## Abstract

Modified melamine (M) resins are a group of amino resins which have a wide range of uses in industrial applications. Due to their crosslinking characteristics and structural complexity modified melamine (M) resins have presented a challenge in the field of characterisation and determination of chemical structures for the last 20 years.

The purpose of my research work was developing methods and determination of hydrodynamic volume of modified melamine (M) resin by size-exclusion chromatography (SEC), and hereby setting separation conditions, columns, standards, mobile phases for modified melamine resins. Modified melamine resins are low-mass oligomeres, which causes problems in separation by SEC. SEC methods are usually applied to molecules with bigger hydrodynamic volume. Better separation was achieved by consecutive connection of multiple columns and appropriate selection of the mobile phase. There are no available SEC standards for modified melamine resins, therefore, polyethylene glycol standards were used at SEC determination of hydrodynamic volume for calibration of water soluble modified melamine resins, and polystyrene standards were used for organic soluble modified melamine resins.

Determination of chromatography conditions using different ranges of columns, mobile phases and sample preparation enabled successful separation of modified melamine resins on HPLC system by the use of MS, RI and PDA detectors. Development and optimisation of the HPLC-MS methods of modified melamine resins was the main task and challenge of this research work. The best chromatography results of separation were achieved for higher modified melamine resins with RP-C18 column, and for partly modified melamine resin with RP-C8. The unmodified melamine resins were separated by using gradient separation of 50 Mm $NH_4COOH$ (MQ/MeOH) on HypersilCarb column. During the method development the influence of ionization, concentration of samples and composition of the mobile phase on the MS spectrum was observed. Decomposition and polymerization of modified melamine resin was studied during chromatography separation and MS detection.

The main part of my PhD research is devoted to monitoring modified melamine resins at different synthesis conditions by HPLC-MS and SEC. With SEC I monitored mass distribution for highly modified melamine resins at different synthesis conditions: temperature and pH. Results show that modified melamine resins with higher hydrodynamic volume are formed at increased temperatures, whereas crosslinking modified melamine resins are formed at lower pH. Decreasing of pH in synthesis results in insolubility of modified melamine resins in most organic and aqueous solvents. The proportion and structures of highly modified melamine resins were determined during the etherification with methanol in synthesis by HPLC-PDA-MS and NMR. One of the tasks was to observe the influence of different syntheses of modifided melamine resins on their hydrodynamic volume and structure. The syntheses were: melamine with carbonyl groups of formaldehyde, polyoxymetyly (paraformaldehide) and mix of formaldehyde and paraformaldehyde in equimolar ratio.
Syntheses were done at the same synthesis conditions. Results show that we can build up a higher hydrodynamic volume of modified melamine resins by addition of formaldehyde to the synthesis.

With preparative HPLC system I fractionated 57 species of commercial highly modified melamine resin. Fractions were analyzed by High Resolution Mass Spectrometry Orbitrap, and $^{13}C$ along with $^{1}H$ NMR and FTIR spectroscopy were used for additional confirmation of end groups and structures. In MS I used electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) as ionization techniques. For detailed structure characterization I used tandem mass spectrometry (MS/MS) experiments and RDB (ring and double bonds) values of product ions as help. NMR studies of isolated fractions confirmed their thermal stability up to 70 °C. Differences in NMR spectrum at temperature increse were explained by the change of conformation. This change is a reversible process as the NMR spectrum remains the same before and after heating. Temperature stability up to 70 °C was confirmed by MS, however, when the temperature of the ion transfer capillary in MS was set above this temperature, sample decomposition occurred.

***Key words:*** Modified melamine resins, HR MS, HPLC-MS, SEC.