

# Examination of Selected Synthesis Parameters for Wood Adhesive-Type Urea–Formaldehyde Resins by $^{13}\text{C}$ NMR Spectroscopy. III

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Received 30 April 1999; accepted 17 August 2000

**ABSTRACT:** The varying polymer structures of wood adhesive-type urea–formaldehyde resins resulting from different formaldehyde/first urea ( $F/U_1$ ) mole ratios used in the first step of resin manufacture were investigated using  $^{13}\text{C}$  NMR. As the  $F/U_1$  mole ratio decreased progressively from 2.40 to 2.10 and to 1.80, the viscosity increase due to polymerization during resin synthesis became faster and resulted in decreasing side-chain branches and increasing free urea amide groups in the resin structure. The resultant UF resins, with the second urea added to an overall  $F/(U_1 + U_2)$  of 1.15, showed viscosity decreases when heated with stirring or allowed to stand at room temperature that were also characteristic with the  $F/U_1$  mole ratios used in resin synthesis. The formaldehyde emission levels of particleboards bonded with the freshly made UF resins showed relatively small but similarly characteristic variations. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2800–2814, 2001

**Key words:** wood adhesive; urea–formaldehyde resins; UF resin chemistry; particleboard bonding

## INTRODUCTION

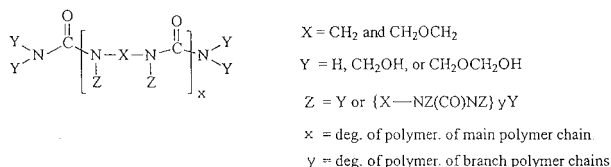
Some details on the polymer chain structure of wood adhesive-type thermosetting urea–formaldehyde (UF) resins based on  $^{13}\text{C}$  NMR data were reported in previous publications.<sup>1–3</sup> UF resins, known for many decades,<sup>4–11</sup> are a major thermosetting wood adhesive in the manufacture of wood composite boards, such as particleboard and medium density fiberboard.<sup>12</sup> The drawbacks of UF resins in these applications are the low water resistance and formaldehyde emission from the wood composite boards.<sup>13–16</sup> The overall formaldehyde/urea ( $F/U$ ) mole ratio used in the manu-

facturing of UF resins, which currently runs at a low value of about 1.15, is a key parameter that determines the formaldehyde emission levels of boards. In general, use of higher  $F/U$  mole ratios in resins improves the wood composite boards' physical performance but results in increases in the formaldehyde emission level. Scavengers are often used to help keep the formaldehyde emission levels in check.<sup>17</sup>

In manufacturing wood adhesive-type UF resins, as described in previous reports,<sup>1–3</sup> urea is employed in two parts: first urea ( $U_1$ ) and second urea ( $U_2$ ). In the first step of resin synthesis, the first urea ( $U_1$ ) is reacted with formaldehyde at an  $F/U_1$  ratio of about 2.10 in a weakly alkaline aqueous medium at an elevated temperature. Mono-, di-, and trihydroxymethylureas, and some of their secondary products containing methyl-

Contract grant sponsor: USDA NRI; contract grant number: 97-35103-5051.

*Journal of Applied Polymer Science*, Vol. 80, 2800–2814 (2001)  
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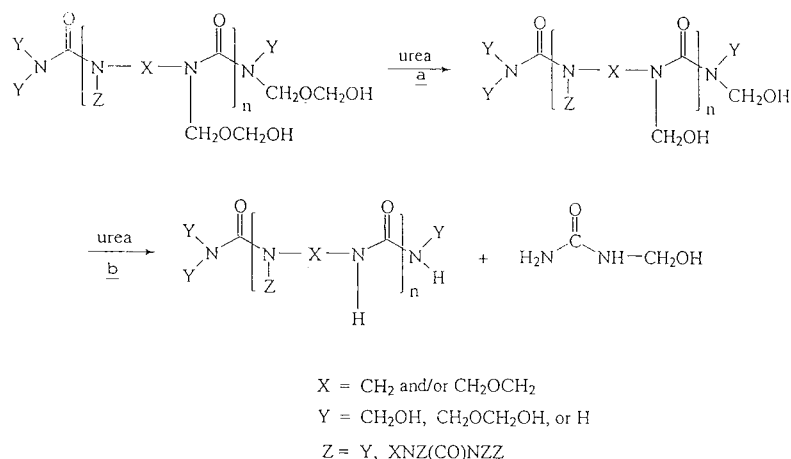
**Figure 1** A schematic representation of UF resin polymer molecules with groups Z's representing possible polymer chain branches that can also form polymer chain branches themselves.

ene-ether bonds, are formed. The hydroxymethylation reactions occurring between urea and formaldehyde are slightly reversible:  $k_1 = 1.1 \times 10^{-4}$  mole/L s and  $k_{-1} = 2.7 \times 10^{-6}$  mole/L s at  $35^\circ\text{C}$  at pH 7.0, the forward reaction being about 40 times faster than the reverse reaction in dilute solutions.<sup>9</sup> In the second step of resin synthesis, the reaction mixture is adjusted to an acidic pH between 4 and 5 and reacted further, where the hydroxymethyl groups attack urea amide nitrogens to form mostly methylene bonds leading to UF resin polymers. During this polymerization reaction, some hydroxymethyl groups split off as formaldehyde because the reverse hydroxymethylation reaction is apparently operative also under the acidic condition and the number of available amide groups in the resin system is decreasing, since the average functionality of urea attainable under this typical UF resin synthesis condition is only about 2.5–2.6.<sup>1,2</sup>

