# $^{13}$C-NMR, $^{13}$C-$^{13}$C gCOSY, and ESI-MS Characterization of Ether-Bridged Condensation Products in *N,N'*-Dimethylurea-Formaldehyde Systems

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Dedicated to Prof. Dr. C. Kreiter on the occasion of his 75th birthday

**ABSTRACT:** The reaction of urea with formaldehyde is the basis for the production of urea-formaldehyde (UF) resins which are widely applied in the wood industry. The presence of ether-bridged condensation products in the UF resin reaction system is an open question in the literature. It is addressed in the present work. The *N,N'*-dimethylurea-formaldehyde model system was studied since it is chemically similar to the UF resin reaction system but allows for a simple elucidation of all reaction products. It was analyzed by $^{13}$C-NMR spectroscopy and ESI-MS. In corresponding NMR and MS spectra, peaks due to methoxymethylenebis(dimethyl)urea and its hemiformal were observed. $^{13}$C-$^{13}$C gCOSY analysis was conducted using labeled $^{13}$C-formaldehyde. The correlation spectra showed evidence for an ether-bridged compound and mass spectra exhibited peaks agreeing with labeled methoxymethylenebis(dimethyl)urea and its hemiformal. Methoxymethylenebis(dimethyl)urea was characterized in *N,N'*-dimethylurea-formaldehyde systems in acidic and slightly basic media. As urea is very similar to *N,N'*-dimethylurea, the results of this work strengthen the assumption that ether-bridged condensation products are likely to form in UF resins. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 3957–3963, 2013

## INTRODUCTION

Applications of urea-formaldehyde (UF) systems have intensely been investigated since they are major binders for the wood industry. While the synthesis process of UF resins has been described elsewhere,[1–3] the mechanism of condensation is still unclear. Condensation pathways involving the formation of methylene bridges are predominant in acidic medium but it is believed that small amounts of ether-bridged condensation products also occur at this pH-range.

Various analytical methods have been applied to investigate the structure of compounds formed during the UF resin synthesis including elemental analysis,[4,5] thin-layer chromatography,[6–8] liquid chromatography,[9,10] infrared spectroscopy techniques,[11,12] Raman spectroscopy, mass spectrometry, and NMR spectroscopy.[13–22] A detailed overview on the efforts and methods used to characterize UF resins is given by Carvahlo et al.[23] Using

NMR spectroscopy Tomita and Hatono[15] confirmed the existence of internal methylene ether bridges, cyclic uron derivatives, in UF resins and referenced their chemical shifts. More recently, $^{13}$C-NMR studies[24,25] proved that strong acidic conditions (and pH higher than 6, ref. 24) favor their formations. However despite extensive investigations, ether-bridged condensation products have not yet been fully characterized or isolated and their existence has still not unambiguously been proven. The large number of products with similar substructures in the UF resin network hinders analytical investigations since similar molecules have similar physical and chemical behavior. For NMR spectroscopy the main difficulty is to distinguish ether-bridged condensation products (A) from methylolmethylenediureas (B) and from methylolurea hemiformals (C) (see Table I). As $^{13}$C peaks of ether-bridged moieties —NR$CH_2$O$CH_2$NR— overlap peaks of methylolurea hemiformal

**Table I.** Analytical Challenge

| A | B | C |
|---|---|---|
| $C_4H_{10}N_4O_3$, 162.15 g mol$^{-1}$ | $C_4H_{10}N_4O_3$, 162.15 g mol$^{-1}$ | $C_2H_6N_2O_2$ [CH$_2$O]$_n$, 90.08 + $n$ 30.03 g mol$^{-1}$ |
| Methoxymethylenediurea | Methylolmethylenediurea | Methylolurea hemiformal |

moieties —NR$CH_2$O[$CH_2$O]$_n$H and as $^{15}$N peaks of —N$RCH_2$OC$H_2$NR— and R—N$CH_2$NR— overlap (or are very close to each other), neither $^{13}$C- nor $^{15}$N-NMR spectroscopy alone can provide a full structural elucidation.

Mass spectrometry, and in particular matrix-assisted laser desorption/ionization-time-of-flight (MALDI-TOF) mass spectrometry, has been used in the last decade for structure analysis of various resins and polymers.[26–29] However, mass spectrometry, gel permeation chromatography/Size exclusion chromatography (GPC/SEC), or elemental analysis do not enable the identification of ether-bridged condensation products, as these and monomethylolmethylenediurea share the same molecular formula.

