

## Co-Polymerization Analysis of Thermosetting Resins using $^1\text{H}$ - $^{15}\text{N}$ - $^{13}\text{C}$ Triple Resonance NMR Spectroscopy

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**ABSTRACT:**  $^1\text{H}$ - $^{15}\text{N}$ - $^{13}\text{C}$  correlation NMR spectroscopy techniques developed to identify and characterize co-polymer fragments in melamine-urea-formaldehyde (MUF) and phenol-urea-formaldehyde (PUF) model systems have been applied to industrially prepared MUF, PUF, and phenol-melamine-formaldehyde (PMF) resins. The NMR data confirm that co-polymers form in a commercially prepared MUF resin manufactured by Momentive Specialty Chemicals Pty. Ltd. Spectra from PUF model reactions were compared with those from a PUF resin and it was determined that PUF co-polymers did not form in the resin prepared using typical temperature and pH. Finally, NMR spectroscopy was used to identify and characterize PMF co-polymer bonds in a phenol-melamine-urea-formaldehyde (PMUF) resin prepared using a procedure from Momentive Specialty Chemicals Pty. Ltd. With these NMR techniques in hand, it is now possible to relate co-polymer structures to properties of commercial thermosets. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** adhesives; copolymers; thermosets; resins; spectroscopy

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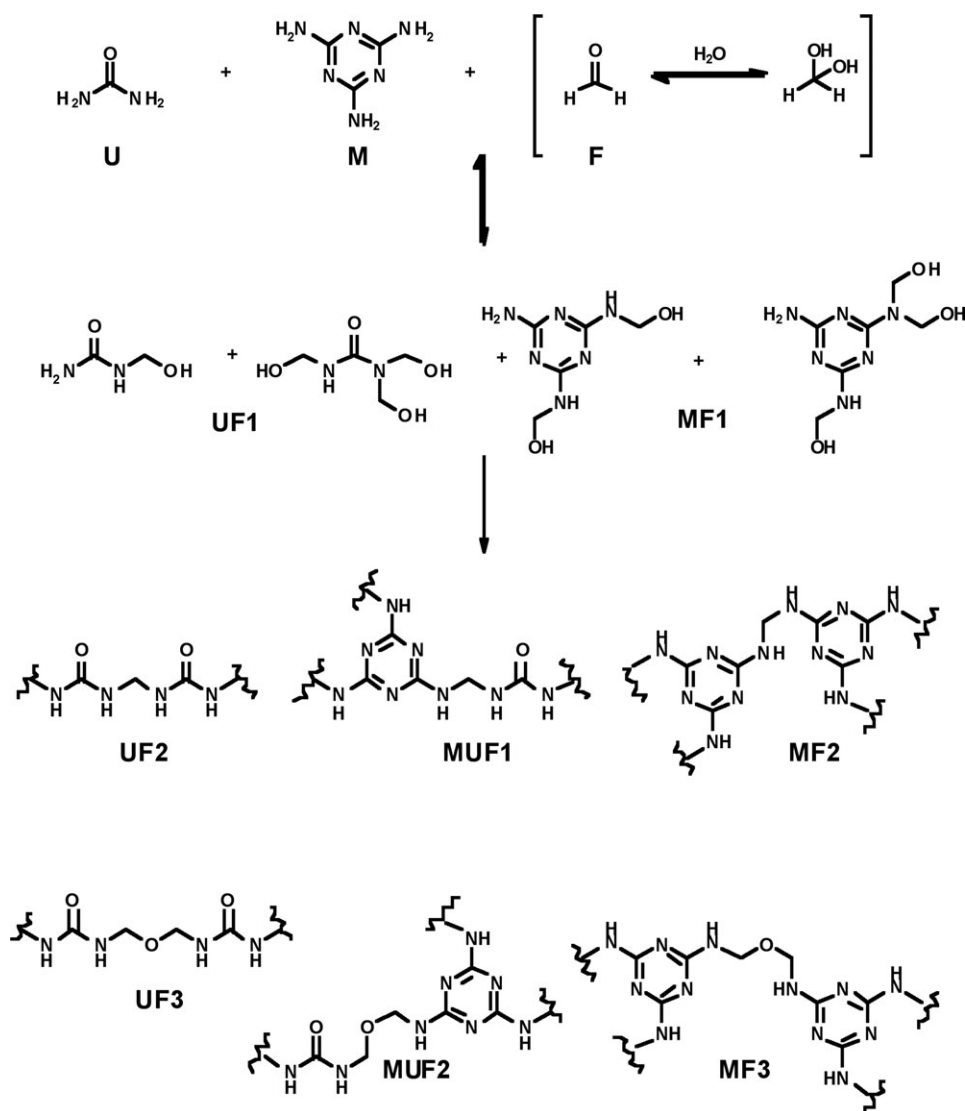
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### INTRODUCTION

