

Demonstration of co-polymerization in melamine–urea–formaldehyde reactions using ^{15}N NMR correlation spectroscopy

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Abstract

Melamine–urea–formaldehyde resins are very important commercially, yet little is known about their structures, and the techniques that have been available to examine this are quite limited. In this manuscript we describe the use of ^1H – ^{15}N HMQC NMR spectroscopy and the development of a doubly-selective ^1H – ^{15}N – ^{13}C CP INEPT NMR experiment, to establish for the first time that melamine and urea co-polymerize with formaldehyde and to identify the ^1H , ^{15}N and ^{13}C chemical shifts of the bridging units. This methodology makes it possible to examine co-condensation in industrial preparations of melamine–urea–formaldehyde resins, in order to correlate structure and function and optimize the manufacturing process.

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1. Introduction

Melamine-urea-formaldehyde (MUF) resins are used in the manufacturing of water-resistant particleboards, papers and laminates. The chemistry of melamine reacting with formaldehyde and of urea and formaldehyde condensations is well known (Fig. 1) [1]. However, there is little direct evidence of co-condensation of melamine and urea with formaldehyde in MUF resins. Low molecular weight co-condensation products have been identified using HPLC/MS [2], but this procedure is not suitable for studying more advanced stages in the polymerization process. MUF resins have been compared with melamine–formaldehyde (MF) and urea–formaldehyde (UF) resins using ^{13}C NMR spectroscopy [3–5]. Mercer and Pizzi [3] assigned two low intensity resonances near δ 154.5 ppm and unique to spectra of MUF resins to co-polymerized species. Tomita and Hse [4,5] did not observe these peaks, but attributed

resonances at δ 158.9 and 160.4 ppm, as well as in the region δ 45–70 ppm, to cross-linked moieties. The individual species were not characterized and the resonances overlap with those of MF and UF resins, limiting precise analyses particularly where line-broadening occurs after extensive polymerization [5]. ^{15}N NMR spectroscopy has also been used to study MF and UF resins [6–8], but when this technique was applied to analyze MUF resins, no unique resonances representing co-polymerization were apparent [9]. As recently as 2004, No and Kim [10] reported that ‘it was difficult to form a conclusion whether any copolymerization occurred between urea and melamine units (in MUF resins)’.

Given the special properties and associated commercial importance of MUF resins, as an initial step towards correlating structure with function we therefore set out to establish procedures to identify and characterize any co-polymerization. ^{15}N NMR correlation spectroscopy was used because indirect detection of nitrogen is 300 times more sensitive than direct methods [11] and the ^{15}N -resonances due to urea and melamine residues have distinct chemical shifts [6].

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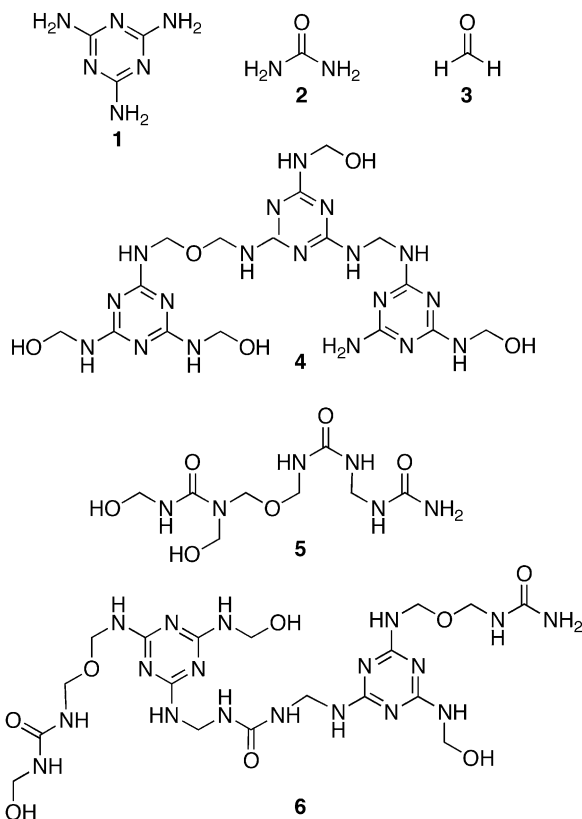


Fig. 1. Melamine (1), urea (2) and formaldehyde (3), and examples of possible structures formed through reaction of melamine and formaldehyde (4), urea and formaldehyde (5), and melamine, urea and formaldehyde (6).

2. Experimental section

2.1. General

^1H - ^{15}N HMQC NMR spectra were recorded on a Varian INOVA 500 spectrometer, using an indirect detection probe with actively shielded z -axis gradients. Doubly-selective ^1H , ^{15}N , ^{13}C CP-INEPT NMR spectra were recorded on a Varian INOVA 600 spectrometer equipped with a PENTA probe.