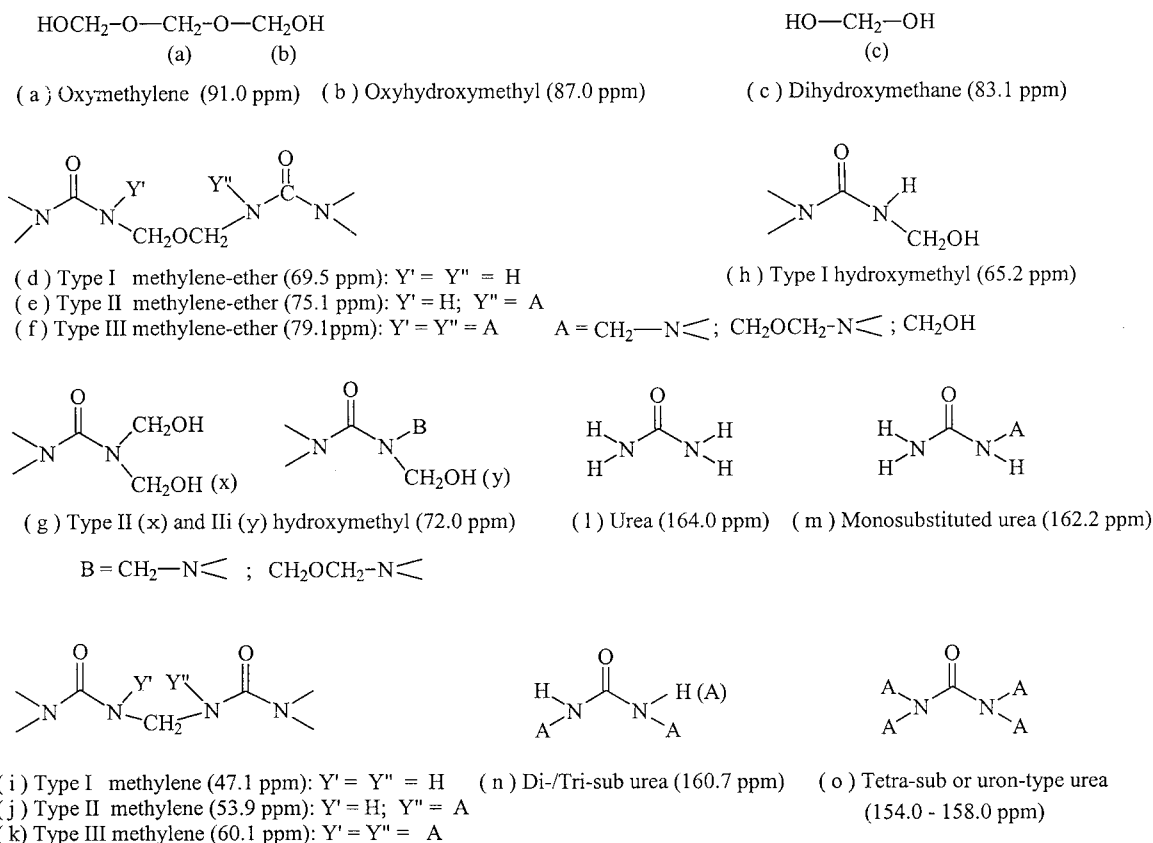
The polymerization reaction in resin synthesis is normally ended when the viscosity of the reaction mixture reaches up to about "W" by the Gardner-Holdt scale ( $\sim 32$  P) at resin solids levels

between 60 and 65% by neutralizing to a weakly alkaline pH. The resulting polymers are polymeric methylene methylene-ether hydroxymethylureas (Fig. 1). The second urea ( $U_2$ ) is then added to attain a combined formaldehyde/urea [ $F/(U_1 + U_2)$ ] ratio value of about 1.15 during the cooling down period, which reacts with the formaldehyde split off in the polymerization step to form various monomeric hydroxymethylureas. It was shown that some hydroxymethyl groups bonded to the polymeric UF resin molecules also cleave and the resultant formaldehyde reacts with the second urea (Fig. 2). In industrial UF resins the extent of this hydroxymethyl group migration at the time of use varies because of the varying temperature and time used in the cooling period as well as the length of time taken in transportation.<sup>3</sup> This migration of hydroxymethyl groups is investigated further in this study.

The major concern of this study is the different UF resin polymer structures resulting from the different  $F/U_1$  mole ratios used in the first step of resin synthesis. As discussed in the previous report,<sup>1</sup> the  $F/U_1$  mole ratio affects various resin synthesis parameters and results in resin having different storage and performance behaviors. For example, higher  $F/U_1$  mole ratios slow down the rate of viscosity increase while lower values increase it in the acidic polymerization step, and  $F/U_1$  mole ratios lower than about 1.85 result in resins having increasingly higher turbidity and non-Newtonian viscosity behaviors as well as reduced wood bonding efficiency. The formaldehyde emission performance also appeared to be affected by this parameter. These various results



**Figure 2** Migration of hemiformal groups (a) and hydroxymethyl groups (b) from polymeric to monomeric UF resin components.



**Figure 3** Chemical structures of molecules and carbon groups occurring in polymeric UF resins with their  $^{13}\text{C}$  NMR shifts identified with lowercase letters from (a) to (o) with respect to peaks identified in Figure 4(a).

indicated that UF resin polymer structures are significantly affected by  $\text{F}/\text{U}_1$  mole ratios, but details were unknown. On the other hand, varying the  $\text{F}/\text{U}_1$  mole ratio results in resins with varying amounts of the second urea due to the similar overall  $\text{F}/\text{U}$  mole ratios used in final resins. The second urea constitutes the monomeric components in the resin relative to the polymeric UF resin components formed in the first step of resin synthesis. The  $\text{F}/\text{U}_1$  mole ratio therefore changes the balance between the two components and can significantly affect the thermosetting curing processes of resins. Thus, a detailed investigation on the  $\text{F}/\text{U}_1$  mole ratio effects was initiated with an intention to find a systematic way to optimization of UF resin compositions. Thus, resin synthesis reactions were carried out with an  $\text{F}/\text{U}_1$  ratio of 1.80, 2.10, and 2.40, the second urea added in corresponding amounts to completely cooled reaction mixtures.  $^{13}\text{C}$  NMR spectra were then obtained on the resin samples before and after stirring/heating at  $60^\circ\text{C}$  for various lengths of time to

estimate the methylene-ether and methylene group-based polymer chain structures from the migration levels of hydroxymethyl groups. Also, the UF resins were evaluated for bonding of particleboards and the formaldehyde emission levels, and also subjected to storage at room temperature over a period of 50 days to probe the effects of different polymer structures on viscosity changes of resin samples.

