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Accurate mass determination of melamine–formaldehyde synthetic polymers after separation on preparative HPLC

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ABSTRACT

Separation of 57 species from solutions of commercial melamines and analysis by high resolution mass spectrometry using electrospray ionisation and atmospheric pressure chemical ionisation is reported. Structures for melamine-based crosslinked polymers were also confirmed with two orthogonal techniques for characterisation of polymers: Fourier Transform Infrared Spectrometry (FTIR) and Nuclear Magnetic Resonance spectroscopy (NMR), respectively.

Accurate mass measurements of melamine–formaldehyde resin structures were achieved in the ppm range, using an internal calibration standard reserpine. Results were within 5 ppm of calculated formulae. Relative isotopic abundances of $[M+H]^+$ ions were evaluated for different fractions. Results were independent of the mobile phase used. NMR studies also confirmed structures of fractions and their thermal stability up to 70 °C. Differences in NMR spectra were explained by change of conformation and it was confirmed that this is a reversible process by reheating samples. Stability at 70 °C was confirmed by MS, since when the temperature of the ion transfer capillary in MS was set above this temperature decomposition occurred.

1. Introduction

Melamine–formaldehyde resins are a group of amine resins which have a wide range of uses in industrial applications. Their main role is that of crosslinker in the industrial coatings field which forms under strongly acidic conditions. Hexa(methoxymethyl) melamine is one type of melamine–formaldehyde resin which is commonly used as a cross-linking agent for polyester-based steel coatings [1]. Two types of crosslink reaction can take place during application, namely co-crosslinking and self-crosslinking. Both occur during film formation of system coating melamine resin. Co-crosslinking enhances flexibility, chemical resistance and weatherability as a consequence of forming covalent bonds between methoxy end groups of the melamine–formaldehyde resin and terminal hydroxyl groups from the polymer [2]. Hardness and solvent resistance are contributed by self-condensation as a side reaction in the coating industry which forms links between two methoxy melamine formaldehyde resins. Mechanical and solvent resistances are mainly defined by the reactivity of the monomer and the extent of crosslinking. The extent of cross- or self-crosslinking in MF cure depends on the selection of MF resin and cure temperature. This has a significant impact on the properties of water-thinnable coating materials and monitoring formulations of high-solid stoving enamels [2–7]. The determination of their chemical structure is therefore very important as it determines their usage.

Due to the structural complexity of MF resins the determination of chemical structures is very challenging and studies have been carried out over the last 20 years. A combination of various analytical techniques is often used for their structural elucidation, for example high field Nuclear Magnetic Resonance (NMR) spectroscopy [8–11] and separation techniques such as High Pressure Liquid Chromatography (HPLC) [12] and Gas Chromatography (GC) [9] with different detectors. In recent years the use of mass spectrometry as detector in synthetic polymer research has increased significantly [13]. Mass spectrometry (MS) has several advantages over other detectors. Its main advantage is that a mass spectrometer is an absolute detector, therefore from a high resolution mass spectrum the elemental composition can be determined, also fragments which correspond to different functional groups can be detected and structural information can be revealed [14].

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Different ionisation techniques have been used (ESI, APCI, FAB, MALDI) [15,16] and different analyzers were employed (Ion Trap, Quadrupole, TOF) [17–19]. Other, mainly spectrophotometric, detectors in combination with MS were also used (e.g. UV–vis, PDA, DAD) [12,15,19]. Some other chromatographic techniques were also used, such as Size Exclusion Chromatography (SEC) in combination with a Refractive Index (RI) detector [15], and Capillary Zone Electrophoresis (CZE) in combination with mass spectrometry [20]. Raman and Fourier Transform Infrared (FTIR) spectroscopy [21,22] and some thermal methods (e.g. Differential Scanning Calorimetry (DSC) [22,23] and Thermogravimetry (TGA) [24] were used as well.

In this paper, we focus on analysis of methylated melamine–formaldehyde resins by high resolution mass spectrometry in order to determine the structure of commercial samples. For this kind of complex mixture the accuracy of the detector is of vital importance. The high resolution Orbitrap mass detector can provide accurate mass, so determination of information on elemental composition and relative isotopic abundance are possible.

To achieve better understanding of the melamine–formaldehyde structure the sample was separated by preparative HPLC and fractions were collected. Different analytical techniques were then employed for structural studies; high-resolution (HR) MS as the main tool, along with ^{13}C and ^{1}H NMR and FTIR spectroscopy.