Unlabeled urea and melamine were provided by Orica Australia Pty. Ltd. Aqueous formaldehyde (20% w/w) was prepared by stirring paraformaldehyde in water adjusted to pH 9.0 with 6 M aqueous sodium hydroxide. ^{15}N -labeled ammonium chloride (98 + atom%) and urea (98 + atom%), ^{13}C -labeled aqueous formaldehyde (20% w/w, 99 + atom%) and 2,4,6-trichloro-1,3,5-triazine were purchased from Sigma–Aldrich Chemical Co. Melamine ^{15}N -labeled at NH_2 was prepared by treating 2,4,6-trichloro-1,3,5-triazine (1.0 g, 5.4 mmol) with ^{15}N -labeled ammonium chloride (2.1 g, 38 mmol) in aqueous sodium hydroxide (13 mL, 3 M), at reflux for 16 h. The mixture was then cooled and the solid that formed was collected by filtration and recrystallized from water adjusted to pH 10.0 with 6 M aqueous sodium hydroxide (yield 0.36 g, 52%). The

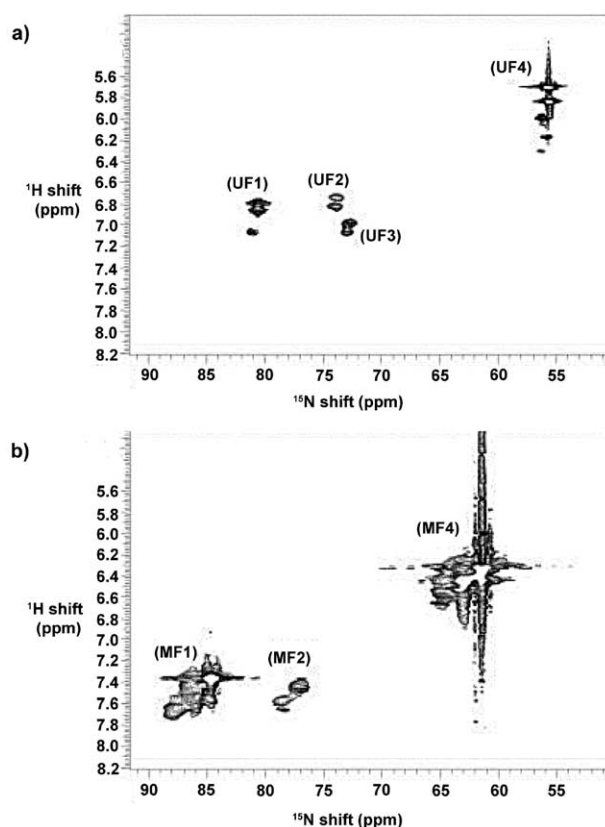


Fig. 2. H - ^{15}N HMQC NMR spectra of (a) urea–formaldehyde and (b) melamine–formaldehyde reaction mixtures.

physical and spectral data of the labeled melamine are consistent with those reported for the unlabeled material.

2.2. Resin preparation and analysis

UF and MF resins were prepared as follows. A mixture of ^{15}N -labeled or unlabeled melamine (126 mg, 1.0 mmol) or urea (90 mg, 1.5 mmol) and aqueous formaldehyde (0.43 mL, 20% w/w, 3.0 mmol) was adjusted to pH 7.0 with 0.5 M aqueous formic acid, and then heated at 363 K for 2 h. It was then cooled and freeze-dried. The residue was dissolved in $^2\text{H}_6$ -DMSO for NMR spectroscopic analysis. MUF resins were prepared in a similar fashion. A mixture of ^{15}N -labeled or unlabeled melamine (63 mg, 0.50 mmol), ^{15}N -labeled or unlabeled urea (45 mg, 0.75 mmol) and ^{13}C -labeled or unlabeled aqueous formaldehyde (0.43 mL, 20% w/w, 3.0 mmol) was adjusted to pH 7.0 with 0.5 M aqueous sodium hydroxide, and then heated at 363 K for 2 h. It was then cooled and freeze-dried. The residue was dissolved in $^2\text{H}_6$ -DMSO for NMR spectroscopic analysis.