In a recent article Despres et al.[30] extensively studied the compounds formed during the synthesis of melamine-urea-formaldehyde (MUF) resins combining $^{13}$C-NMR and MALDI-TOF analyses. No peak corresponding to methylene bridges was observed in the $^{13}$C-NMR spectra of the first stage (UF stage) of the synthesized resin. As peaks with chemical shifts between 50 and 90 ppm were observed—chemical shifts known to belong to the secondary carbon atoms of methylol groups and possibly also to ether-bridged condensation products—Despres et al. (Ref. 30) concluded that the resin contained ether-bridged condensation products. This is convincing as the MALDI-TOF spectra exhibit peaks corresponding to condensation products (about 1400 Da).

Using a simplified but chemically similar system may help to confirm the presence or absence of ether-bridged products in UF resins. $N,N'$-Dimethylurea is an appropriate substitute for urea in the study of UF reactions as $N,N'$-dimethylurea and urea react with formaldehyde in a very similar way. Like urea, $N,N'$-dimethylurea is involved in addition reactions as well as in condensation reactions. Since tetra substitution only occurs to a very limited extent if it occurs at all, only a few structures are possible in the $N,N'$-dimethylurea-formaldehyde system. This work brings to light evidence for the existence of an ether-bridged condensation product in a dimethylurea-formaldehyde model system for the first time. Combining electrospray ionization mass spectrometry (ESI-MS), $^{13}$C-NMR, and further NMR correlation experiments

(gradient correlation spectroscopy $^{13}$C-$^{13}$C gCOSY on $^{13}$C-labeled samples) allowed characterizing this product.

## EXPERIMENTAL

### Chemicals

### Sample Preparation

A large number of samples were prepared at various formaldehyde to dimethylurea molar ratios (FA : DM-U molar ratio) and various pH-values. Dimethylurea was added to formaldehyde and the pH of the samples was adjusted using aqueous sodium hydroxide and formic acid solutions. Buffer salts—sodiumdihydrogen phosphate dihydrate and disodium hydrogen phosphate dihydrate—at a concentration of 0.1 $M$ were added to the samples with a pH value of 7.5. The samples were equilibrated at the appropriate temperature for at least one day prior to the analysis. Three replicates of each sample were prepared and analyzed.

For practical reasons the pH value of the formaldehyde solution for the $^{13}$C-labeled samples was adjusted to approximately pH 3 and was not further adjusted in the samples. Three samples at FA:DM-U molar ratio of 1:1 were prepared and stored at 25°C. The first sample (Sample I) contains exclusively $^{13}$C-labeled formaldehyde solution, the second sample (Sample II) contains a mixture 40 mol %/60 mol % of a $^{13}$C-labeled formaldehyde solution and formaldehyde Solution B, the third sample (Sample III) contains exclusively the non-labeled formaldehyde Solution B. An overview of these samples is given in Table II. Three replicates of each sample were prepared and analyzed.

**Table II.** Overview of the Dimethylurea-Formaldehyde Samples I, II, and III

| Sample | Molar ratio FA:DM-U | | Aqueous formaldehyde solution inserted | |
|---|---|---|---|---|
| I | 1 : 1 | 100% | 0.2 g g$^{-1}$ FA in H$_2$O | 99% $^{13}$C-labeled |
| II | 1 : 1 | 40% | 0.2 g g$^{-1}$ FA in H$_2$O | 99% $^{13}$C-labeled |
| | | 60% | 0.3 g g$^{-1}$ FA in H$_2$O | Non-labeled |
| III | 1 : 1 | 100% | 0.3 g g$^{-1}$ FA in H$_2$O | Non-labeled |

**Table III.** List of the Dimethylurea Species Occurring in this Work: Name, Abbreviation, Formula, Molar Mass, and Structure

| Name | Abbreviation | Formula | Molar mass (g mol$^{-1}$) | Structure |
|---|---|---|---|---|
| N,N′-Dimethylurea | DM-U | $C_3H_8N_2O$ | 88.1 | |
| Monomethyloldimethylurea | DM-MMU | $C_4H_{10}N_2O_2$ | 118.1 | |
| Monomethyloldimethylurea hemiformal | DM-HF-1 | $C_5H_{12}N_2O_3$ | 148.1 | |
| Methylenebis(dimethyl)urea | DM-MDU | $C_7H_{16}N_4O_2$ | 188.2 | |
| Methoxymethylenebis(dimethyl)urea | DM-Ether | $C_8H_{18}N_4O_3$ | 218.3 | |
| Methoxymethylenebis(dimethyl)urea hemiformal | DM-Ether-HF-1 | $C_9H_{20}N_4O_5$ | 248.3 | |
| 3,5-Dimethyl-[1,3,5]-oxadiazinan-4-on | DM-Uron | $C_5H_{10}N_2O_2$ | 130.2 | |
| 1,3,5-trimethyl-[1,3,5]-triazinan-2-on | Triazinan | $C_6H_{13}N_3O$ | 143.2 | |

