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Original scientific paper

Molar-mass distribution of urea–formaldehyde resins of different degrees of polymerisation by MALDI-TOF mass spectrometry

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Abstract: This paper describes some results obtained in an investigation of urea–formaldehyde (UF) resins of different degrees of polymerisation by matrix-assisted laser desorption/ionisation time-of-flight (MALDI-TOF) mass spectrometry (MS). MALDI-TOF MS proved to be an appropriate technique for analyzing these types of polymers, bearing in mind that the results of the analysis correspond with previous physical and chemical measurements. This technique enables a relatively swift determination of the degree of polymerrisation through the monitoring of key changes in the structure of a polymer. Thus, in the analysis of UF resins, it may be possible to monitor a decrease in the intensity of the monohydroxymethyl urea (MMU) signal, which corresponds to an increase of the mass spectra values in the mass range of higher homologues, above 1000 g mol^{-1}. A noticeable difference concerns the signal intensities in the higher mass ranges (up to 1400 g mol^{-1}), which corresponds to more branched and longer homologues of the polymers. Especially, a significantly more intensive signal of MMU was registered. The average molecular weight (*MW)* of the examined samples was between 936 and 1324 g mol^{-1}, with a maximal deviation of 20 %, depending on the ratios of the reactants.

Keywords: urea-formaldehyde resins; molar ratio; molecular structure; degree of polymerisation; MALDI-TOF.

INTRODUCTION

Urea–formaldehyde, UF, resins are the most important type of adhesives in the wood industry. They are widely used for the production of wood-based composite panels, such as particleboards, fibreboards and plywood.[1]

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UF resins are based on a manifold reaction of two monomers, urea and formaldehyde.[2] By using different reaction and preparation conditions, a more or less innumerable variety of condensed structures is possible.[3] In the application stage, UF resins are still soluble or dispersed in water. They also can be supplied in the form of spray-dried water-soluble powders. Such structures consist of linear or branched polymeric molecules of various molecular masses. After hardening, UF resins form insoluble three-dimensional networks of thermosetting duromers.[4]

Although UF resins consist of only two main components, *i.e.*, urea and formaldehyde, they present a broad variety of possible reactions and structures.[5] This variety leads to a wide range of molar mass distributions in UF resins, from low molar mass molecules up to more or less polymeric structures. The highest molar masses in UF resin cannot be clearly determined, but it is estimated that molar masses of 100000 to 500000 g mol^{-1} can successfully describe the macromolecule structure of UF resins.[3,6–8]

From the viewpoint of end-use applications of UF resins, the molar mass distribution is a very important chemical characteristic, having an influence on several important properties of the resin, such as: viscosity, flow ability, penetration into the wood surface,[9,10] distribution on the wood furnish (particles or fibres), water dilute ability,[11] *etc*. The molar mass distribution can be determined by means of gel permeation chromatography (GPC),[12] but it is very difficult because an increase in the molecular weight of the soluble macromolecules and in the degree of branching leads to the formation of insoluble products.[13] In addition, analysis of the structural components can be performed by various spectroscopic methods, such as: infrared (IR);[14–19] nuclear magnetic resonance (NMR), *i.e.*, ^{1}H-NMR,[20–23] ^{13}C-NMR,[14,24–28] ^{15}N-NMR[9,30] and Raman spectroscopy.[31]

Matrix-assisted laser desorption/ionisation time-of-flight (MALDI-TOF) mass spectrometry has greatly expanded the use of mass spectrometry towards large molecules and has been demonstrated to be a powerful method for the characterization of both synthetic and natural polymers. This technique is usually combined with a time-of-flight (TOF) mass analyzer, which has the advantages of being capable of providing a complete mass spectrum per event, having a virtually unlimited mass range, requiring a small amount of analyte and relatively low cost equipment.[32–34]

Generally, the polycondensation structures of UF resins have not been studied thoroughly by the MALDI-TOF technique. Therefore, the objective of this research was a MALDI-TOF investigation of the molar mass distribution of UF resin samples obtained from the same reactor batch, but having three different degrees of polymerisations.

EXPERIMENTAL

Preparation of urea–formaldehyde (UF) resins with various viscosities

Urea–formaldehyde resins were synthesized *via* the reaction between formalin at a concentration of 47.69 % and urea by DUKOL Ostrava (the Czech Republic). Four samples of about 1 L, designated as I, II, III and IV, were taken from the same reactor batch when the viscosity values showed that different degrees of polymerisation had been attained. Samples I–III were prepared at an F:U molar ratio of 2:1. Sample IV was prepared by modification of sample III by the addition of formaldehyde to give an F:U ratio of 1.45:1. All the samples were kept in a refrigerator before further use.