3. Results and discussion

^1H - ^{15}N HMQC NMR spectra recorded of UF and MF resins are illustrated in Fig. 2 and the assignments of the

Table 1

Assignments of resonances observed in spectra of urea–formaldehyde, melamine–formaldehyde and urea–melamine–formaldehyde reaction mixtures

	Assignment	^{15}N shift (ppm)	^1H shift (ppm)
(UF1)	(urea)- NHCH_2OH	80–81	6.7–7.1
(UF2)	(urea)- NHCH_2NH -(urea)	73.5–74.5	6.7–6.9
(UF3)	(urea)- $\text{NHCH}_2\text{OCH}_2\text{NH}$ -(urea)	72–73	6.9–7.1
(UF4)	(urea)- NH_2	54–56	5.6–6.3
(MF1)	(melamine)- NHCH_2OH	84–88	7.2–7.7
(MF2)	(melamine)- NHCH_2NH -(melamine)	76.5–77.5	7.4–7.6
(MF4)	(melamine)- NH_2	60–64	6.2–6.7
(MUF1)	(urea)- NHCH_2NH -(melamine)	72.3	6.6
(MUF2)	(urea)- $\text{NHCH}_2\text{OCH}_2\text{NH}$ -(melamine)	71.3	6.7
(MUF3)	(urea)- NHCH_2NH -(melamine)	74.8	6.9
(MUF4)	(urea)- $\text{NHCH}_2\text{OCH}_2\text{NH}$ -(melamine)	76.7	6.9

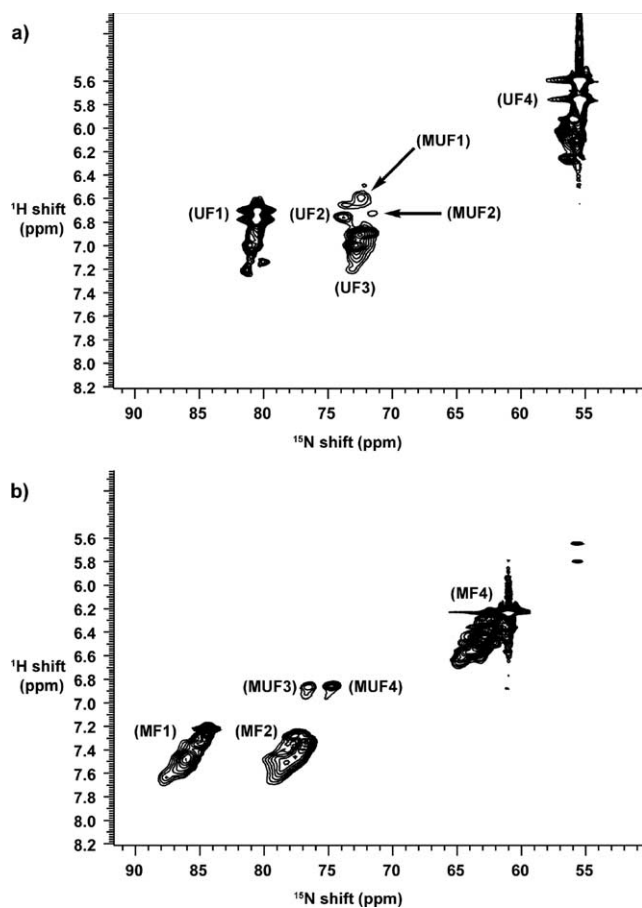


Fig. 3. ^1H - ^{15}N HMQC NMR spectra of urea-melamine-formaldehyde reaction mixtures prepared using (a) ^{15}N -labeled urea and (b) ^{15}N -labeled melamine.

resonances are shown in Table 1. The samples were prepared by treating aqueous solutions of formaldehyde (20%, w/w) with either urea or melamine, at pH 7.0 and 363 K, for 2 h. In each case the ratio of reactive nitrogen to formaldehyde was 1:1. The crude product mixtures were freeze-dried and the spectra of the residues were recorded in $^2\text{H}_6$ -DMSO. The ^{15}N - and ^1H -chemical shifts of the resonances observed in the spectra all correspond to those previously obtained using 1D NMR methods [6,7,9].

^1H - ^{15}N HMQC NMR spectra were also recorded of MUF resins. These are illustrated in Fig. 3 and the assignments of the resonances are also shown in Table 1. The samples were prepared as described above for the UF and MF resins, except that a 3:2 ratio of urea to melamine was used instead of either melamine or urea, and in separate experiments either the melamine or the urea was ^{15}N -labeled (at NH_2) in order to distinguish signals attributable to that component. Consequently the signals observed in Fig. 3a arise from urea residues and those in Fig. 3(b) are due to melamine. In addition to those observed for UF resins, Fig. 3(a) shows correlations between ^{15}N resonances at δ 71.3 and 72.3 ppm, and ^1H resonances at δ 6.7 and 6.6 ppm, respectively. Similarly, other than those seen with MF resins, Fig. 3(b) shows correlations between ^{15}N resonances at δ 74.8 and 76.7 ppm, and ^1H resonances at δ 6.9. These must be due to co-polymerization, and by analogy with the chemical shifts of the resonances of UF and MF systems, they correspond to the linking moieties. However, it was not possible to distinguish between methylene- and dimethylene ether-bridges on the basis of the available data.