## NMR Measurements, Analysis, and Chemical Shift Assignment

Measurements were carried out on a Varian 400 MHz Inova Unity NMR spectrometer, a Bruker 400 MHz Avance III or a 600 MHz Avance NMR spectrometer.

Peak assignment was based on Steinhof's $^1$H- and $^{13}$C-NMR study[32] of the formaldehyde-dimethylurea system. A capillary containing sodium 3-trimethylsilyl-1-propanesulfonate (DSS) in $D_2O$ was used as reference for $^1$H- and $^{13}$C-NMR measurements. The chemical shift of DSS was itself assigned in reference to tetramethylsilane (TMS): $^1$H-NMR ($D_2O$): $\delta = 0.018$ ppm; $^{13}$C-NMR ($D_2O$): $\delta = -2.66$ ppm.

Typical qualitative proton decoupled $^{13}$C-NMR spectra were recorded at a frequency of 100 MHz (alternatively 150 MHz) with an acquisition time between 0.9 and 1.4 s, a relaxation time of 2 s, a 20–36 kHz sweep width, and a 45° pulse width. At least 256 scans were recorded.
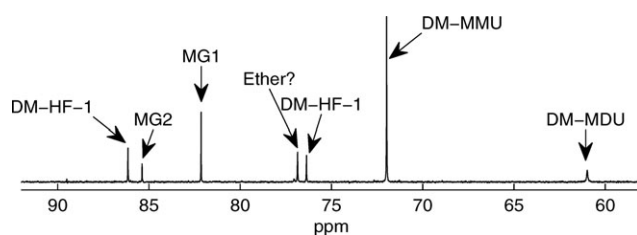
Typical experimental conditions for the $^{13}$C-$^{13}$C gCOSY spectra were: 100 MHz, 0.15 s acquisition time, 7×7 kHz (alternatively 5×5 kHz), sweep width, 2 s relaxation time, a 45° pulse width, 16 scans, and 512 increments. The resolution in F1 was typically 0.13 ppm.

## ESI-MS Analysis and Sample Preparation

ESI-MS spectra were recorded on an Esquire 3000+ Quadrupol Ion Trap (Bruker). The samples were injected at a sample flow rate of 120 μL/h using a capillary voltage of 4000 V. The measurements were carried out with a drying gas flow rate of
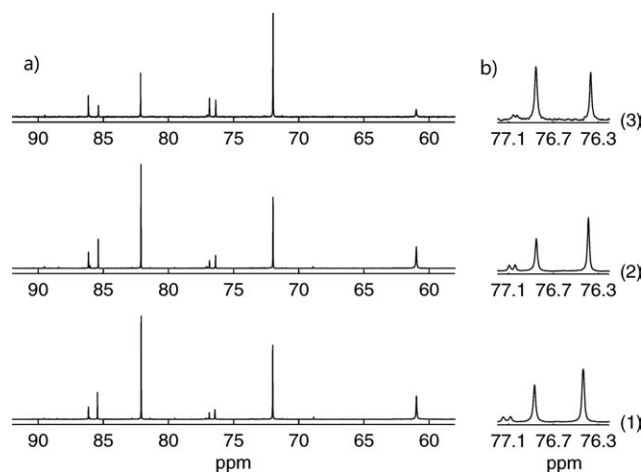


**Figure 1.** Example of the CH$_2$ range of a $^{13}$C-NMR spectrum of a formaldehyde-dimethylurea sample (FA:DM-U molar ratio of 1:1, pH approximately 4.3, $t = 22°C$). Spectrum recorded on a Varian 400 MHz NMR spectrometer.