Definitions of various chemical structures occurring in UF resin polymers and their  $^{13}\text{C}$  NMR chemical shift values are shown in Figures 3 with the corresponding spectral peaks marked in Figure 4.<sup>18-20</sup> The one key uncertainty that arises in interpretation of spectral data is the chemical shift overlap of Types II and III hydroxymethyl groups at 72.0 ppm. Type III hydroxymethyl groups, by their substituent effects, cause the neighboring methylene and methylene-ether groups appear as groups with higher degrees of branching. Although Type III hydroxymethyl groups by themselves constitute polymer chain

branches in resin structure, the labile nature of hydroxymethyl groups makes it desirable to quantify them and obtain polymer chain structures unencumbered by them. The method for solving this dilemma used in previous studies<sup>2,3</sup> was adding the second urea after the reaction mixture was completely cooled down to first suppress the migration of hydroxymethyl groups and then subjecting the resins at elevated temperatures, up to 70°C, to effect a controlled maximum extent migration of hydroxymethyl groups possible without resulting in much disturbance in other resin properties for accurate NMR measurements. Type II/III hydroxymethyl group contents of the resin samples, at 72.0 ppm, were determined, which decreased with the heat treatment time. The optimum final value was employed, assuming residual Type III hydroxymethyl groups are negligible, to obtain the approximate polymer chain structures of resins in terms of methylene and methylene-ether bonds. The residual levels of Type II/III hydroxymethyl groups remained to be a problem in this approach, and therefore a further refinement of the heat treatment method was experimented in this study using a milder temperature 60°C. The heat treatment used in the earlier study (70°C) was somewhat severe, resulting in formation of some methylene-ether bonds and some cloudiness in resin samples which could have distorted the <sup>13</sup>C NMR analysis results.

Because of the limited solubility in water or many other organic solvents and the varying migration extent of hydroxymethyl groups as discussed above, <sup>13</sup>C NMR spectroscopy is uniquely suited for molecular structure characterizations of UF resins.<sup>1-3,18-23</sup> On the other hand, quantification results can include the spectral effects of spin relaxation times that would vary with hydrodynamic changes of UF polymer molecules.<sup>24,25</sup> Considering the fact that UF polymers are only partially soluble in water and cannot be diluted too much in NMR sample preparations, some such errors would be unavoidable in most cases and might become serious with decreasing polymer solubilities. In this study, however, the UF resin sampling was made in the range that gave relatively good solubilities in terms of the F/U<sub>1</sub> ratio and extent of polymerization, and the spectral quantifications and discussions were made only with necessary methylenic carbons—all of which had very short spin-lattice relaxation times compared with the pulse delay time used. The quantitative arguments made in this study

therefore appears to be well justified. Urea carbonyl carbons were quantified separately from methylenic carbons and although the pulse delay was less than their spin-lattice relation times, the results were in line with the expectation useful in comparing the differently substituted carbonyl carbons

## EXPERIMENTAL

Reagent grade urea, sulfuric acid, sodium hydroxide, and a fresh industrial grade 50% formaldehyde solution kept at 60°C in the laboratory were used. All pH adjustments were made using 4.0% sulfuric acid and 8.0% sodium hydroxide solutions, and the pH drifts were maintained within ±0.1.

### Synthesis of Resin Sample 2.10 Series Using an F/U<sub>1</sub> Ratio of 2.10

The resin synthesis was carried out according to the procedure described earlier.<sup>1-3</sup> A 3150-g aliquot of 50% formaldehyde solution was charged into a stirred reactor and, after adjusting the pH to 7.8, heated to 70°C, the first urea, 1500 g, was added over a period of 15 min (F/U<sub>1</sub> = 2.10). The temperature of the reaction mixture was then allowed to rise to 90°C and maintained at the temperature for 30 min with intermittent external cooling to eliminate the exothermic heat. Then, the pH of the reaction mixture was lowered to 4.5 and the polymerization reaction conducted at 95°C until viscosity "X" was reached (approximately 120 min), when it was neutralized to pH 7.8 and cooled to ~4°C to obtain Sample 2.10a. Then, the second urea (1237 g) was added to attain the final F/U mole ratio of 1.15, stirred for an hour and slowly warmed up to room temperature to obtain Sample 2.10b. Both samples were then stored at 4°C for about three days until analyses.

For the heat treatment for expediting the migration of hydroxymethyl groups to the second urea, a 800-g aliquot of this resin was put in a reactor and stirred and heated to 60°C over a period of 40 min and maintained at the temperature for 90 min to obtain Sample B2.10c (400 g), and it was stirred for an additional 60 min at 60°C to obtain Sample 2.10d (400 g). The decreasing viscosity changes were recorded during the heat treatments. The heat-treated resin samples were cooled to and stored at 4°C for about three days until analyses. All samples were sent over-

night to the testing laboratory for  $^{13}\text{C}$  NMR analyses.

#### Synthesis of Resin Sample 2.40 Series Using an F/U<sub>1</sub> Ratio of 2.40

The procedure used was the same as the one used above except that the first urea was reduced to 1313 g (F/U<sub>1</sub> = 2.40) to obtain Sample 2.40a. To compensate for the slower polymerization reaction rate at this higher F/U<sub>1</sub> ratio, the reaction was conducted at pH 4.10, still the time being lengthened to 140 min. The second urea was increased to 1426 g (F/U = 1.15) to obtain Samples 2.40b. Similar heat treatments of this resin sample resulted in Samples 2.40c and 2.40d, which were similarly analyzed.

#### Synthesis of Resin Sample 1.80 Series Using an F/U<sub>1</sub> Ratio of 1.80

The procedure used was generally the same as the one used for the Sample 2.10 series with the amount of the first urea increased to 1750 g (F/U<sub>1</sub> = 1.80) and the second urea decreased to 989 g (F/U = 1.15). One modification specifically made was dividing the first urea into two parts to minimize the turbidity developing in the resin during the polymerization step, which normally begins when the F/U<sub>1</sub> ratio is lowered to about 1.85. Thus, the first part of the first urea (1500 g) was reacted with formaldehyde in the alkaline pH, followed by the similar acidic polymerization reaction until 10 min after a viscosity "B" was obtained (approximately 30 min at 95°C and pH 4.5). Then, the reaction mixture was neutralized back to pH 7.8 and the second part of the first urea (250 g) was added and reacted for 20 min at 90°C at the weakly alkaline pH. The reaction mixture was then acidified to pH 4.50 and reacted at 90°C until a viscosity of "W" was reached (approximately 30 min) to obtain Sample 1.80a. Samples 1.80b, 1.80c, and 1.80d were then obtained, and analyzed similarly as for Sample 2.10 series. All Sample 1.80 series resins showed a very light turbidity, which was much less than in resins made without the modification of splitting the first urea.

#### Room Temperature Storage and Viscosity Measurements

Resin Samples 2.40b, 2.10b, and 1.80b were filled in Gardener–Holdt viscosity measurement tubes

(10.65 mm diameter × 108 mm long), and allowed to stand at room temperature (~23°C) over a period of 50 days in December and January. The viscosity was measured (and turbidity observed) periodically.