The samples were tested for viscosity, dry matter content, pH value, gel time and pot life. The obtained results are presented in Table I.

In order to determine the dry matter content, 2.0 g of resin were dried in a laboratory oven at 105 ± 2 °C until constant mass was reached.

The viscosity of the four UF resins was determined by the Brookfield method. The test values registered on the Brookfield instrument together with factors based on the employed combination of the type of rotating spindle and the rotation speed were used to calculate the viscosity in Pa s.

The pH value of each UF resin sample was determined by inserting a glass electrode directly into the emulsion.

The gel time of the resins containing hardener was determined by the boiling water test. The time measurement began when a test tube containing approximately 2.0 g of resin together with the hardener ammonium sulphate (1 % based on the adhesive dry matter) was immersed into boiling water. The resin in the test tube was gently stirred throughout the test. The gel time was taken as the time elapsed from immersion of the test tube until hardening of the resin, when stirring was no longer possible.

The densities of the resins were determined at 20 °C using a pycnometer of 25 mL nominal volume, the exact volume of which was determined using distilled water.

Preparation of the MALDI matrix

A saturated solution of α-cyano-4-hydroxycinnamic acid (CHCA) was prepared by dissolving the matrix in 50 % acetonitrile with 0.10 % trifluoracetic acid. The solution was vortexed thoroughly and sonicated in a water bath for several minutes at room temperature. The solution was used for the preparation of samples for MALDI-TOF MS. All employed chemicals were of p.a. purity, originating from Sigma-Aldrich (St. Louis, WI, USA).

Matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry

An aliquot of each sample solutions containing an internal standard was combined 1:1 with the CHCA matrix and mixed thoroughly. Aliquots (0.50 μL) of the mixtures were spotted onto a 100-spot sample plate (Applied Biosystems) and air-dried. Mass analysis was performed in the positive ion reflector mode using a 200 Hz frequency pulsed N_2 laser operating at 327 nm. Five spectra at each of 10 randomly selected positions were accumulated per spot between 170 and 500 g mol^{-1} using the MS positive ion reflector mode acquisition method. Calibration of the instrument was realised using Calibration mixture 2 as the external standard. To generate spectra with high mass accuracy, an internal calibration was performed.

Sample preparation

For the analysis of silver clusters, 1.0 mg mL^{-1} solutions in 0.10 % trifluoracetic acid were prepared. 0.50 μL of these solutions was placed onto 0.50 μL of CHCA solution on the target.

Data analysis

Samples of the UF resins (I–IV) were mixed with the CHCA matrix in ratios of 1:100 and 1:10, v/v. The concentration of CHCA was 10 mg mL^{-1}, diluted in a 1:1 acetonitrile and water solution. After dilution, 0.50 μL volumes of samples were placed on the MALDI plate. Samples were air dried and analyzed on a 4800 Plus MALDI TOF/TOF analyser (Applied Biosystems, Foster City, CA, USA) in the positive mode. Data Explorer, version 4.9, was used for the analysis of the recorded spectra. Ions of the CHCA matrix were used for internal calibration, based on the theoretically calculated masses of CHCA monomers, dimers and trimers at *m*/*z* 190.05 (molecular formula $C_{10}H_7NO_3$), 379.09 (molecular formula $C_{20}H_{14}N_2O_6$) and 568.14 (molecular formula $C_{30}H_{21}N_3O_9$), respectively. The mass spectrum of the matrix alone was recorded in order to eliminate the signals generated by the matrix itself. Baseline correction and Gaussian smoothing was applied to each mass spectrum.

Positively charged ions were analysed in the reflector mode using delayed ion extraction. The spectra were recorded with a 200 Hz frequency data-sampling rate. Unless otherwise stated, the extraction delay time was 150 ns and deflection was used to suppress ions up to *m*/*z* 500. The spectra were recorded using the reflector mode of the TOF analyzer under delayed extraction conditions, thus improving the mass accuracy and resolution. The extraction voltage was 20 kV in all cases. Other instrument parameters were tuned for optimal resolution. All instrument high voltages were left on between all analyses to ensure a stable instrument performance. After short interruptions (< 7 min), while exchanging the sample plate, the high voltages of the instrument were switched on 50 min prior to spectra acquisition. The applied laser intensity was between 10 and 30 % of the maximum available laser power.