To accomplish this, a doubly-selective ^1H - ^{15}N - ^{13}C CP-INEPT NMR experiment was developed, to correlate the ^1H - ^{15}N resonance pairs with the ^{13}C resonances of the corresponding directly-bonded carbons. The method used was similar to one proposed by Gudat [12], except that the initial transfer of magnetization between ^1H and ^{15}N was achieved by selective excitation of the ^{15}N resonance by doubly-selective cross-polarization, using matched continuous wave pulses set to an RF field strength of ~ 40 Hz and a pulse duration of 10 ms on the ^1H and ^{15}N channels. This was followed by polarization transfer from the selectively excited ^{15}N to the directly bonded ^{13}C by ^{15}N , ^{13}C -INEPT (Fig. 4). ^{13}C -Labeled formaldehyde was used to increase sensitivity. As a control, correlation of the ^1H and ^{15}N resonances of the NHCH_2OH moiety of hydroxymethyl-melamine, at δ 7.4 and 85 ppm, respectively, was found to be with a ^{13}C resonance having the known chemical shift of δ 64 ppm [1,4,5]. Each of the four MUF ^1H - ^{15}N resonance pairs (Fig. 3) was then examined to establish the ^{13}C chemical shift of the adjacent carbon. Then from the assignment of ^{13}C resonances at δ 67 and 68 ppm to an ether bridge, and at δ 47 ppm to a methylene link [1,4,5], the chemical shifts of the resonances of each of the $\text{H}-\text{N}-\text{CH}_2$ fragments were determined and these are summarized in Fig. 5.

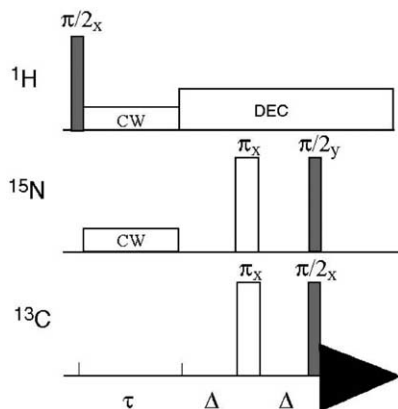


Fig. 4. Pulse sequence used in the ^1H - ^{15}N - ^{13}C CP-INEPT NMR experiment.

4. Conclusion

In summary, ^{15}N NMR correlation spectroscopy has been developed as a tool to study MUF resins. Through the identification of resonances unique to cross-linked species, copolymerization has been established. Moreover, the ^1H , ^{15}N and ^{13}C chemical shifts of all four of the possible H–N–C fragments of the bridging groups have been assigned. With this methodology it should now be possible to determine the extent of co-condensation in industrial preparations of MUF resins, in order to correlate resin structure with function and optimize the manufacturing process.

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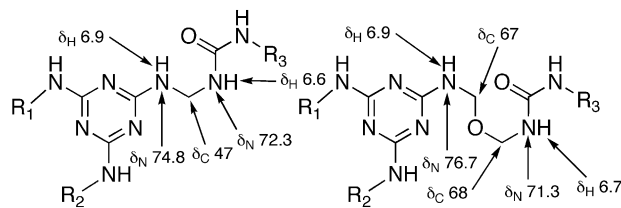


Fig. 5. Methylene and dimethylene ether links between melamine and urea moieties.

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References

- [1] Pizzi A. *Advanced Wood Adhesives Technology*. New York: Marcel Dekker; 1994. Chapters 2–3.
- [2] Nussender JJ, Aarts VMLJ, Brandts PM, Mattheij J. *DSM Technical Information Sheet: Skill Centre Melamine*. October, 1998.
- [3] Mercer TA, Pizzi A. *Holzforsch. Holzverw* 1994;46:51–4.
- [4] Tomita B, Hse C-Y. *Mokuzai Gakkaishi* 1995;41:349–54.
- [5] Tomita B, Hse C-Y. *Mokuzai Gakkaishi* 1995;41:490–7.
- [6] Ebdon JR, Heaton PE, Huckerby TN, O'Rourke WTS, Parkin J. *Polymer* 1984;25:821–5.
- [7] Ebdon JR, Hunt BJ, O'Rourke WTS. *Br Polym J* 1987;19:197–203.
- [8] Andreis M, Koenig JL. *Adv Polym Sci* 1995;124:191–237.
- [9] Angelatos AS, Burgar MI, Dunlop N, Separovic F. *J Appl Polym Sci* 2004;91:3504–12.
- [10] No BY, Kim MG. *J Appl Polym Sci* 2004;93:2559–69.
- [11] Kaji H, Miura N, Schmidt-Rohr K. *Macromolecules* 2003;36:6100–13.
- [12] Gudat D. *J Magn Reson Ser A* 1995;112:246–9.