Thermosetting resins are defined as resins that change irreversibly under the influence of heat<sup>1,2</sup> and are used in the manufacture of wood adhesives, laminates, dinnerware, and paper additives.<sup>3,4</sup> The principle types of thermosets are urea-formaldehyde (UF), melamine-formaldehyde (MF), phenol-formaldehyde (PF), and combinations thereof. Urea, melamine, and phenol monomers are often combined during production to incorporate the desired physical properties of each homo-polymer resin. For example, melamine-urea-formaldehyde (MUF) resins utilize the cost-effective, strong UF component with the hydrophobic durable properties of melamine-formaldehyde (MF) resins. When compared with a UF resin, an MUF resin has better bond performance, and therefore lower formaldehyde emission.<sup>5–8</sup> Tohmura et al.<sup>5</sup> attributed improved performance to stronger bonds formed between formaldehyde and melamine than urea and not to co-polymerization. At present, the increase in durability has been attributed to the addition of melamine but not to the formation of cross-links between urea and melamine moieties. The ability to identify and characterize melamine-urea cross-links in commercially prepared resins is necessary to assess the benefits of MUF co-polymers compared with MF/UF mixtures.

The identification of co-polymer bridges when multiple monomers are used has been problematic due to the similar chemical environment of co-polymer and homo-polymer cross-links. Researchers have previously used  $^{13}\text{C}$  NMR spectroscopy to investigate the formation of co-polymers in MUF resins. However, the reported  $^{13}\text{C}$  NMR chemical shifts in MUF co-polymer linkages overlapped with those reported for the corresponding homo-polymer. For example, literature assignments for the methylene link in UF systems range from  $\delta$  45.5–49.1 ppm<sup>4,9–11</sup> in the  $^{13}\text{C}$  NMR spectrum, which are very similar to the  $^{13}\text{C}$  resonance assignments for the methylene link in MF resins ( $\delta$  47.0–49.8 ppm).<sup>9</sup> Similarly, the  $^{13}\text{C}$  NMR resonances reported for UF dimethylene-ether links ( $\delta$  67.5–71.1 ppm)<sup>4,9–11</sup> completely overlap the reported  $^{13}\text{C}$  NMR chemical shift assignments for dimethylene-ether links ( $\delta$  68.0–71.0 ppm) in MF resins.<sup>9,11</sup>

Like the MUF system, phenol and urea can potentially condense to form methylene and dimethylene ether links.<sup>12,13</sup> Co-polymerization in phenol-urea-formaldehyde (PUF) resins has been investigated using  $^{13}\text{C}$  NMR spectroscopy,<sup>12,14–16</sup> MALDI-TOF mass spectrometry<sup>13</sup> as well as a combination of these techniques.<sup>17</sup> Tomita and Hse<sup>14</sup> used  $^{13}\text{C}$  NMR spectroscopy to identify  $^{13}\text{C}$  resonances of methylene bridges from  $\delta$  40.6 to 44.7



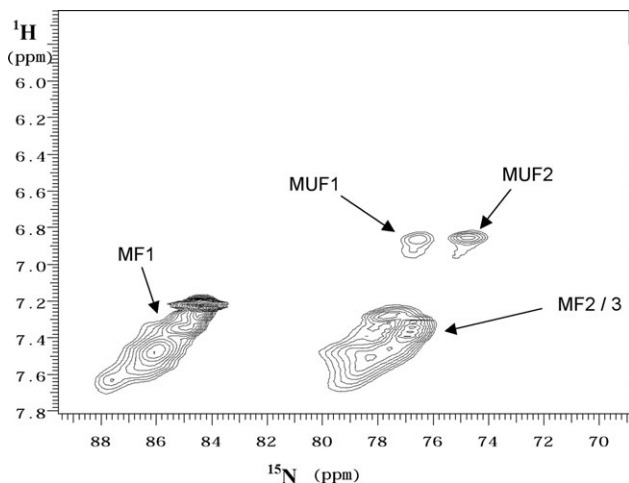
**Scheme 1.** Reaction of urea (U), melamine (M), and formaldehyde (F) [which exists as formalin in  $\text{H}_2\text{O}$ ], forming hydroxymethyl-urea (UF1) and -melamine (MF1) derivatives. Possible condensation products are homo-polymers (UF2, UF3, MF2 and MF3), as well as co-polymers (MUF1 and MUF2).