**Figure 2.** CH$_2$ range of the $^{13}$C-NMR spectra (1) of Sample I, (2) of Sample II, and (3) of Sample III, after equilibration for a few days. The spectra were recorded on a Bruker 600 MHz NMR spectrometer. (a) overview, (b) zoom.
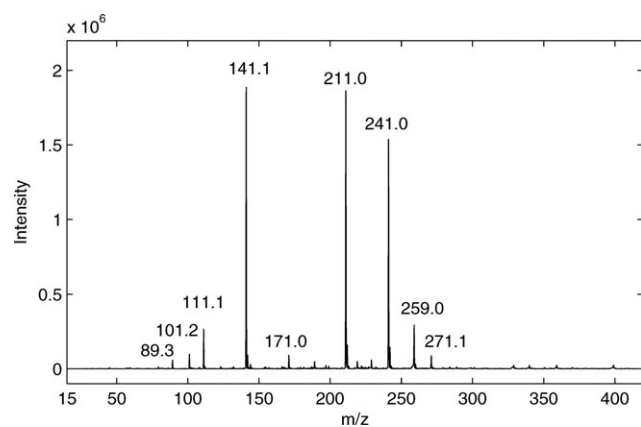
**Figure 3.** ESI-MS spectrum of Sample III (unlabeled) after equilibration for a few days.

3 L/min at 300°C and a nebulizer pressure of 4 psi. The system was operated in the positive mode and at a mass range of $m/z$ 15–800 with a mass target of $m/z$ 100. The calibration of the mass spectrometer was done using Agilent's APPI tune mix.

The following dilutions were done immediately prior to measurement: 20 $\mu$L of the sample were diluted in 10 mL of distilled water and 10–12 mg of sodium thiocyanate was added. Fifty microliters of this solution were then diluted with 450 $\mu$L of distilled water. Each sample was analyzed three times. Blank experiments were conducted with the distilled water used for the dilutions.

### Chemicals Species: Names, Structures, and Abbreviations
Table III lists all formaldehyde-dimethylurea species that occur in this study.

### RESULTS AND DISCUSSION

#### Observations in the Formaldehyde-Dimethylurea System
The CH$_2$ region of the $^{13}$C-NMR spectrum was found to be the most appropriate to investigate the presence of ether-bridged condensation products. Based on Steinhof's work,[31] peaks were assigned as follows (Figure 1): at 61 ppm the CH$_2$ carbon atoms of methylenebis(dimethyl)urea, at 72 ppm the CH$_2$ carbon atoms of monomethyloldimethylurea, 77 and 86.5 ppm are characteristic for the CH$_2$ carbon atoms of monomethylolbis-
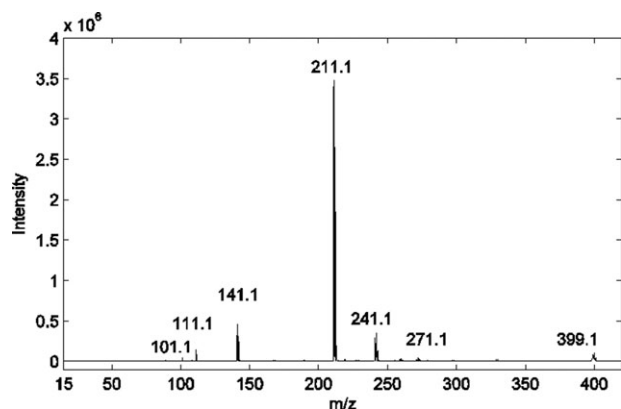


**Figure 4.** ESI-MS spectrum of Sample II (40 mol% labeled) after equilibration for a few days.
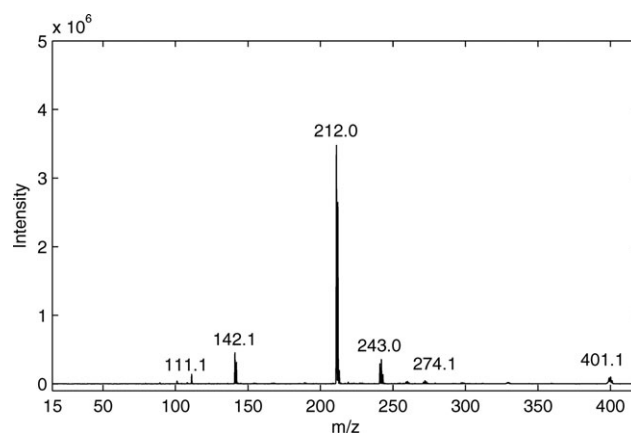