The spectra were acquired without a low mass gate and each spectrum represents an average of at least 100 single laser shots.

RESULTS AND DISCUSSION

Physical characteristics of UF resins

The characteristics of UF resins (Table I) showed no significant differences between samples I–III, except for the viscosity, sample III having a viscosity of 555 mPa s, while the viscosities of samples I and II were 218 and 281 mPa s, respectively. All the determined physical properties were significantly increased for sample IV in comparison to the other samples, which clearly distinguishes sample IV from samples I–III. The viscosity of sample IV was 2052 mPa s, a value 3 to 9 times higher when compared with the other samples. It will be quite evident later that increased content of higher homologues increased the viscosity of this resin.

TABLE I. The characteristics of the UF resins (Samples I–IV)

No.	Property	UF Sample			
		I	II	III	IV
1	Dry matter, %	53.7	53.6	53.8	65.6
2	Brookfield viscosity (at 20 °C), mPa s	218	282	555	2052
3	pH	7.8	7.9	8.0	7.7
4	Gel time, s	58	59	58	59
5	Density, g cm^3	1.24	1.24	1.25	1.30

Degree of polymerisation

The recorded spectra of samples I–IV (Figs. 1 and 2), obtained on the MALDI-TOF/TOF instrument, implicate a close relationship between viscosity, dry matter content and degree of polymerisation of the UF resin samples. A comparison of spectra revealed sample I had the lowest degree of polymerisation and also the lowest viscosity.

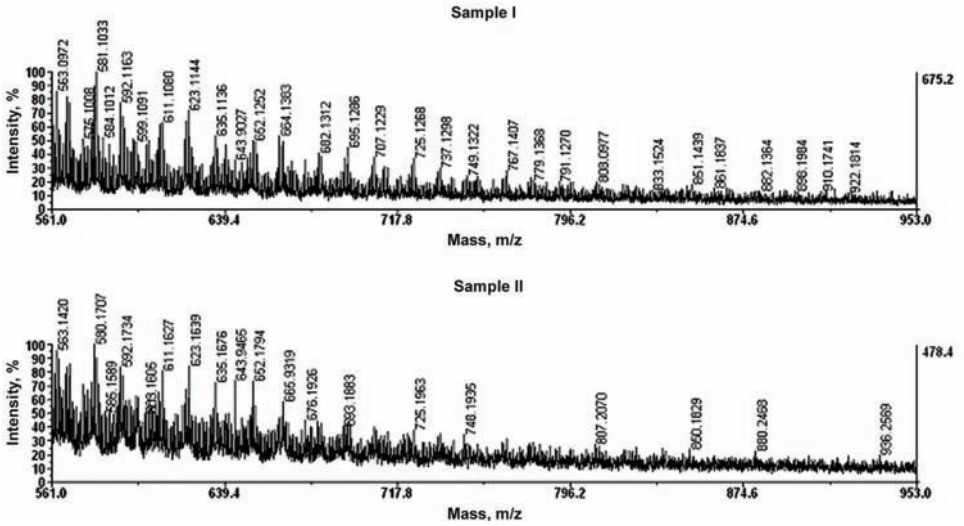

Fig. 1. MALDI-TOF Mass spectra of samples I and II in the *m*/*z* range 561–953.

Results of the analysis showed that samples I and II had similar degrees of polymerisation, but with a slightly higher amount of branching in sample I, as indicated by its more pronounced mass signals in the *m*/*z* range 561–953 (Fig. 1). Although, both samples had a similar dry matter content, they differed in viscosity, with sample II having an approximately 30 % higher viscosity than sample I.

Due to its higher viscosity, an increased amount of homologues with a higher degree of polymerisation is to be expected in sample II. However, the difference between the signal intensity of the higher homologues in samples I and II was negligible (also when compared with samples III and IV).

The dry matter content of samples I, II and III were similar. On the other hand, the viscosity of sample III was almost twice that of samples I and II. A higher viscosity implies a higher degree of polymerisation, which can be observed in the mass spectrum of sample III, shown in Fig. 2.

In addition, three times more intense signals in the same mass range of the higher polymerisation homologues were registered for sample III (data not given) than for samples I and II (shown in Fig. 1).

According to its physical and chemical parameters, sample IV had no similarities with samples I–III, having an almost one order of magnitude higher viscosity compared with the other three samples, a 10 % higher dry matter content and a significantly increased degree of polymerisation of higher homologues, as shown in Fig. 2.