#### Particleboard (PB) Preparation and Strength and Formaldehyde Emission Tests

Particleboard manufacturing and testing procedures were the same as those reported earlier from this laboratory.<sup>2,3,26</sup> Resin samples were freshly prepared and aged for 2 days at room temperature (Samples 2.40b, 2.10b, and 1.80b). To explain briefly: single-layer PBs were made with dried core-layer wood particles obtained from Georgia-Pacific Corporation PB plant in Louisville, Mississippi. A rotary drum blender, forming box, and Williams-White hot press were used. The hot pressing was done at 163°C for 3 min. Two PB panels (506 × 506 × 12.65 mm) with a target board density of 801 kg/m<sup>3</sup>-density (50 lb/ft<sup>3</sup>) were made for each resin. For the formaldehyde emission tests, the hot-pressed PBs were first equilibrated for 24 h in the laboratory and eight test pieces (69.6 × 126.5 mm) were cut from each board, wrapped in a plastic bag, and sent to the Composite Panel Association's testing laboratory (Gaithersville, MD)<sup>27</sup> for the standard 2 h desiccator tests.<sup>27</sup> In this desiccator test, the samples are edge-sealed with molten wax, aired for 24 h, and the amount of formaldehyde emitted over a period of 2 h at 75°F is measured. The board samples, providing a total exposed board face area of 0.141 m<sup>2</sup> in each test, are placed in a closed desiccator along with 25 mL water placed in a shallow beaker, which absorbs the formaldehyde emitted. The test results are reported in μg formaldehyde/mL water. The internal bond and bending strengths of boards were measured after equilibrating samples for three weeks in a constant humidity chamber to about 10% moisture content in accordance with the American Society for Testing and Materials Procedure D 1037.<sup>26</sup>

#### Procedure for $^{13}\text{C}$ NMR Spectra and Calculation of Carbon Group Values

Test samples were prepared by mixing 2.0 g of resin and 1.0 g of deuterium oxide. Spectra were obtained with a Techmag 360 MHz NMR Spectrometer using a pulse width of 22 μs (80°) and an ample pulse delay of 10 s to secure quantitative results at least for all methylenic carbons (Spec-

**Table I Percentage Values for Various Methylenic and Carbonyl Carbons of UF Resin Samples Determined Using  $^{13}\text{C}$  NMR Spectroscopic Method and Formaldehyde Emission Values of Bonded Particleboards<sup>a</sup>**

Groups (ppm)	Synthesized/Heat-Treated Urea-Formaldehyde Resin Samples											
	2.4a	2.4b	2.4c	2.4d	2.1a	2.1b	2.1c	2.1d	1.8a	1.8b	1.8c	1.8d
91.0	2.31	0.79	0.79	0.85	1.23	0.52	0.83	0.65	0.98	0.36	0.41	0.40
87.0	8.00	0.24	0.27	0.25	4.84	0.19	0.46	0.37	3.13	0.10	0.20	0.20
83.1	10.49	0.28	0.20	0.62	7.39	0.29	0.29	0.39	4.13	0.28	0.37	0.26
79.1	3.20	2.66	2.43	1.87	1.90	2.22	1.85	2.12	2.74	2.15	2.28	2.05
75.1	7.15	4.98	3.76	3.97	6.69	4.82	4.74	4.07	5.40	4.50	4.58	4.21
69.5	8.52	6.79	7.67	8.12	9.18	7.27	8.92	9.32	10.57	8.92	9.50	9.58
72.0	17.04	17.91	11.89	10.51	18.24	18.52	12.83	11.97	16.50	15.19	11.68	11.35
65.2	11.87	35.01	40.20	40.36	15.39	29.66	34.26	35.11	18.91	26.70	29.40	30.56
60.1	6.52	4.64	4.84	4.23	5.81	4.48	2.71	4.56	5.39	4.29	4.88	2.75
53.9	19.50	21.06	19.33	19.53	21.40	23.79	23.26	20.59	22.28	25.81	23.50	24.70
47.4	5.40	5.64	8.65	9.69	7.93	8.24	9.85	10.85	9.97	11.70	13.20	13.94
164.0	0.00	28.01	23.32	16.70	0.00	26.39	23.36	21.61	0.00	25.08	21.81	20.76
162.2	0.95	23.58	28.94	37.35	1.83	18.44	25.60	27.62	5.11	15.91	23.50	24.75
160.7	94.29	45.86	45.47	44.02	94.63	54.03	49.51	49.21	90.77	56.78	53.02	52.88
158.0	4.76	2.55	2.26	1.93	3.54	1.14	1.53	1.56	4.12	2.23	1.67	1.61
CH <sub>2</sub> O <sup>a</sup>	—	0.60	—	—	—	0.70	—	—	—	0.72	—	—

<sup>a</sup> Sample numbers are as defined in the text and chemical structures and chemical shifts are shown in Figures 3 and 4(a). Formaldehyde emission values ( $\mu\text{g}/\text{mL}$ ) were from 2-h desiccator method described in the text.

tral Dada Services, Inc., Champaign, IL). Decoupling power was kept on during the acquisition and off during the delay to suppress the nuclear Overhauser effect.<sup>24</sup> The  $^{13}\text{C}$  NMR relaxation times,  $T_1$ , measured on UF resin samples similar to Sample 2.10b by the inversion-recovery method,<sup>25</sup> were 1.4–6.2 s for urea carbonyls, 1.1 s for methanediol, 5.8 s for methanol present as impurity, and 0.16 s or less for all other methylenic carbons.<sup>2</sup> Normally, about 400 scans were accumulated. Spectral peaks were integrated and urea carbonyls and methylenes were separately quantified as percentages, assuming no formaldehyde losses during resin syntheses had occurred.

#### Calculation Method of UF Polymer Structures

The calculation procedure described in previous reports<sup>2,3</sup> was slightly modified. To explain briefly: from the spectral integration values of heat-treated Resin Samples 2.40d, 2.10d, and 1.80d, the methylene and methylene-ether group percentage values were obtained (Table I), and the

former and one half of the latter values were combined by I, II, or III types of bonds. Each of these values was then multiplied with the respective  $F/U_1$  mole ratio value used in synthesis to obtain the bond contents per mole of the first urea. The total of all bond type values ( $a$ ) was then converted to the degree of polymerization value ( $n$ ) using the appropriate equation,  $n = 1/(1 - a)$ .<sup>28</sup> The number of polymer chain branches per polymer molecule was then obtained for each bond type by multiplying the bond type values with the degree of polymerization ( $n$ ) and then with 1.0 for Type III and 0.5 for Type II bonds. For Type I bonds, 2.0 branches were assigned regardless of the bond content. The combined, total number of polymer chain branches per polymer molecule was then divided by the degree of polymerization to obtain the total polymer chain branch number per urea ( $U_1$ ) unit. This procedure includes the residual Type II hydroxymethyl groups as branches, although their levels in appropriately heat-treated UF resins would be relatively low. Other calculation methods are further discussed in the discussion section.