**Figure 5.** Experimental ESI-MS spectrum of Sample I (labeled) after equilibration for a few days.

(dimethyl)urea hemiformals. The peaks at 82 and 85.5 ppm were assigned to methylene glycol (MG1) and poly(oxymethylene) glycol (MG2), respectively (Figure 1). When two main peaks in the hemiformal range (76–77 ppm) were observed, only one peak (that does not belong to a methylene glycol or to a poly(oxymethylene) glycol compound) was found at 86.5 ppm. This observation is in accordance with the presumed presence of an ether-bridged product. Indeed it is expected that the resonance of the CH$_2$ carbon atoms of a —CH$_2$OCH$_2$— bridge should have a chemical shift similar to the resonance of the carbon atom —CH$_2$O[CH$_2$O]$_n$H ($n \geq 1$) of a hemiformal moiety. It is likely that one of the two peaks at approximately 77 ppm belongs to the hemiformal of monomethylolbis(dimethyl)urea and that the other belongs to methoxymethylenebis(dimethyl)urea. From the peaks' height at 76–77 ppm and at 86 ppm, it can be concluded that the peaks at 76.4 and 76.8 ppm belong to the hemiformal of dimethylmonomethylolurea and to methoxymethylenebis(dimethyl)urea, respectively.

The peak at approximately 76.8 ppm which is presumably attributed to ether-bridged moieties is relatively small. To facilitate further analysis, a short qualitative study was carried out to determine the conditions under which the peak is maximized. The influence of the pH on the composition was studied at 22°C and a FA:DM-U molar ratio of 1:1. Samples with a pH between 3.5 and 9.5 were prepared. The compound of interest was found to
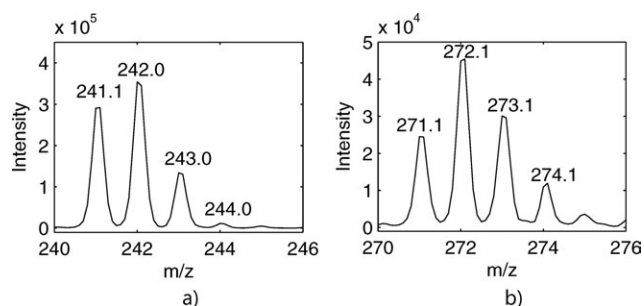


**Figure 6.** Experimental ESI-MS spectrum of Sample II (40 mol% labeled) after equilibration for a few days. Zoom on isotope peaks (a) at 241 Da, (b) at 271 Da.
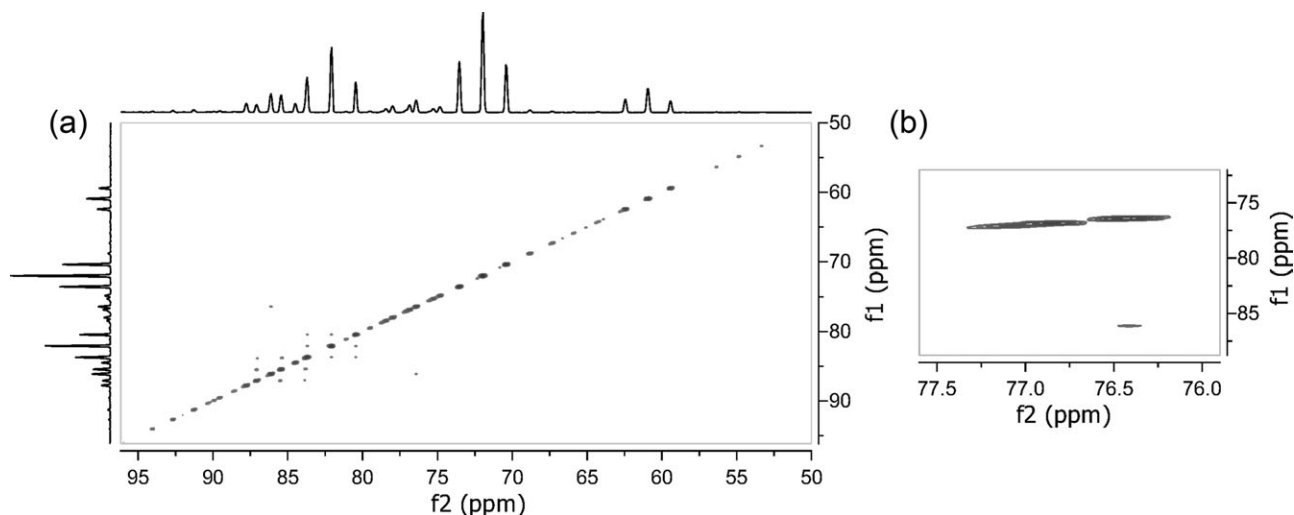
**Figure 7.** ^{13}C-^{13}C gCOSY spectrum. Spectrum recorded on a Varian 400 MHz NMR spectrometer. (a) overview. (b) zoom.