ppm. However, their studies used hydroxymethylphenol and not phenol. Pizzi and coworkers<sup>12</sup> assigned three resonances for carbons in phenol-urea co-polymer bridges. These  $^{13}\text{C}$  NMR shifts were due to methylene links, *para*-Ph- $\text{CH}_2$ -NH-(urea) at  $\delta$  44.2 ppm, *para*-Ph- $\text{CH}_2$ -N( $\text{CH}_2$ )-(urea) at  $\delta$  49.2 ppm, and *ortho*-Ph- $\text{CH}_2$ -NH-( $\text{CH}_2$ )-(urea) at  $\delta$  46.4 ppm. However, these assignments can overlap with those of UF and PF particularly when line-broadening occurs after extensive cross-linking.<sup>9</sup> Despite the extensive research reported for PUF co-polymer analysis, experts in the field have different views to whether or not co-polymerization occurs in PUF resins.<sup>12,17,18</sup> It is also important to note that process conditions greatly influence the polymerization process.<sup>4,18,19</sup> and presumably variations in resin protocols can affect cross-linking including the formation of co-polymers.

Phenol-melamine-formaldehyde (PMF) methylene co-polymer linkages were reported by Maciejewski et al.<sup>20</sup> but the purpose

of the study was to make precursors for dendritic macromolecules. In another study, the  $^{13}\text{C}$  resonances of co-polymer methylene links were reported but these links were formed by reacting methylolphenols with an excess of melamine.<sup>21</sup> Furthermore, phenol is often combined with a MUF resin<sup>22</sup> further complicating NMR spectral analysis. To the best of our knowledge PMF co-polymer links have not been identified in commercial resins and the  $^{15}\text{N}$  chemical shifts of such links are also unknown.

We previously reported the development of  $^1\text{H}$ - $^{15}\text{N}$ - $^{13}\text{C}$  triple resonance NMR spectroscopy techniques that were used to identify and characterize co-polymer bridges in MUF reactions,<sup>23</sup> diisocyanate-urea-formaldehyde model systems<sup>24</sup> and cross-links in cellulose model-urea-formaldehyde reactions.<sup>25</sup>  $^{15}\text{N}$ -Labeled monomers were employed and  $^1\text{H}$ - $^{15}\text{N}$  HMQC NMR spectroscopy experiments were used to detect co-polymer cross-peaks. Reaction products with overlapping  $^{13}\text{C}$  resonances



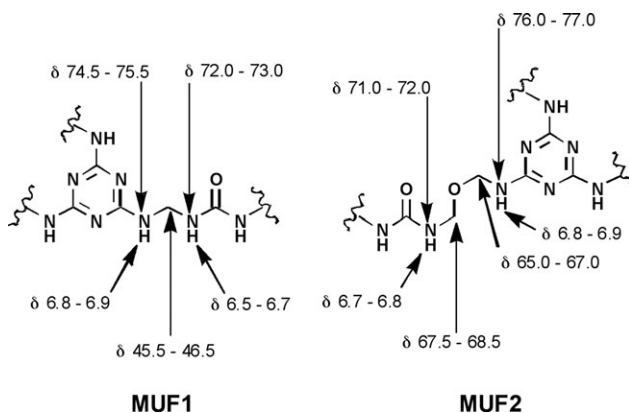
**Figure 1.**  $^1\text{H}$ - $^{15}\text{N}$  HMQC NMR spectrum of MUF reaction products using  $^{15}\text{N}$ -labeled melamine.<sup>23</sup>

had distinct  $^1\text{H}$ - $^{15}\text{N}$  correlations demonstrating that  $^1\text{H}$ - $^{15}\text{N}$  HMQC NMR spectroscopy is a powerful tool in elucidating amino resin structures. To fully characterize co-polymer bridges, the  $^{13}\text{C}$  resonance is correlated with its directly bonded nitrogen by a  $^1\text{H}$ - $^{15}\text{N}$ - $^{13}\text{C}$  triple resonance experiment<sup>23</sup> where selective heteronuclear Hartman-Hahn polarization transfer is used to excite specific  $^1\text{H}$ - $^{15}\text{N}$  pairs followed by non-selective INEPT polarization transfer from  $^{15}\text{N}$  to the directly bonded  $^{13}\text{C}$ . The NMR techniques used to investigate model systems can now be applied to resins made using industrial process conditions. Therefore, the aim of the present work was to use  $^1\text{H}$ - $^{15}\text{N}$ - $^{13}\text{C}$  NMR correlation spectroscopy to identify and characterize co-polymer bridges in resins prepared using commercial protocols.

