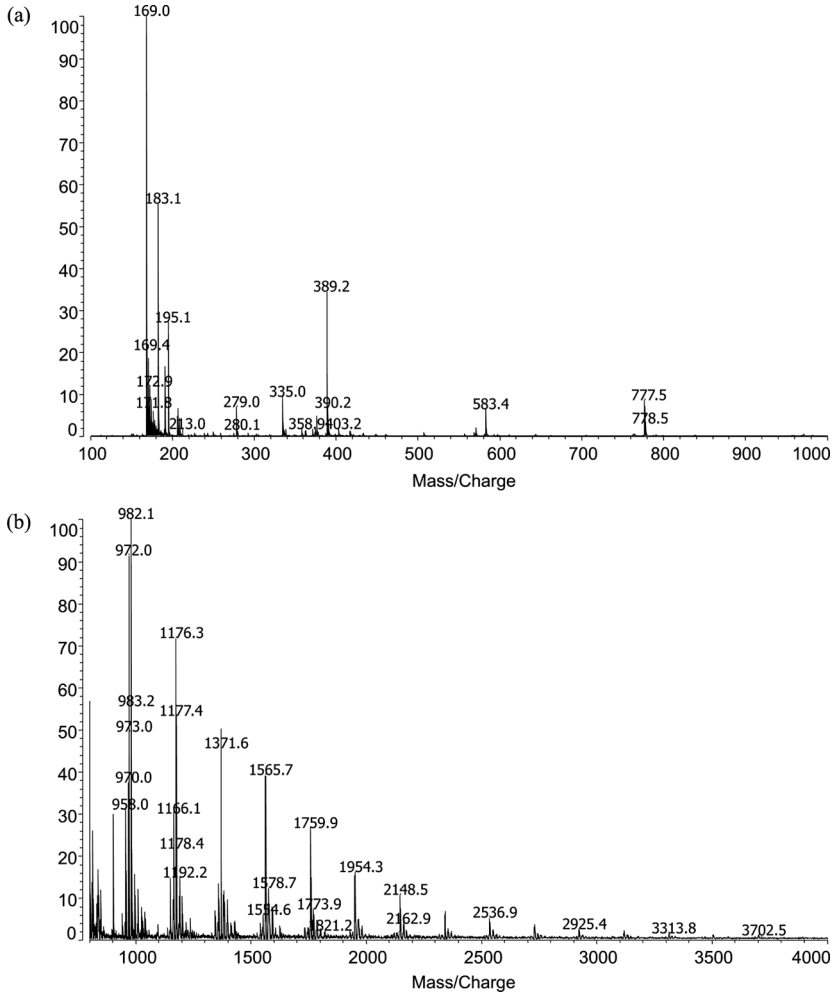

Figure 5. MALDI-mass spectra of a high molecular weight resin showing (a) a low scan range dominated by fragments and matrix (169) and (b) a scan range above m/z 900 where no more fragmentation occurs.

and thus an exact determination of molar masses is impossible. An independent calibration was attempted by hyphenation of the GPC columns to a mass spectrometer. Since THF (and most other GPC solvents) cannot be used in ESI mass spectrometry, a modification of the standard method had to be made. In preliminary tests it could be shown that a mixture of THF/methanol (50/50) produced almost the same spectra as chloroform/methanol (50/50), and therefore an equal amount of