form mainly in acidic or slightly basic media (Supporting Information Figure S1). The relative height of the peak at 76.8 ppm compared to that of the methylene-bridged, of the methylol, and of the neighbor peak at 76.4 ppm was found to be similar in all mixtures with a pH between 3.5 and 5.5.

The influence of the temperature was studied at a FA:DM-U molar ratio of 1:1 and at a pH of approximately 4.3. The ^{13}C-NMR spectra recorded after keeping the mixtures for three days at 22°C, 40°C, or 60°C are provided in the Supporting Information Figure S2. It was observed that the peak at 76.8 ppm was very small—if present at all—in the spectrum of the mixture at 60°C. For lower reaction temperatures this peak becomes larger. No significant variation of the relative height was observed for the peak at 76.8 ppm compared to the $CH_2$ peaks of the methylene-bridged and of the methylol compounds. Little difference in the size of the $CH_2$ peak at approximately 76.8 ppm was observed between samples obtained at 22°C and 40°C.

The influence of the FA:DM-U molar ratio was studied at 22°C and at a pH of approximately 4.3. Spectra of samples with a FA:DM-U molar ratio of 1:1, 2:1 and 4:1 are provided in the Supporting Information Figure S3. A slight shift of the peak from 76.8 to 77.0 ppm was observed when increasing the molar ratio. At higher molar ratios the relative amount of methylene-bridged condensation products decreases since methylolation is favored. It was observed that the relative height of this peak compared to the $CH_2$ peaks of the methylol compounds decreases slightly with increasing molar ratio.

To summarize it was found at 22°C, a FA:DM-U molar ratio of 1:1 and a pH of approximately 4.5, that sufficient compound giving rise to a peak at 76.8 ppm (presumably attributed to ether-bridged moieties) was formed to enable characterization.

### NMR and ESI-MS Results

The Samples I, II, and III were analyzed by ^{13}C-NMR and ESI-MS. The ^{13}C-NMR spectra of all three samples were similar (Figure 2); in all spectra two main peaks at 76.4 and 76.8 ppm are observed. The ESI-MS results are given in Figures 3–5, the
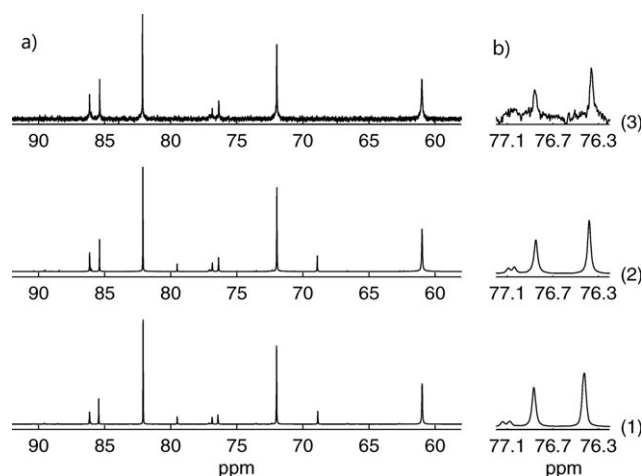


**Figure 8.** $CH_2$ range of the ^{13}C-NMR spectra for the Samples (1) I, (2) II, and (3) III after equilibration for about 4 weeks. The spectra were recorded on a Varian 400 MHz NMR spectrometer. (a) overview, (b) zoom.
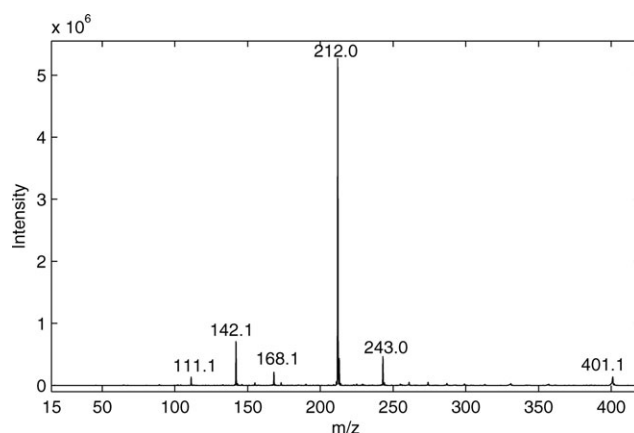