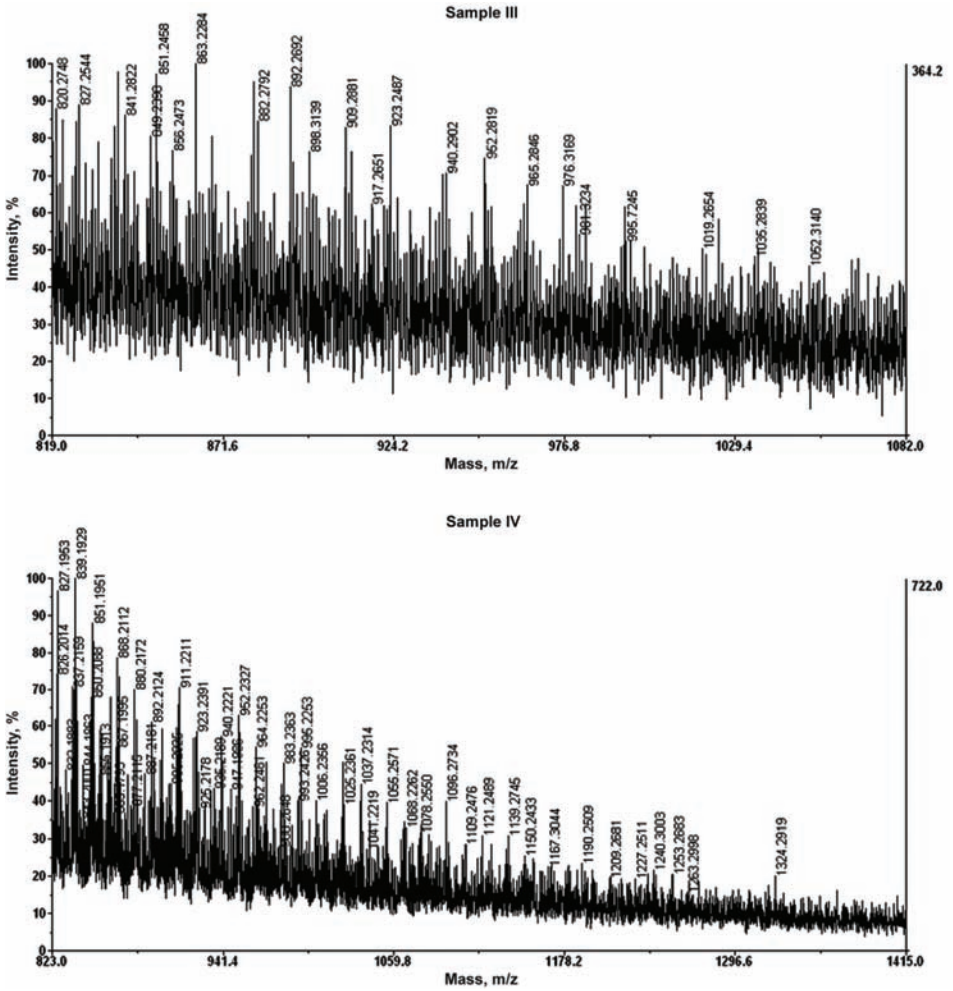

Fig. 2. MALDI-TOF Mass spectra of sample III (maximum registered polymer mass 1052 g mol^{-1}) and sample IV (maximum registered polymer mass 1324 g mol^{-1}).

Comparison of the polymer structures of samples I, II, III and IV

Higher homologue products of the polymerisation processes, which are registered in the *m*/*z* range 200–1200, may be described through a combination of the residues in the general structure. Confirmation of such structures was based

on both external and internal calibration. The external calibration was applied on the mass spectra shown in Figs. 1 and 2, with an experimental error of 0.10 g mol^{-1} of the mass value. In addition, the mass spectra were internally calibrated (see later in the text Figs. 5–7) using signals originating from the ions of the CHCA matrix, which increased the mass measurement accuracy to 5 ppm (third of the four decimal digits of the mass value). Accurate mass measurement leads to a better determination of the elemental ion composition and, in this sense, the molecular formula of a link can be established. As the polymers consisted of a series of links, it was impossible to determine the molecular formulas of all the polymers. However, it was possible to determine the constitutive elements of the polymer structure.