## RESULTS AND DISCUSSION

### Polymer Structure Interpretation of UF Resin Samples from $^{13}\text{C}$ NMR Data

The optimization of  $^{13}\text{C}$  NMR measurement condition as used in this study and the overall chemical and polymer structures of UF resin components in terms of polymeric methylene–methylene–ether hydroxymethylureas were discussed in previous publications.<sup>2,3</sup> To explain briefly: the amide nitrogens of urea units in polymeric UF resin molecules are singly or doubly bonded to methylene and methylene–ether groups to form branched polymer chain structures (Fig. 1). Type I and Type II hydroxymethyl groups are bonded to urea nitrogens of polymer chain ends and Type III hydroxymethyls to internal urea nitrogens (Fig. 3). Types II and III hydroxymethyls overlap in  $^{13}\text{C}$  NMR as discussed above. Furthermore, in  $^{13}\text{C}$  NMR spectra of UF resin samples obtained prior to the addition of the second urea (Samples 2.40a, 2.10a, and 1.80a), the hemiformal groups present exert  $\beta$ -substituent effects on the hydroxymethyl groups to which they are bonded, making the latter overlap with methylene–ether groups. This complication mostly disappears with the addition of the second urea (Samples 2.40b, 2.10b, and 1.80b), allowing the measurement of methylene–ether bond contents relatively accurately. All  $^{13}\text{C}$  NMR data of a-, b-, c-, and d-series resin samples are reported in Table I, and spectra of resins 1.80 and 2.40 series also shown with assigned peaks in Figures 4(a) and 4(b).

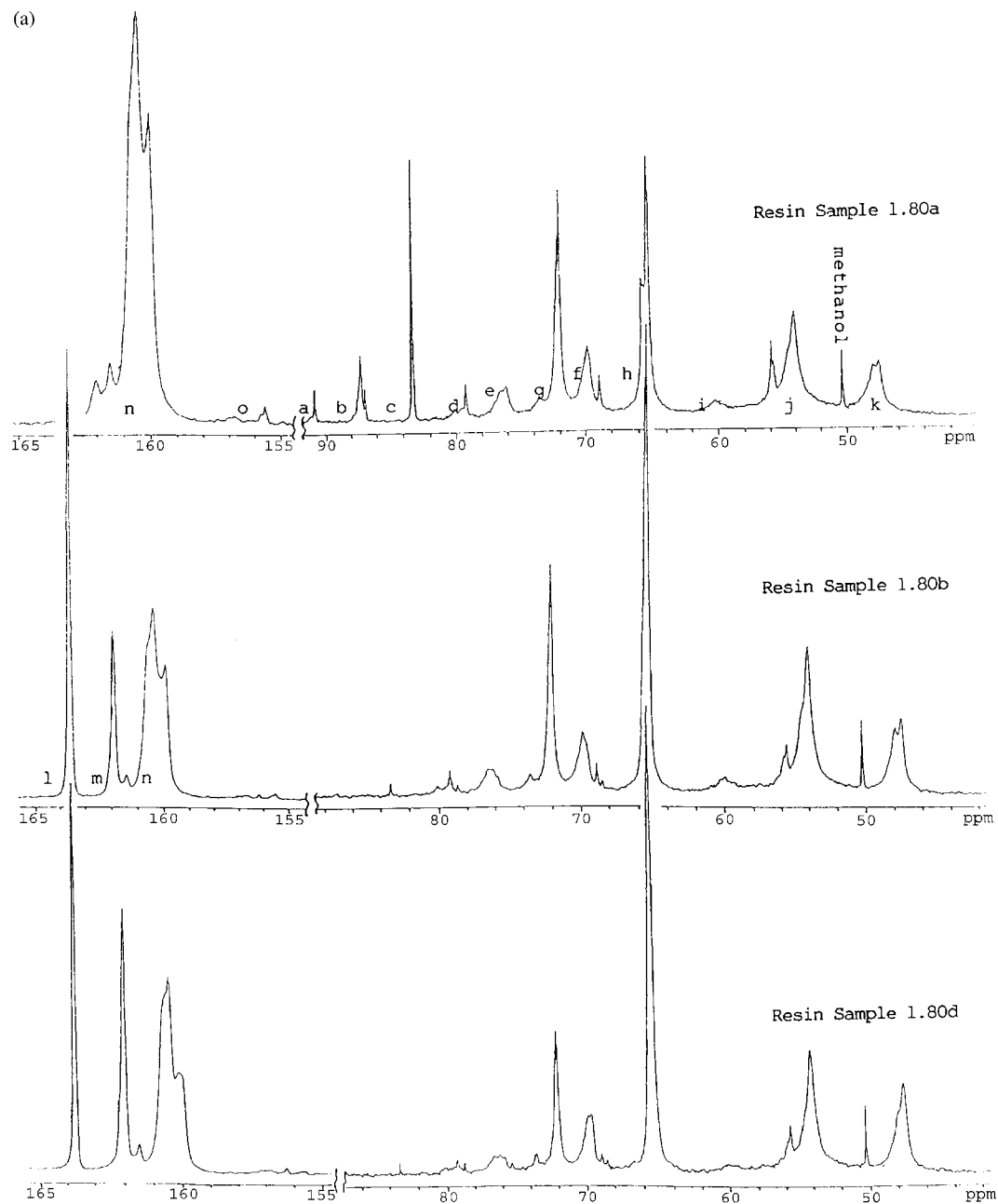
Types II/III hydroxymethyl groups bonded to polymeric UF molecules decrease when resin samples were aged or heat treated, i. e., they migrate to the second urea to form Type I hydroxymethyls. A similar migration of Type I hydroxymethyl groups from the polymeric UF polymers would occur, although they are indistinguishable and not measurable in  $^{13}\text{C}$  NMR. Type III hydroxymethyl groups, present at varying extents on polymeric UF resin molecules, exert  $\beta$ -substituent effects on neighboring methylenes and methylene ethers, making the latter bond groups appear as higher types. This prevents the calculation of polymer chain branching structures based on the methylene and methylene–ether bonds. Although Type III hydroxymethyl groups can be viewed as branches, their level can change or decrease to low values during the resins' lifetimes due to their migration to the second urea. This uncertainty can be largely minimized by es-

timating Type III hydroxymethyl groups by heat-treating resin samples to completely migrate them to the second urea, as discussed below.