**Figure 9.** ESI-MS spectrum of Sample I (labeled) after equilibration for about 4 weeks.
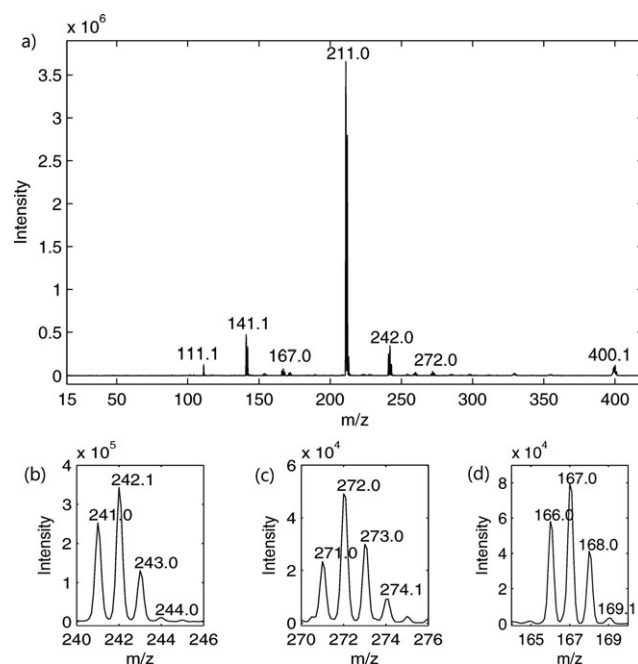
**Figure 10.** ESI-MS spectrum of Sample II (40 mol% labeled) after equilibration for about 4 weeks. (a) overview, (b–d) zoom.



**Figure 11.** ESI-MS spectrum of Sample III (unlabeled) after equilibration for about 4 weeks.

corresponding tables are provided in the Supporting Information Tables S1–S3.

The peaks at 219 and 241 Da in the ESI-MS spectra of the unlabeled Sample III (Figure 3) match to the molar mass of methoxymethylenebis(dimethyl)urea adducts with additional $H^+$ and $Na^+$, respectively. The peak at 271 Da matches the molar mass of its hemiformal adduct with $Na^+$. In the ESI-MS spectrum of the labeled Samples I (Figure 4), peaks at 243 and 274 Da are observed. It is assumed that these peaks correspond to products with 241 and 271 Da and two or three $^{13}$C-labeled formaldehyde units, respectively. This supports the identification of these peaks as methoxymethylenebis(dimethyl)urea and its hemiformal. In Sample III which is prepared using a mixture of 40 mol %/60 mol % $^{13}$C-labeled/unlabeled formaldehyde, the results of the ESI-MS spectra (Figure 5) are expected to contain three peaks for a compound with two formaldehyde $-CH_2O-$ units and four peaks for a compound with three formaldehyde units. The expected relative intensities of these peaks are 100%, 133%, and 44% in the first case and 100%, 200%, 67%, and 22% in the second case assuming statistical distributions. In the ESI-MS spectra of the 40 mol % labeled Sample II, two peaks at 241 and 271 Da were observed. The relative intensities of the isotope peaks at 241, 242, and 243, respectively, were approximately 100%, 121%, and 46% (Figure 6) indicating that this compound contains two formaldehyde $-CH_2O-$ units. In each ESI-MS spectrum, a peak at 271 Da is also observed; this peak is assumed to belong to the methoxymethylenebis(dimethyl)urea hemiformal adduct. The relative intensities of its isotope peaks at 271, 272, 273, and 274 Da, as shown in Figure 6, are approximately 100%, 186%, 121%, and 49% respectively. This is a strong evidence for a compound containing three formaldehyde units.
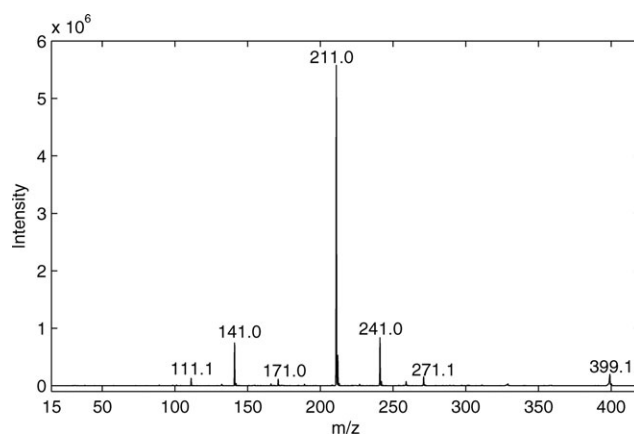
Further, $^{13}$C-$^{13}$C gCOSY spectra were recorded for the Sample I prepared with the $^{13}$C-labeled formaldehyde solution. One $^{13}$C-$^{13}$C gCOSY spectrum is given as an example in Figure 7. A crosspeak at 76.4/86 ppm was observed and the resonances were assigned to the $CH_2$ carbon atoms of the $-N(CH_3)CH_2O-$ and of the hemiformal groups of monomethyloldimethylurea hemiformal, respectively. Unlike for the peak at 76.4 ppm, no crosspeak for the $^{13}$C resonance at 76.8 ppm is observed. Since the two peaks at 76.4 and 76.8 ppm have approximately the same height in the $^{13}$C-NMR spectra (see Figure 2), it can be concluded that the absence of a crosspeak is not attributable to a low concentration of this species.