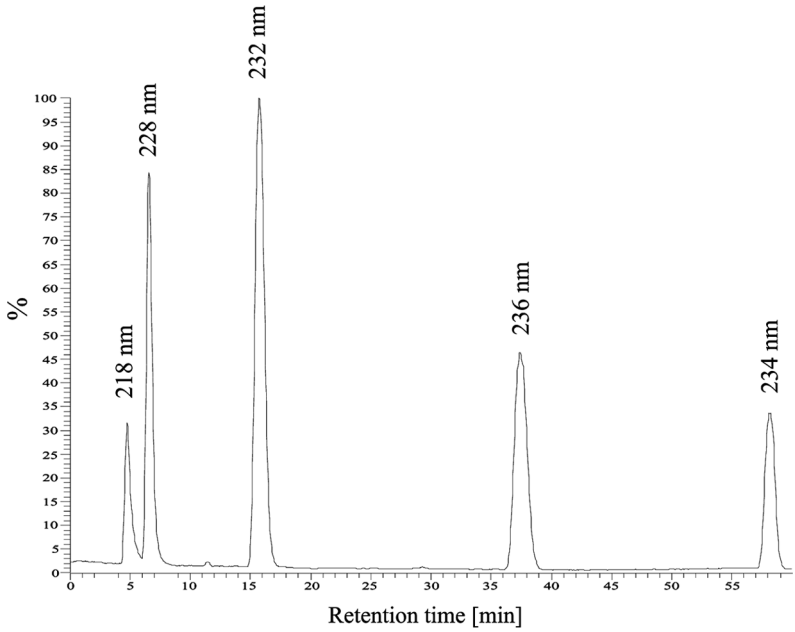

Figure 6. HPLC/UV chromatogram of an oligomeric resin showing the shift of UV absorption maxima with increasing degree of polymerization.

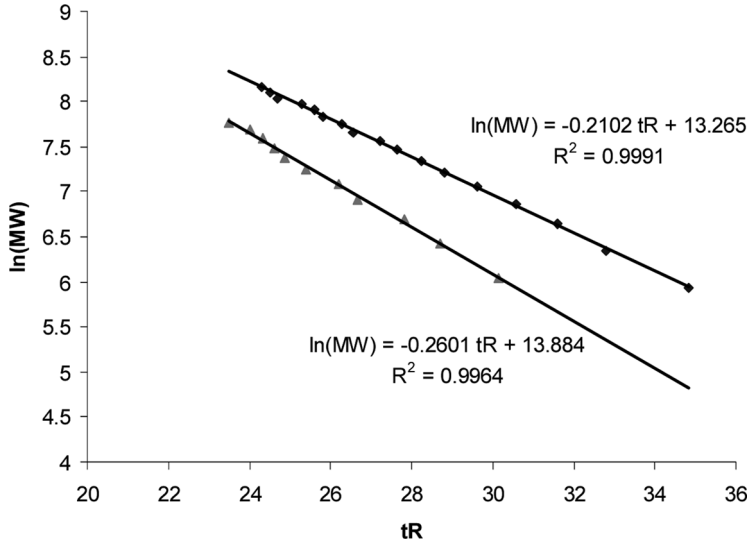

Figure 7. GPC calibration curves for the linear melamine resin with amino end groups (upper curve) and methoxymethyl groups (lower curve) obtained from mass spectrometry.

methanol was supplied to the eluent leaving the GPC column by means of a HPLC pump prior to entering the ESI source of the mass spectrometer. With this modification, we could determine a linear calibration curve for the melamine resin bearing no methylol or methoxymethyl groups in the range of 350 to 3500 g/mol (Figure 7). When this calibration is applied to a polystyrene standard with 2400 g/mol, its calculated molar mass would be 4800 g/mol, thus resulting in an error of 100%. The reason for this delayed elution of melamine resins is probably the polarity of the amino and hydroxyl groups, which make up the majority of the end groups. This hypothesis is also supported by the calibration curve calculated for the melamine oligomers containing methoxymethyl groups (Figure 7), which