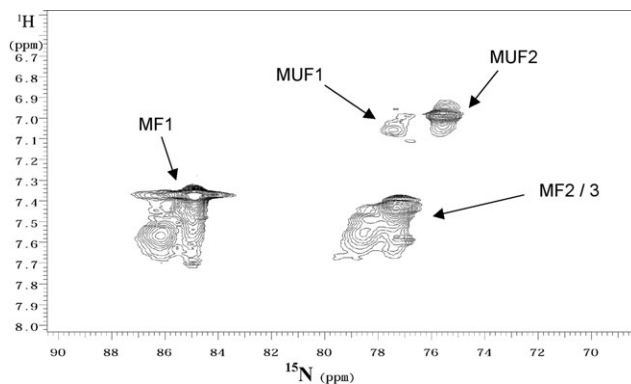
## EXPERIMENTAL

### Melamine-Urea-Formaldehyde (MUF) Resin Sample

$^{15}\text{N}$ -Labeled melamine was made using a reported method.<sup>23</sup> The labeled melamine was then incorporated into an MUF resin using a procedure supplied by Momentive Specialty Chemicals Pty. Ltd.<sup>26</sup> The resin was made on a 20 g scale with a 20% substitution of melamine with melamine  $^{15}\text{N}$ -labeled at  $\text{NH}_2$ .



**Figure 2.**  $^1\text{H}$ - $^{15}\text{N}$ - $^{13}\text{C}$  resonances for methylene (MUF1) and dimethylene-ether (MUF2) linked MUF co-polymers.<sup>23</sup>



**Figure 3.**  $^1\text{H}$ - $^{15}\text{N}$  HMQC NMR spectrum of MUF commercial resin sample using  $^{15}\text{N}$ -labeled melamine.

A sample was removed from the reaction mixture and cooled in liquid nitrogen. The water was removed on a freeze dryer and the remaining residue was dissolved in  $^2\text{H}_6$ -DMSO for NMR analysis.

### Phenol-Urea-Formaldehyde (PUF) Resin Sample

$^{15}\text{N}$ -Labeled (98+ atom%) urea, aqueous  $^{13}\text{C}$ -labeled formaldehyde (20% w/w, 99+ atom%) and unlabeled phenol were purchased from Sigma-Aldrich Pty Ltd, Castle Hill, Australia. Phenol (1.0 mmol, 94 mg), NaOH (0.35 mmol), and  $^{13}\text{C}$ -labeled aqueous formaldehyde (20% w/w, 99+ atom%, 180 mg) solution were stirred together at  $30^\circ\text{C}$ . After 10 min,  $^{15}\text{N}$ -labeled urea (98+ atom%, 0.24 mmol, 14.4 mg) was added and the reaction mixture was heated to  $90^\circ\text{C}$  over 30 min. Another 15 mg of the formaldehyde solution was then added to the reaction. The mixture was stirred at  $90^\circ\text{C}$  for a further 10 min. The reaction mixture was then cooled in liquid nitrogen and freeze-dried before being dissolved in  $^2\text{H}_6$ -DMSO for NMR analysis.

### Hydroxymethylphenol-UF Sample

Hydroxymethylphenol was made by mixing phenol (1.36 mmol, 128 mg) with aqueous formaldehyde (20% w/w, 99+ atom%) solution. The pH was adjusted to 11 with 3 M NaOH solution and the mixture was stirred at room temperature for 20 min. Urea (5.31 mmol, 319 mg) was then added and the pH of the solution was adjusted to 3 with formic acid. The PUF reaction was then heated to  $80^\circ\text{C}$  for 20 min. The resulting mixture was cooled and then freeze-dried. The dried residue was then dissolved in  $^2\text{H}_6$ -DMSO for NMR analysis.

### Phenol-Melamine-Formaldehyde (PMF) Resin Sample

The reactions conditions for the preparation of the PMF sample were supplied by Momentive Specialty Chemicals Pty. Ltd. and were conditions in the first stage of phenol-melamine-urea-formaldehyde (PMUF) resin formula used for the manufacturing of plywood.<sup>26</sup>  $^{15}\text{N}$ -Labeled (98+ atom%) melamine and  $^{13}\text{C}$ -labeled formaldehyde (20% w/w, 99+ atom%) solution were used to enhance NMR signals. To simplify the NMR spectrum, the resin sample that was analyzed by NMR spectroscopy was taken after the melamine addition and before any urea was added to reaction. Therefore, any detected co-polymerization would be due to melamine-phenol and not melamine-urea copolymers.