### Heat Treatment Results of UF Resin Samples Used for $^{13}\text{C}$ NMR Analyses

The heat treatment temperature (60°C), used for heat treating resin Samples 1.80b, 2.10b, and 2.40b, was chosen to minimize the side reactions observed in the earlier study,<sup>2</sup> while allowing the hydroxymethyl group migration to complete within a reasonably short time period. Furthermore, the heat-treated resins would be similar to freshly made industrial resins where a relatively long cooling time was taken after the addition of the second urea for various reasons. Heat-treated samples, both Samples c-series (1.5 h treatments) and d-series (2.5 h treatments), did not show any turbidity increase, except Sample 1.80d, which showed a small increase in turbidity. The viscosity decreases observed in the heat treatments [Fig. 5(a)] were similar to the general downward trend observed at 70°C reported in the previous study, arising from the migration of Type II/III hydroxymethyl groups from polymeric UF molecules to the second urea. The viscosity decreases were characteristic with the F/U<sub>1</sub> mole ratios used in resin syntheses, an indication that different polymer chain structures resulted from different mole ratios used in syntheses. Overall, the low viscosity values and the very low or no turbidity of the resin samples obtained during and after the heat treatments indicate that the  $^{13}\text{C}$  NMR experiments, obtained with a long pulse delay time, would not incur too much quantitative inaccuracies from suspended solid particles or molecular movement limitations. Further heat treatments at 60°C were observed to increase the turbidity in resin samples significantly but these were not studied.

The  $^{13}\text{C}$  NMR results of heat-treated resin samples (Table I) showed various functional group level changes that in general agreed with those of earlier studies. Formaldehyde and hemiformal species were reduced to very low values before any heat treatment, i.e., in Samples b-series, resulting in increasing Type I hydroxymethyl groups. This destruction of ether-type bonds of hydroxymethyl formal groups presented in samples of the a-series is also shown by the significant decreases in the total methylene-ether group levels in samples of the b-series. Meanwhile, the migration of Type II/III hydroxymethyl

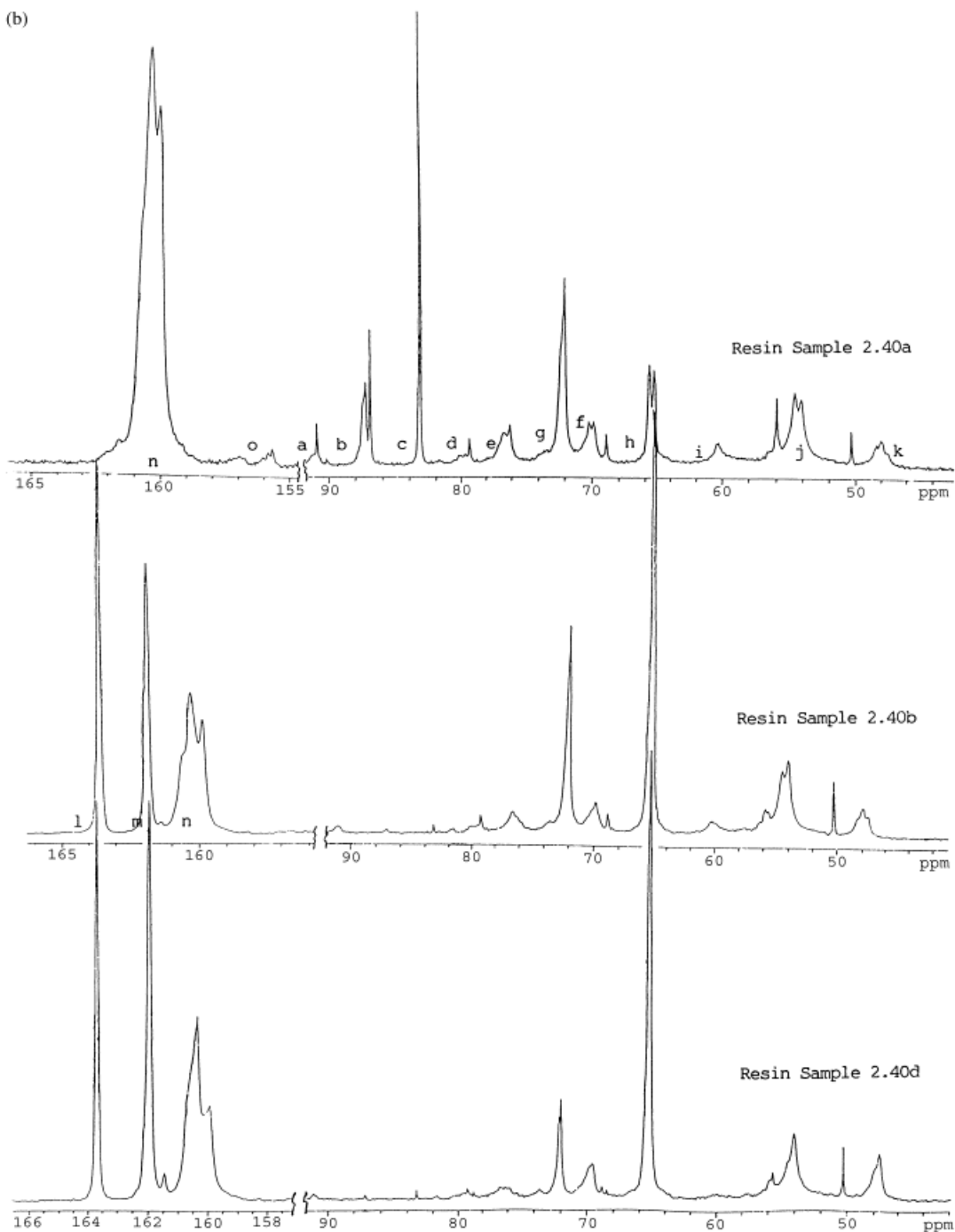


**Figure 4(a)**  $^{13}\text{C}$  NMR spectra of Resin Samples 1.80a, b, and d with peaks identified with lowercase letters from (a) to (o) in accordance with the chemical structures shown in Figure 3.