Rather, the lack of the crosspeak suggests that this compound does not have a hemiformal structure $-CH_2O[CH_2O]_nH$ with $n \geq 1$. The secondary carbon atom of the compound at 76.8 ppm has a chemical environment similar to that in a hemiformal group, as indicated by its chemical shift. This compound most likely has a symmetrical $-CH_2OCH_2-$ structure. This peak at 76.8 ppm can therefore be assigned to the secondary carbon atom of the ether-bridge of methoxymethylenebis(dimethyl)urea. The peaks at 241 and 271 Da in the ESI-MS spectra are then assigned to methoxymethylenebis(dimethyl)urea and to the methoxymethylenebis(dimethyl)urea hemiformal adduct, respectively.

The $^{13}$C-NMR and ESI-MS measurements of all Samples I, II, and III, were repeated about 4 weeks after the initial measurements. NMR and mass spectra were similar to those recorded initially (see Figures 8–11, corresponding tables are provided in the Supporting Information Tables S4–S6). The $CH_2$ peak of methoxymethylenebis(dimethyl)urea at 76.8 ppm was still visible in all spectra. In all mass spectra, the peaks of methoxymethylenebis(dimethyl)urea and its hemiformal were observed. These compounds were found to be stable at 22°C.

In the NMR spectra of the labeled and 40 mol % labeled samples, Samples I and II respectively, two small peaks are observed at 68.9 and 79.5 ppm. These compounds were assigned in the literature[31] to 1,3,5-trimethyl-[1,3,5]-triazinan-2-on and to 3,5-dimethyl-[1,3,5]-oxadiazinan-4-on, respectively. In the

corresponding mass spectra, a small peak at 166 Da can be observed. The relative intensity of its isotope peaks at 166, 167, 168, and 169 Da (Figure 10) in the Sample II indicates that this compound contains two formaldehyde units. The number of formaldehyde units as well as the mass of the sodium adduct support the assignment of this peak to 1,3,5-trimethyl-[1,3,5]-triazinan-2-on.

## CONCLUSIONS

Using a combination of ESI-MS, $^{13}$C-NMR and $^{13}$C-$^{13}$C gCOSY techniques, methoxymethylenebis(dimethyl)urea has been characterized. This compound was found to be stable at 22°C. It was only observed in acidic and slightly basic media in N,N'-dimethylurea–formaldehyde systems. Until now ether-bridged condensation products have not been characterized in UF resins, but these products are believed to occur. This study of N,N'-dimethylurea-formaldehyde systems provides information on the structure of UF resins. N,N'-dimethylurea is very similar to urea, and undergoes similar chemical reactions with formaldehyde. Since the protection of two active sites of urea by methyl groups in dimethylurea changes the reactivity of the active sites, no conclusion on the quantity of ether-bridged condensation products present in UF resin can be extrapolated. From the results of this study it is however to expect that ether bridges occur in UF resins too, when condensation occurs in acidic medium.

## ACKNOWLEDGMENTS

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