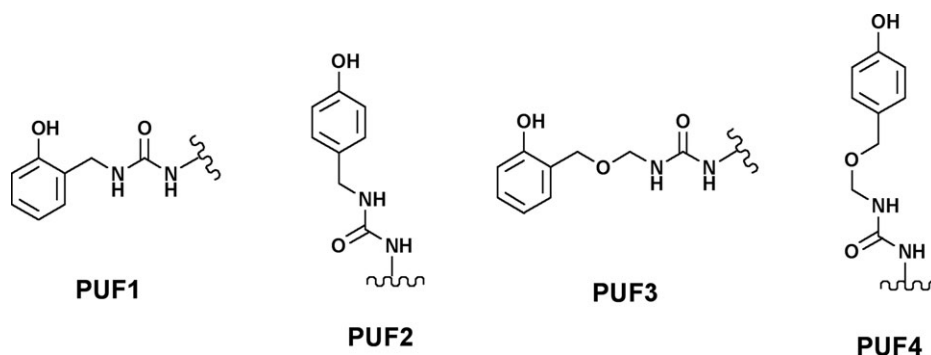


Figure 4. Possible PUF co-polymer products.

## RESULTS AND DISCUSSION

### Melamine-Urea-Formaldehyde (MUF) Resin Analysis

The chemistry of formaldehyde condensing with melamine and urea is well known and produces methylene and dimethylene-ether linked species (Scheme 1). Model studies identified and characterized methylene and dimethylene-ether linked co-polymers (MUF1 and MUF2, Scheme 1).<sup>23</sup> In these studies,  $^1\text{H}$ - $^{15}\text{N}$  NMR spectra of homo-polymer reactions (UF and MF) were compared with those of MUF reactions. The  $^{15}\text{N}$ - and  $^1\text{H}$ -chemical shifts of the resonances observed in the homo-polymer spectra (not shown) all correspond to those previously obtained using 1D NMR spectroscopic methods.<sup>10,27,28</sup>  $^{15}\text{N}$ -Labeled melamine was used in resin preparation to identify  $^1\text{H}$ - $^{15}\text{N}$  correlations observed in spectrum for the MUF reaction (Figure 1), which were not evident in the MF reaction. In Figure 1, cross-peaks arise from melamine moieties only because the melamine is  $^{15}\text{N}$ -labeled and the urea is not. The two co-polymer correlations have  $^{15}\text{N}$  resonances at  $\delta$  74.5–75.5 and 76.0–77.0 ppm, and  $^1\text{H}$  resonances at  $\delta$  6.8–6.9 and 6.8–6.9 ppm, respectively (Figure 1). Each of the  $^1\text{H}$ - $^{15}\text{N}$  co-polymer cross-peaks were doubly selected in a series of one-dimensional triple resonance,  $^{13}\text{C}$ -detected experiments to determine the chemical shift of the carbon in each co-polymer bridge. Similarly,  $^{15}\text{N}$ -labeled urea (spectrum not shown) was used in reactions with unlabeled melamine to fully characterize the co-polymer bridges. The chemical shift assignments of the H-N-C co-polymer MUF bridges are shown in Figure 2.<sup>23</sup>

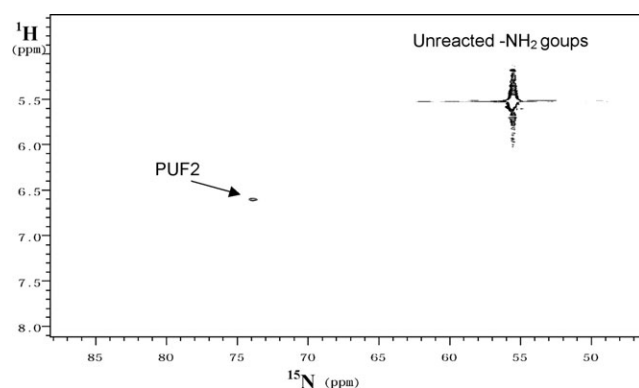


Figure 5.  $^1\text{H}$ - $^{15}\text{N}$  HMQC NMR spectrum of a hydroxymethylphenol-UF reaction sample.