groups in samples of the c-series reached a relatively high level, and it proceeded only slightly further in samples of the d-series as a result of an additional one hour of heat treatment, with the value reaching 6.53% for Resin Sample 2.40d, 6.27% for Resin Sample 2.10d, and 5.15% for Resin Sample 1.80d. The total values of methylene and methylene-ether groups, respectively, re-

mained relatively constant in all heat-treated samples, indicating that, first of all, no significant polymerization or depolymerization reaction had occurred during the heating in the weakly alkaline pH. On the other hand, individually, the Types II and III methylene-ether or methylene groups were decreased in general while the Type I methylene-ether or methylene groups in-

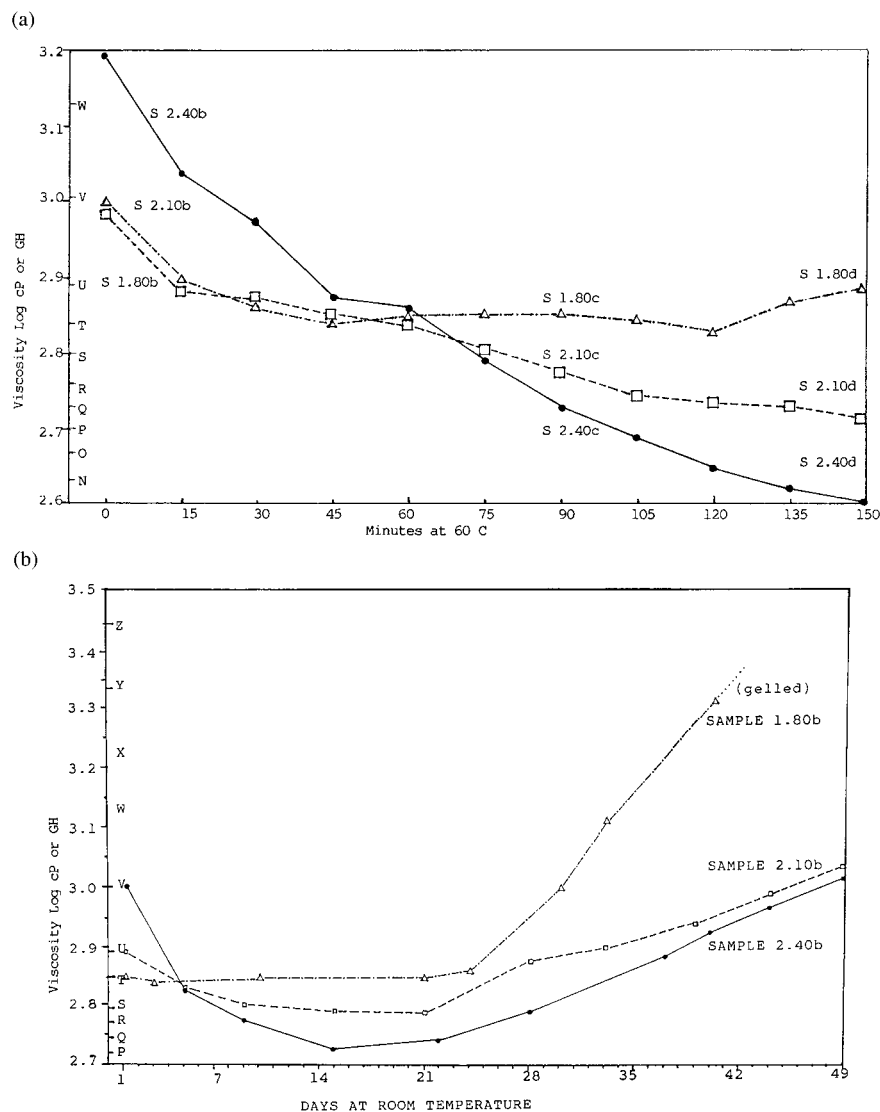




**Figure 4(b)**  $^{13}\text{C}$  NMR spectra of Resin Samples 2.40a, b, and d. The decrease of free formaldehyde and hemiformal species (peaks a–c) by reacting with the second urea to increase monosubstituted urea (peak m) can be clearly seen.

creased in samples of the d-series in comparison with samples of the b-series, with the average values of increases or decreases reaching 4.56% for Resin Sample 2.40d, 4.66% for Resin Sample 2.10d, and 2.97% for Resin Sample 1.80d. These

methylene–ether and methylene level changes are directly ascribable to the migration of Type III hydroxymethyl groups to the second urea giving; therefore, partial estimated values in resin samples of the b-series. Estimation of total Type III



**Figure 5(a)** Viscosity changes of Resin Samples 1.80b, 2.10b, and 2.40b during the stirring/heating treatments at 60°C for 2.5 h with the sampling points for c- and d-series resin samples indicated. **(b)** Viscosity changes of Resin Samples 1.80b, 2.10b, and 2.40 during the room temperature storage for 50 days.

hydroxymethyl group values requires the knowledge of their levels in the residual Type II/III hydroxymethyl group values in the samples of the d-series. Although there would be no primary reason to suggest a preferential migration of Type II or III hydroxymethyl groups in the heat treatments, an examination of overall data indicated that it was reasonable to assume the residual levels of Type II/III hydroxymethyl groups, 10.51–11.97% in samples of the d-series, appear to harbor negligible amounts of Type III hydroxymethyl groups, as discussed below further.

#### Effects of $F/U_1$ Mole Ratios on the Resin Formation and Resin Polymer Chain Structures

The methylene-ether/methylene group ratios obtained for the resins were relatively constant—17–18%:83–82%—not affected by the  $F/U_1$  mole ratios. The degree of polymerization ( $n$ ), calculated on the basis of total methylene and methylene-ether bond contents per mole of the first urea ( $U_1$ ), was 37.0 for Sample 2.40d, 12.4 for Sample 2.10d, and 8.90 for Sample 1.80d (Table II). The cause of these differences is partly traceable to the similar end point made in resin syntheses

**Table II Polymer Structure Calculation Results of Resin Samples 2.40, 2.10, and 1.80 for the Number of Polymer Chain Branches per Mole of the First Urea ( $U_1$ ) Before (Sample b-Series) and After (Samples d-Series) Stirring/Heating Treatments at 60°C for 2.5 h<sup>a</sup>**