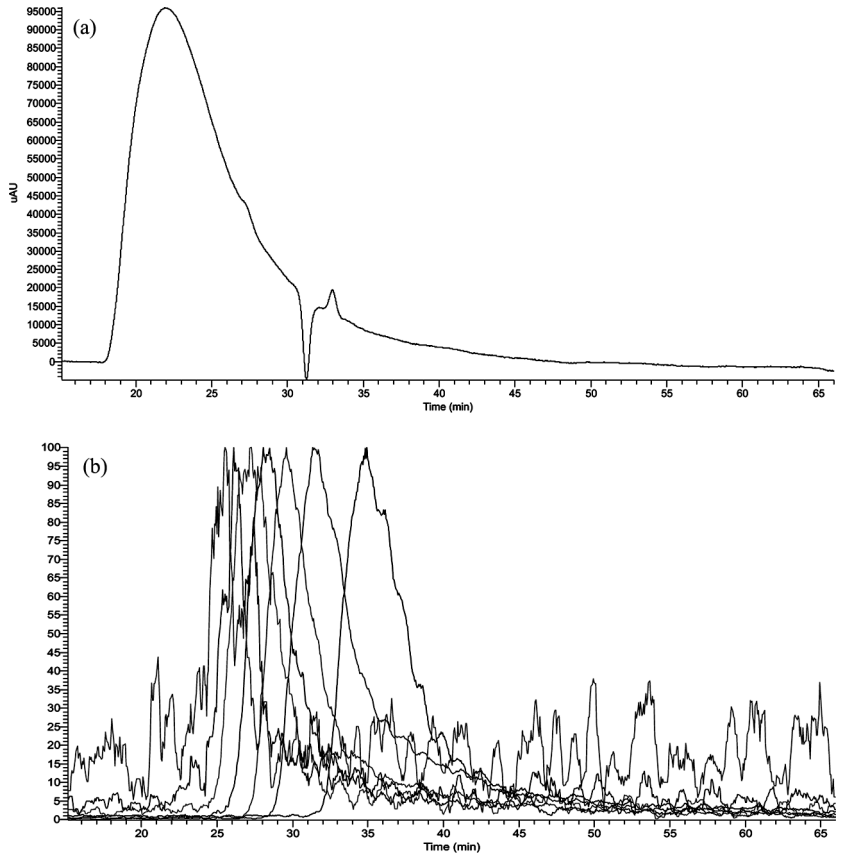

Figure 8. (a) GPC chromatogram of resin cured in toluene with a conventional UV detector at 232 nm (detector delay of 1 min added); (b) GPC/MS chromatogram showing the extracted ion traces for several oligomers (dp = 2, 4, 6, 8, 10, 12, 15).

is in accordance with the polystyrene standard. When the first MS calibration is applied to the GPC/UV results of the linear melamine resin cured in toluene, the weight average molar mass is 6330 g/mol, the number average molar mass is 3906 g/mol, the polydispersity index is 1.62, and the highest molar masses detected are around 13000 g/mol. Figure 8(a) shows the GPC results obtained with a UV detector, and in Figure 8(b) the extracted ion chromatograms for several oligomers as detected with mass spectrometry are displayed.

Pyrolysis

Pyrolysis was used to characterize a high molar mass sample of the linear melamine formaldehyde resin. Figure 9 shows that the polymer is degraded to its monomer level and that the most abundant product is TMM. But methylmelamines with higher and lower degrees of methylation are also formed. Pentamethylmelamine can be explained assuming a thermal cleavage to the methylene linkages between the melamine rings, similar to the one observed in mass spectrometry (Figure 3), resulting in the formation of a new methyl group. The formation of 2,4,6- and 2,2,4-trimethylmelamine indicates that methyl groups can also be cleaved off during the thermal degradation process. Because pyrolysis yields only a few products but with high intensities, it is extremely suitable for the identification of linear melamine formaldeyhde resin in composites, even if present only in low percentages (data not shown).

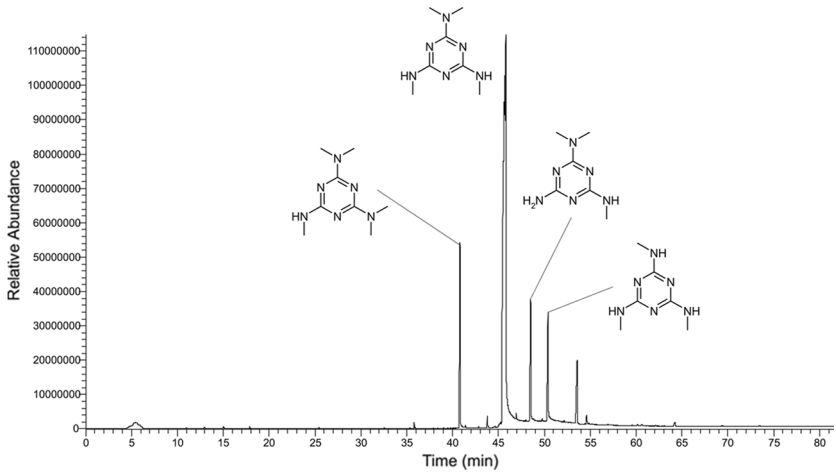

Figure 9. Pyrolysis-GC/MS analysis of a fully cured resin; the main products are due to breaking of the methylene linkages.

CONCLUSIONS

A broad variety of methods for the characterization of a novel type of resinous material has been presented. Although there are methods for each stage of the production of the resin there is no method that can be used exclusively throughout the production process. The most versatile method in our opinion is ESI-MS, which gives structural information as well as molar mass data (although only relative). Whenever there is the need for more detailed information, MS should be coupled to chromatography in order to obtain higher resolution of data or molar mass distributions. GPC can be used to determine molar masses and distributions but care must be taken with the calibration used, especially because other than steric exclusion interactions occur. Once the material is not soluble anymore, pyrolysis-GC/MS was shown to be a powerful technique whenever the task is to identify the material in a composite, even if there are only small quantities present.

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