The true mass and molecular formula were determined using the signals of the highest intensity in order to identify the structure of the higher homologues. Within the observed mass range and according to the signal intensity, it is possible to determine the type of homologue and the preferred form of branching. NMR research indicated that the formation of mono-, di- and tri-hydroxymethyl urea under alkaline conditions amounts to 45–60 % and partial polymerisation to dimethyl ethers to 10–20 % (*i.e.*, –NH–CH_2OH 45–60 % and –$N(CH_2OH)_2$ 10–15 %).[35] In addition, 10–15 % of the formaldehyde remained unreacted. The formation of methylol groups mostly depended on the F/U molar ratio, with higher molar ratios increasing the tendency to form highly methylolated species.[36,37]

The significant intensive signal of MMU can be seen at *m*/*z* 91 in the MALDI-TOF mass spectra of samples I–IV shown in Fig. 3. Some examples of polymer chains of ether homologues are demonstrated in Figs. 4 and 5, from which, it is possible to determine the representative type of molecular structure originating in the branching process and growth of the polymer chains. This might reveal if the method of synthesis favours the creation of ether or methyl bonds and, furthermore, allow an estimation of the preferred number of hydroxyl groups per number of carbons in the chain. As expected, the highest MMU intensity of 68,000 was registered for sample I, in comparison to sample IV, with an MMU intensity of 22000. Contrary to sample IV, which had an increased ratio of higher homologues, sample I had increased amounts of simple MMU structures, 3.1 times higher when compared to sample IV, suggesting poor branching in sample I and a high degree of polymerisation of sample IV. The relations between samples II and III were similar to those of samples I and IV. Thus, sample III had a higher ratio of higher polymer structures in comparison to sample II, while sample II had a 2.7 times more intensive MMU signal when compared to sample III.

Structures **A**, **B** and **C** shown in Fig. 5 may also belong to structures with hydroxymethyl groups with secondary and tertiary amines in different positions. Thus, the molecular formulas of structures **A** $C_8H_{18}N_4O_5$, **B** $C_9H_{20}N_4O_6$ and **C** $C_{10}H_{22}N_4O_7$ would have to be preserved. Mass spectra showing the intensity of the structures **A**, **B** and **C** are shown in Fig. 6.