With the  $^1\text{H}$ - $^{15}\text{N}$ - $^{13}\text{C}$  chemical shifts of the co-polymer links in hand, we then set-out to determine whether co-polymerization occurs in a commercial MUF resin. A resin was therefore made with 20%  $^{15}\text{N}$ -labeled melamine<sup>23</sup> using a commercial protocol supplied by Momentive Specialty Chemicals Pty. Ltd.<sup>26</sup> The  $^1\text{H}$ - $^{15}\text{N}$  HMQC NMR spectrum from the model studies (Figure 1) was then compared with the spectrum obtained from the resin sample that was made using a commercial recipe (Figure 3).<sup>26</sup> The two  $^1\text{H}$ - $^{15}\text{N}$  NMR correlations observed in the model MUF co-polymer experiment (Figure 1, MUF1 and MUF2) are also evident in the NMR spectrum of the commercial resin sample (Figure 3, MUF1 and MUF2), indicating the formation of dimethylene-ether (MUF2) and methylene (MUF1) cross-links. Therefore co-polymerization occurred in the MUF resin made following the protocol of Momentive Specialty Chemicals Pty. Ltd.<sup>26</sup>

### Phenol-Urea-Formaldehyde (PUF) Resin Analysis

Having shown the effectiveness of  $^{15}\text{N}$  NMR correlation spectroscopy for the characterization of MUF co-polymers, the technique was then applied to the structural analysis of PUF resins. The possible PUF co-polymers are shown in Figure 4. Initially, model reactions were analyzed by NMR spectroscopy. It has been reported that reacting hydroxymethylphenol with urea results in co-polymer PUF linkages.<sup>14,29</sup> By eliminating formaldehyde, co-polymer linkages are presumably favored because urea can only react with hydroxymethylphenol. Therefore,

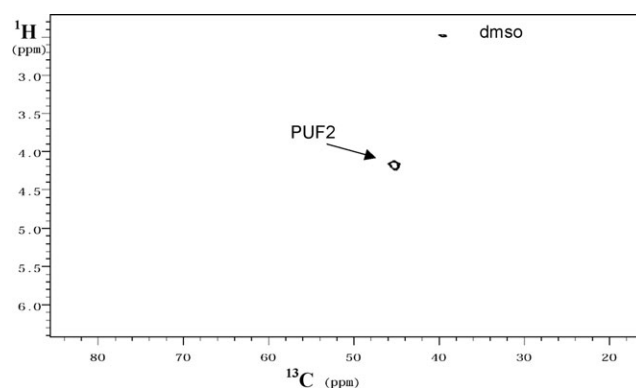
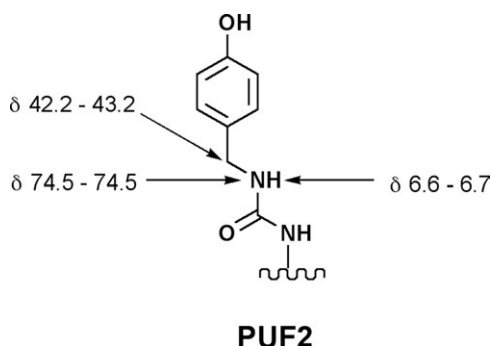
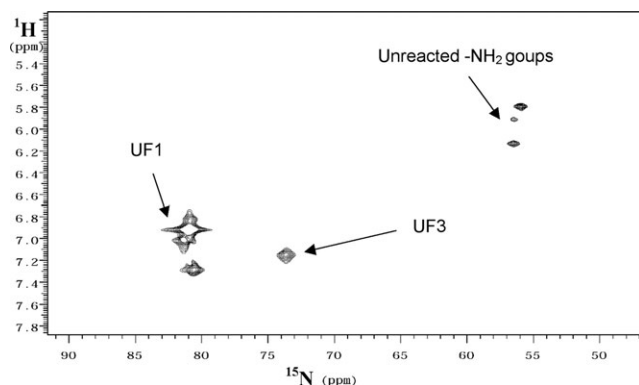


Figure 6.  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of a hydroxymethylphenol-UF reaction sample in the solvent DMSO.