2. Experimental

2.1. Material

For this study the commercially available sample Komelol MM 90/GE, which is based on melamine–formaldehyde resin, was used. The molecular structure is governed by the molecular ratio of melamine (M) to formaldehyde (F) to monoalcohol (A). In the first step M is converted to methylol melamine with formaldehyde under acidic conditions and then etherified with a large excess of methanol (MeOH) [25]. A sample was synthesised as described in previous publications by Marcelli and citations included in this paper [26]. The average molar mass distribution measured by SEC was 360 Da with polydispersity (PDI) of 1.28 (THF Sigma–Aldrich, 5 μm SDV, 300 × 7.5 mm PSS Germany) at 30 °C. A sample was dissolved in MeOH (Merck, Germany) in a concentration of about 90 mg/mL, injected and separated on a Waters 600E HPLC preparative system equipped with a preparative Alltima C18 column (250 × 22 mm, 5 μm) with gradient elution and a gradient consisting of MeOH and water. The composition of mobile phase changed linearly from 40% MeOH to 100% MeOH over 115 min. Mobile phase flow was 10 mL/min and a UV detector at 240 nm was used. Seventy five peaks were obtained and collected in separate fractions. A Millipore Milli-Q water purification system was used to purify the water. Each fraction separated was then examined by analytical HPLC using an Alltima C18 column (150 × 4 mm, 5 μm) to check for the full width at half maximum (FWHM) of separated peaks. The area % for all peaks was below 50%. Only peaks with an area above 5% were further characterised by HPLC–MS, NMR and FTIR.

2.2. Instrumentation

2.2.1. NMR spectroscopy

Solvent was evaporated from each HPLC fraction by rotary evaporator to visual dryness and then used for further characterisation by NMR. Samples were dissolved in acetonitrile-d_3 (CD_3CN, CIL) at a concentration of approximately 10 mg/mL. Experiments were performed on a Bruker Avance III 500 MHz NMR spectrometer fitted with a 5 mm PATXI probe. The residual protonated solvent signal was used as a reference peak in ^{1}H NMR spectra at 1.94 ppm and in ^{13}C NMR spectra at 1.32 and at 118.26 ppm. Sensitivity-enhanced ^{1}H–^{15}N 2D heteronuclear single quantum coherence (HSQC) and heteronuclear multiple bond coherence (HMBC) experiments were carried out at 25 °C. The temperature stability of samples was also studied by NMR. Samples were placed in an NMR tube and the NMR probe was heated to 25 °C, 30 °C, 50 °C and 70 °C. ^{1}H NMR measurements were performed 5 min after the temperature had stabilised. NMR processing was done using Bruker TopSpin software version 3.2.

2.2.2. Mass spectrometry

HPLC-MS experiments were performed on a Dionex Ultimate 3000 system (Thermo Scientific) coupled with a Thermo Q Excative mass spectrometer (Thermo Scientific). The Dionex Ultimate 3000 UV detector (Thermo Scientific) wavelength was set at 235 nm. 1 μL of sample was injected with a Dionex Ultimate 3000 Autosampler onto a Merck Chromolith C18 column (100 mm × 4.6 mm, 2.7 μm). The temperature of the column was maintained at 30 °C. Two different chromatography conditions with a linear gradient were used (Fig. 1(a)). Four minutes were allowed for column conditioning. UV chromatograms for separate fractions are presented in Fig. 1(b).

Two ionisation techniques for MS analysis were used. The instrument resolution was set on 140,000 with detection m/z window in the range 200–2000 and an automatic gain control (AGC) target of 1×10^6. A pre-scan was performed in the m/z range 100–4000, which confirmed that no significant peaks were above the m/z 2000 and below 200, therefore the above mentioned range was used for mass spectrometry. Electrospray ionisation (ESI) was employed at spray voltage 3.8 kV and capillary temperature was set at 70 °C, 270 °C and 350 °C. Atmospheric Pressure Chemical Ionisation (APCI) was used with a source temperature of 350 °C and discharge current of 3.4 μA. Both ionisation sources used nitrogen as sheath gas with a flow of 40 arbitrary unit (a.u.), auxiliary gas flow 15 a.u. and sweep gas flow 10 a.u. Thermo Scientific software Xcalibur version 2.2.SP1.48 was used for data acquisition and processing. Calculated results with an error <5 ppm were displayed.

2.2.3. FTIR

Sample solutions previously used for NMR were deposited onto an ATR diamond crystal and analysed using a Nicolet 6700 FTIR spectrometer (Thermo Scientific). Spectra were collected after acetonitrile-d_3 had evaporated from the crystal. The spectral range of measurement was from 7000 to 650 cm^{-1}. All analyses were acquired with 200 scans and an instrument resolution of 4.0 cm^{-1}.

3. Results and discussion

3.1. Technology

The functional groups of this type of MF resins are free methylol groups, etherified methylol groups and unsubstituted NH groups from the amides. The general structure of this type of melamine resin can be written as $M_nF_xMe_y$ in which M represents melamine (1,3,5-triazine-2,4,6-triamine), F represents formaldehyde (CH_2O) and Me represents the methyl end group as shown in Fig. 2. The purpose of this research was to characterise and determine the composition of this complex but widely used industrial mixture with high resolution mass spectrometry. Structural complexity of MF resin was confirmed by higher polydispersity (PDI) by SEC analysis of melamine–formaldehyde resins.