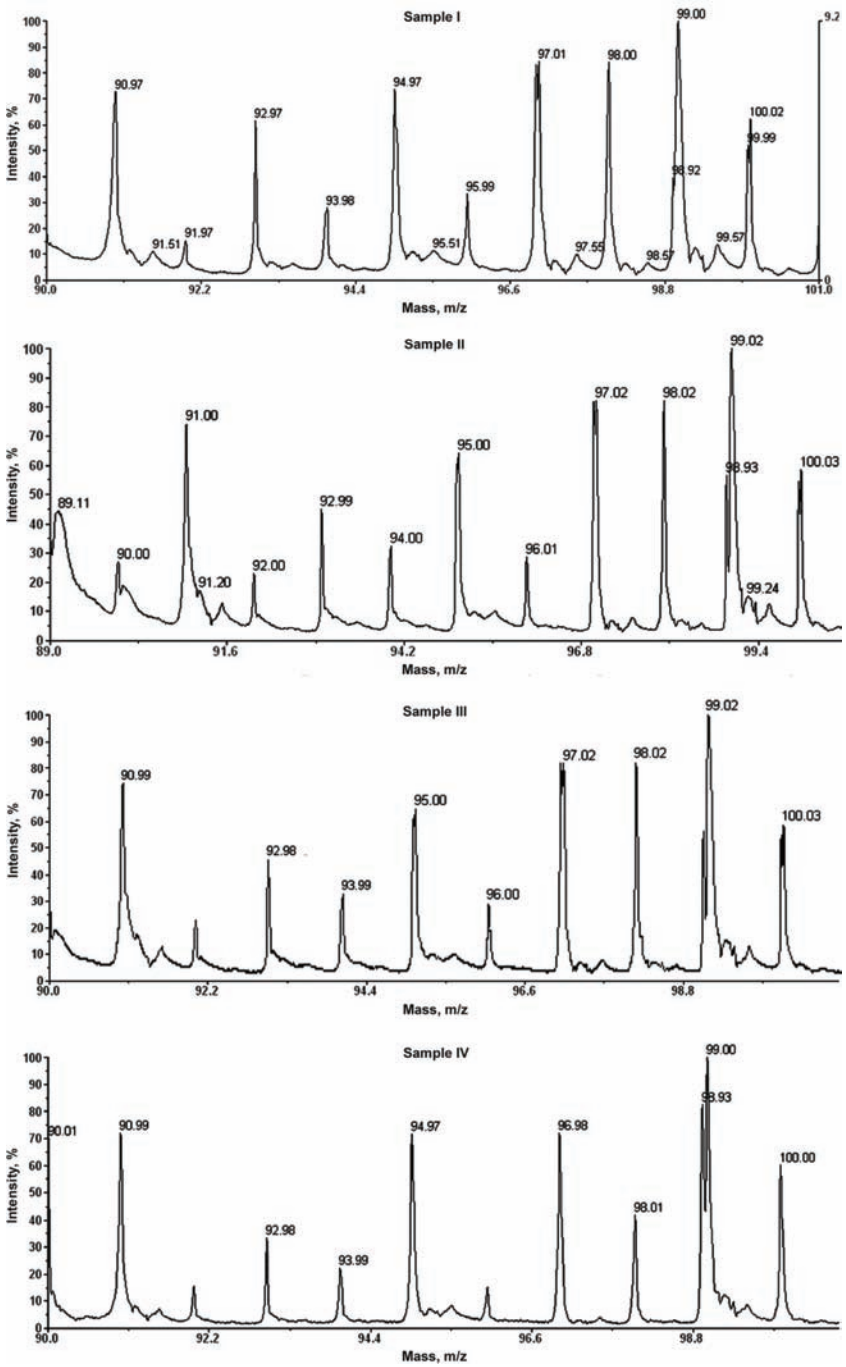

Fig. 3. MALDI-TOF Mass spectra of samples I–IV, with a significant intense signal of monohydroxymethylurea (MMU) at *m*/*z* 91.