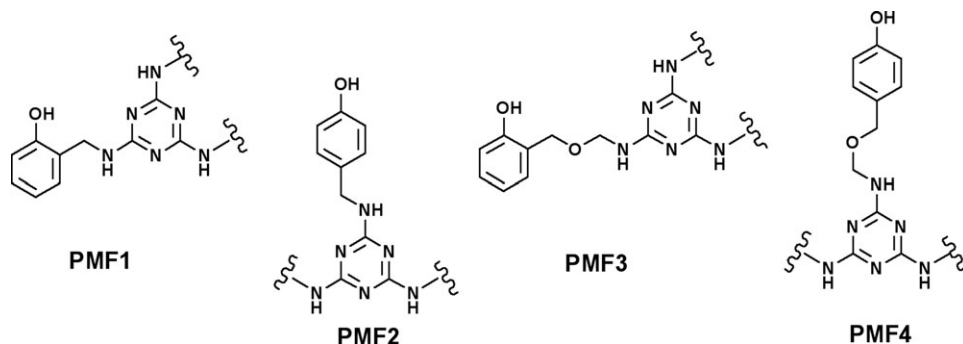


**Figure 7.**  $^1\text{H}$ - $^{15}\text{N}$ - $^{13}\text{C}$  resonances for methylene (PUF2) linked PUF co-polymers.

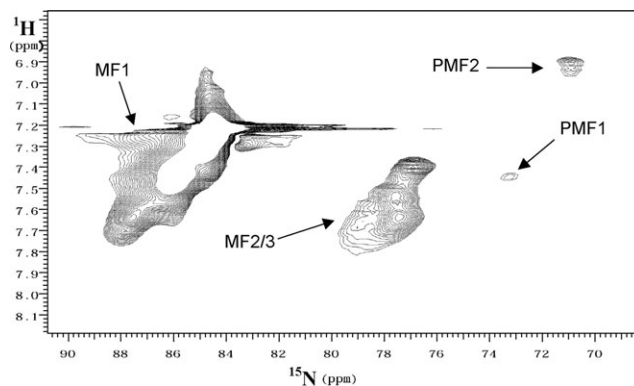


**Figure 8.**  $^1\text{H}$ - $^{15}\text{N}$  HMQC NMR spectrum of a PUF resin.<sup>12</sup>

hydroxymethylphenol was made *in situ* and was then added to urea without additional formaldehyde. This reaction was performed in acidic conditions as reported in the co-polymer studies performed by Tomita et al.<sup>29</sup> The  $^1\text{H}$ - $^{15}\text{N}$  HMQC spectrum of the reaction sample is shown in Figure 5. The cross-peaks with  $^{15}\text{N}$  shifts from  $\delta$  53.0 to 57.0 ppm are due to unreacted urea-NH<sub>2</sub> groups. The  $^1\text{H}$ - $^{15}\text{N}$  correlation at  $\delta$  73.5–74.5 ppm/ $\delta$  6.6–6.7 ppm does not correspond to known UF reaction products<sup>23</sup> and is therefore due to a PUF co-polymer. Because there is only one co-polymer correlation it was not necessary to employ  $^1\text{H}$ - $^{15}\text{N}$ - $^{13}\text{C}$  correlation NMR spectroscopy as a  $^1\text{H}$ - $^{13}\text{C}$  correlation is sufficient for characterization of a single moiety.



**Figure 9.** Possible PMF co-polymer products.

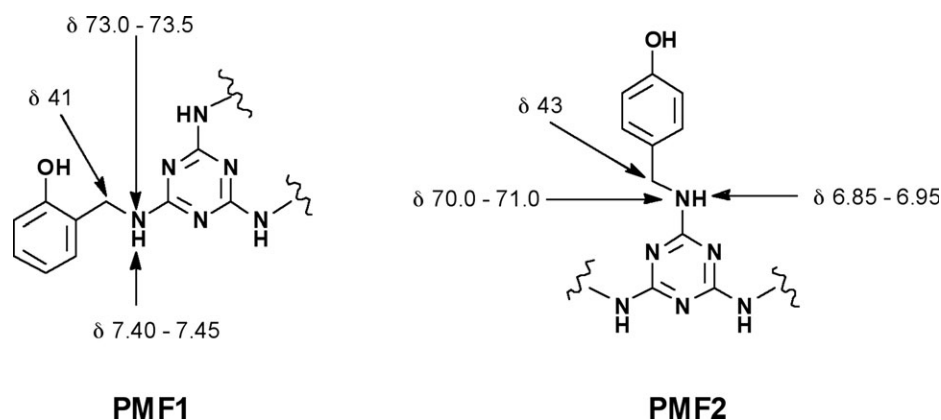


**Figure 10.**  $^1\text{H}$ - $^{15}\text{N}$  HMQC NMR spectrum of PMF commercial resin sample using  $^{15}\text{N}$ -labeled melamine.