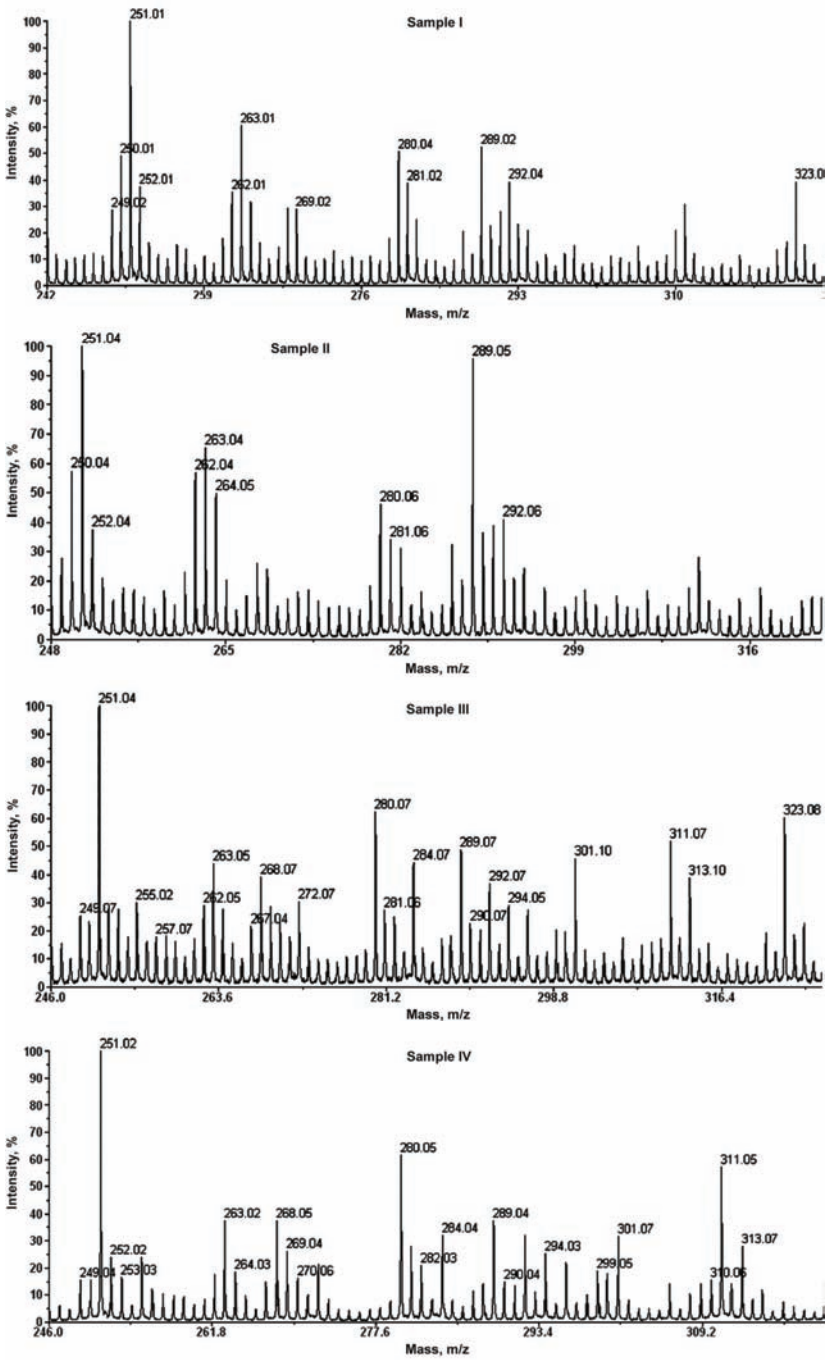

Fig. 4. Molecules formed through reaction of urea and formaldehyde under alkaline conditions, registered in the *m*/*z* range of 250–312.

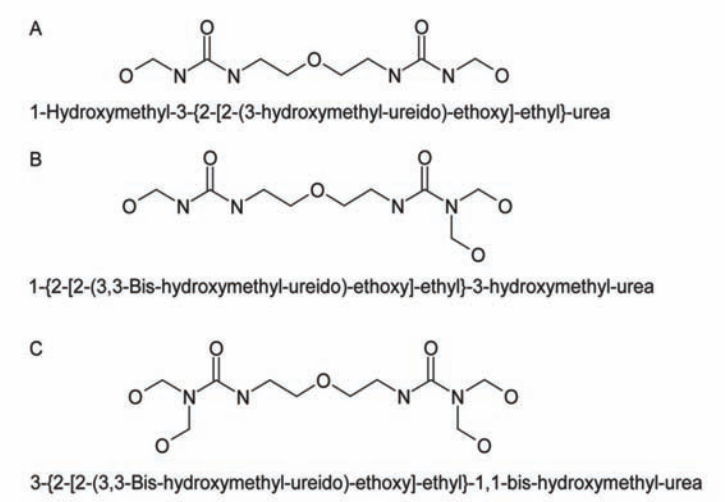

Fig. 5. Molecules formed through reaction of urea and formaldehyde under alkaline conditions, registered in the *m*/*z* range of 250–312. The associated theoretical *m*/*z* values for structures **A**, **B** and **C** are 251.14, 281.14 and 311.16, respectively.

The mass spectrum of sample IV for the selected region is shown in Fig. 6. Identical mass spectra were obtained for samples I–III. According to the signal intensity of the ion structures **A**, **B** and **C**, it may be concluded that the homologues containing ether bonds are more abundant than those of homologues with methylene bonds are. It may also be concluded that the most intensive signals in the spectra belong to structures with terminal di- and tetrahydroxymethylene groups (structures **A** and **C**). The calculation of molecular formulas in regards to the

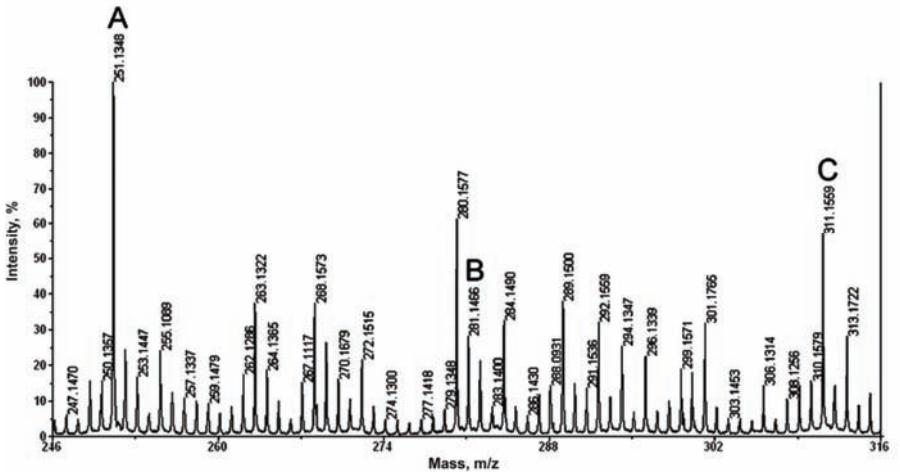

Fig. 6. MALDI-TOF Mass spectra of sample IV with the **A**, **B** and **C** structures designated.

measured molecular masses for structures **A**–**C** were possible because a maximum measurement error of 5 ppm was achieved.

Methylene bridges, branching polymer structures, are present over the whole spectrum and signify the difference between peaks of 12 g mol^{-1} or 12.0072 g mol^{-1} as measured and shown in Fig. 7.

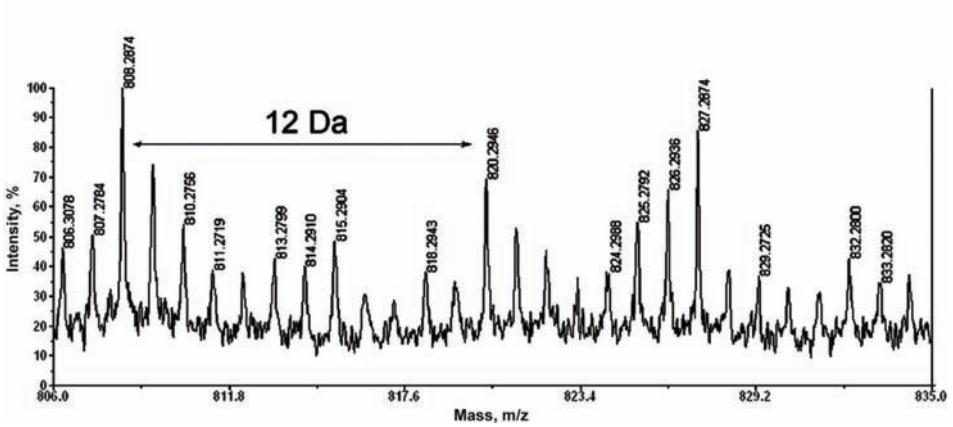

Fig. 7. MALDI-TOF Mass spectrum of sample IV with noticeably constant differences of 12 g mol^{-1} between the most intensive signals in the spectrum.

CONCLUSIONS

This paper describes some results obtained in an investigation of urea–formaldehyde (UF) resins of different degrees of polymerisation by MALDI-TOF mass spectrometry. Each of the four samples gave a contribution to the elucidation of the establishment of the molar masses of the resins. The interpretation and combination of the results led to following conclusions:

1) The average *MW* of the examined samples I–IV of UF resin was between 936 and 1324 g mol^{-1}, with a maximal deviation of 20 %, depending on the ratios of the reactants.

2) The signal intensities and their positions regarding samples I–IV showed no differences. The only noticeable difference concerned the signal intensities in the higher mass ranges (up to 1400 g mol^{-1}), which corresponds to more branched and longer homologues of the polymers.

3) Sample IV had, by far, the highest degree of branching and polymerisation when compared to samples I–III, which was evidenced as it was the polymer giving the highest recorded mass of 1324 g mol^{-1} and multiple higher signal intensities in the *m*/*z* range of 250–1000.

4) MALDI-TOF proved to be an appropriate technique for analyzing these types of polymers, bearing in mind that the results of analysis corresponded with the results of physical and chemical measurements (dry matter content, viscosity,

gel time, *etc*.). For routine polymer analysis, this technique enables a relatively swift and simple determination of the degree of polymerisation, through the monitoring of key changes in the polymer structure. It may be possible to monitor a decrease in the intensity of the MMU signal, which corresponds to an increase of the mass spectra values in the mass range of higher homologues, above 1000 g mol^{-1}.

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И З В О Д

РАСПОДЕЛА МОЛАРНЕ МАСЕ УРЕА–ФОРМАЛДЕХИДНИХ СМОЛА РАЗЛИЧИТОГ СТЕПЕНА ПОЛИМЕРИЗАЦИЈЕ ОДРЕЂЕНА МАСЕНОМ СПЕКТРОМЕТРИЈОМ MALDI-TOF

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У циљу карактеризације четири узорака уреа–формалдехидне (УФ) смоле, коришћена је метода масене спектроскопије MALDI-TOF (матрицом потпомогнута ласерска десорпција/јонизација-време прелета). Као један од видова анализе полимера, поменута техника омогућује релативно брзо одређивање степена пилоконденсације путем праћења кључних промена у структури полимера. При анализи узорака УФ смоле утврђено је да смањење интензитета ММУ сигнала одговара повећању вредности масеног спектра у опсегу виших хомолога изнад 1000 g mol^{-1}. Значајна разлика односи се на интензитет сигнала при вишем масеном опсегу (до 1400 g mol^{-1}), што одговара разгранатијим и дужим полимерним хомолозима. Средња *Mw* испитиваних узорака налази се у опсегу од 936 до 1324 g mol^{-1}, са максималном девијацијом од 20 % у зависности од компоненти.

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