The  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of the same sample is shown in Figure 6. The spectrum of the hydroxymethylphenol-urea-formaldehyde reaction sample has one  $^1\text{H}$ - $^{13}\text{C}$  cross-peak not due to a UF species at  $\delta$  42.2–43.2 ppm/ $\delta$  4.1–4.3 ppm. A carbon with a chemical shift at  $\delta$  42.2–43.2 ppm is indicative of a methylene link in the *para*-phenolic position.<sup>14,29</sup> From analysis of this NMR data, it is clear that the cross-peak labeled PUF2 in Figures 5 and 6 are due to a PUF co-polymer *para* linkage. The H-N-C resonance assignments of a phenol-urea co-polymer (PUF2) are now known and shown in Figure 7. To determine whether this co-polymer occurs in the presence of formaldehyde, a PUF resin sample was prepared using typical pH and temperature and the resulting  $^1\text{H}$ - $^{15}\text{N}$  HMQC NMR spectrum is shown in Figure 8. Only cross-peaks arising from UF reactions products<sup>23</sup> were observed indicating that co-polymers had not formed. Although co-polymers did not form using the described protocol, these NMR techniques can now be used to determine if co-polymers form with other PUF resins.

#### Phenol-Melamine-Formaldehyde (PMF) Resin Analysis

Strategies developed for the structural analysis of the MUF and PUF resins were then used to assess co-polymerization in PMF resin samples. The possible melamine-phenol co-polymer linkages that could form through the *ortho* and/or *para* position on phenolic residues during condensation with melamine are shown in Figure 9. The commercial protocol employed was again supplied by Momentive Specialty Chemicals Pty. Ltd.<sup>26</sup>



**Figure 11.**  $^1\text{H}$ - $^{15}\text{N}$ - $^{13}\text{C}$  resonances for methylene linked PMF co-polymers.

The sample studied by NMR spectroscopy was taken at an intermediate stage of the resin process before any urea was added to resin to eliminate the possibility of melamine-urea co-polymers thus simplifying the NMR spectrum.

Figure 10 displays the  $^1\text{H}$ - $^{15}\text{N}$  NMR spectrum of the PMF sample. By comparing this NMR spectrum to one obtained from MF reaction products (Figure 1), two new cross-peaks are apparent and are therefore due to co-polymers. To identify the co-polymer links by characteristic carbon chemical shift, the two cross-peaks labeled PMF1 and PMF2 were double selected and correlated to the adjacent carbon. This three bond correlation was achieved by employment of the  $^1\text{H}$ - $^{15}\text{N}$ - $^{13}\text{C}$  triple resonance experiment originally designed for the characterization of MUF co-polymer bridges.<sup>23</sup> The cross-peak labeled PMF1 ( $\delta$  73.0–73.5 ppm/ $\delta$  7.40–7.45 ppm) was correlated to a carbon with a resonance of  $\delta$  41 ppm indicating that this cross-peak is due to methylene links at the *ortho* position.<sup>20</sup> The other co-polymer cross-peak PMF2 ( $\delta$  70.0–71.0 ppm/ $\delta$  6.85–6.95 ppm) was correlated to a carbon with resonance  $\delta$  43 ppm, which is indicative of a methylene link at the *para* position.<sup>20</sup> The PMF methylene co-polymer bridges have thus been identified in a commercial PMUF resin and the chemical shifts of the methylene linkages are summarized in Figure 11.

## CONCLUSION

NMR techniques developed to study MUF model reactions were applied to commercial thermosets.  $^1\text{H}$ - $^{15}\text{N}$  HMQC NMR spectra of MUF model reaction products were compared with spectra obtained from resins manufactured using industrial conditions. From these comparisons it is evident that co-polymerization can and does occur in commercial MUF resins. Furthermore,  $^1\text{H}$ - $^{15}\text{N}$  NMR correlation spectroscopy as well as  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectroscopic data showed that PUF co-polymers did not form when typical alkali conditions were employed.  $^1\text{H}$ - $^{15}\text{N}$ - $^{13}\text{C}$  triple resonance NMR spectroscopy was also used to assign  $^1\text{H}$ - $^{15}\text{N}$ - $^{13}\text{C}$  fragments in PMF co-polymers.

Methods have therefore been established that can be used to monitor process conditions that lead to co-polymers and those that result in homo-polymer mixtures. It is now possible to relate the chemical structures of thermosetting resins to their

physical properties enabling the assessment of co-polymerization and the optimization of manufacturing processes.

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