	Sample 2.40			Sample 2.10			Sample 1.80		
	d	dB	b	d	dB	b	d	dB	b
Type III M/ME	0.125	4.63		0.119	1.47		0.068	0.61	
Type II M/ME	0.517	9.56		0.473	2.92		0.483	2.16	
Type I M/ME	0.331	2.00		0.327	2.00		0.337	2.00	
Total	0.973	16.19		0.919	6.39		0.888	4.77	
DP	37.0			12.35			8.93		
Total branch/ $U_1$	(0.438)			(0.517)			(0.534)		
Side branch/ $U_1$	0.384			0.355			0.310		
Type I HM/ $U_1$	0.285		0.285	0.323		0.323	0.341		0.341
Type II(IIi) HM/ $U_1$	0.126		0.126	0.126		0.126	0.102		0.102
Free amide group/ $U_1$	0.027		-0.007	0.068		0.046	0.091		0.071
Total branch/ $U_1$	0.438			0.517			0.534		
Type Ii HM, mig.			0.109			0.089			0.053
Type II HM, mig.			0.034			0.022			0.020
Total branch/ $U_1$			(0.547)			0.606			(0.587)
Side branch/ $U_1$			0.493			0.444			0.363
Functionality $U_1$			2.65			2.56			2.33
M/ME group ratio	82:18			83:17			83:17		

<sup>a</sup> Types of groups are as defined in the text and Figure 3. M: methylene bonds. ME: methylene-ether bonds. HM: hydroxymethyl groups. DP: degree of polymerization. dB: number of polymer chain branches per molecule.  $U_1$ : one mole of the first urea. mig.: Migrated HM groups in heat treatments. b and d: Resin Samples b- and d-series. Side branch: number of polymer chain branches excluding the number of linear portion branches. Calculation methods were discussed in the experimental and results and discussion sections.

using the viscosity of reaction mixture as the measure of advancement. For all three resin formulas, the same 50% formaldehyde solution was used without any added water to compensate for the different amounts of water going in. Resins with higher  $F/U_1$  ratios resulted in more dilute systems, resulting in higher degrees of polymerization in the first step. On the other hand, the amount of the second urea added, which decreases the viscosity of resulting resins, is greater with higher  $F/U_1$  ratio resins, and this compensation results in similar final viscosities and overall average molecular weights for the three different resin samples. (The final viscosity was slightly higher for Sample 2.40b than Samples 2.10b or 1.80b, but this cannot be used to directly explain the molecular weight differences.) Overall, the degree of polymerization values based on the first urea observed appears to be within the range where polymer structure comparisons can be made with appropriate adjustments.

In accord with earlier results,<sup>2,3</sup> the polymerization reaction time was longest for Sample 2.40

and shortest for Sample 1.80. Although the dilution factor mentioned above could be considered for it, the major reason for the slower reaction rates of higher  $F/U_1$  mole ratio resin systems appears to be the decreasing availability of urea amide/imide nitrogens for hydroxymethyl groups to react to form methylene bonds. The overall functionality of the first urea under the condition, i.e., availability of urea amide/imide nitrogens, has been known to be near 2.50 and only slightly variable depending on the reaction condition. The functionality of the first urea, calculated from Samples a-series after taking into account the hemiformal factor derived from Samples b-series, shows it decreases as the  $F/U_1$  ratio decreases: 2.65 for Sample 2.40; 2.56 for Sample 2.10, and 2.33 for Sample 1.80. Thus, the accessibility of urea nitrogens increases as the  $F/U_1$  ratio increases, to a limited extent, but it should be noted that when the  $F/U_1$  mole ratio increases to about 2.60 or higher, very little polymerization occurs, indicating that the functionality of 2.65 observed is near at the maximum value attainable in syn-

theses of typical wood adhesive-type UF resins. The functionality of the first urea, also related to the number of polymer chain branches discussed below, indicates that on average there are one polymer chain branches for every three urea molecules in UF resin polymers.

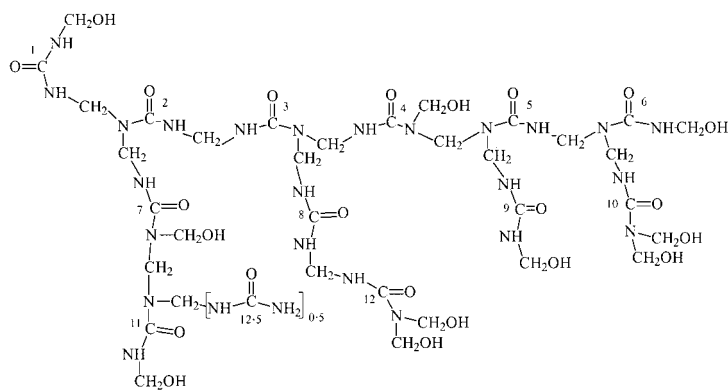
In the very high  $F/U_1$  mole ratio regimes, the polymerization reaction is made to go by acidifying the reaction mixture to about pH 1, where uron-type methylene-ether bonds are formed extensively with increased functionality for urea. The resulting uron group-containing UF resins have been known for many years and their NMR data reported recently,<sup>23</sup> but they are generally unsuitable as wood adhesives for various reasons. In this regard, it should be noted that all three UF resins of this study showed small levels of the urea carbonyl peak at near 158.0 ppm, corresponding to tetrasubstituted, possibly, uron structures. The uron-type as well as ordinary methylene-ether levels in UF resins, showing little changes in the heat treatments, raises an intriguing question regarding their formaldehyde emission potential in wood composite manufacturing and therefore ways to control their levels.

The results of calculation for the number of polymer chain branches and other data based on the heat-treated, d-series resin samples are reported in Table II. The number of polymer branches per mole of the first urea calculated using the methylene and methylene-ether bond contents showed an increasing trend as the synthesis  $F/U_1$  mole was decreased: 0.437 for Sample 2.40, 0.517 for Sample 2.10, and 0.534 for Sample 1.80. A direct comparison of the values is unfair, however, due to the degree of polymerization factor included in assigning two chain ends to Type I methylene and methylene-ether bond values in the calculation. Excluding this factor gives the values for the number of side-chain branches: 0.388 for Sample 2.40, 0.355 for Sample 2.10, and 0.310 for Sample 1.80—a lower number of side-chain branches for lower  $F/U_1$  mole ratio resins. In other words, the extent of side-chain branching is about one for every 2.82 urea units for Sample 2.10, which represents the typical UF resins currently used in the industry, and it decreases to 2.57 units for  $F/U_1$  ratio 2.40 and increases to 3.22 units for  $F/U_1$  ratio of 1.80. The maximum side-chain value would be 1.0 for polymer chains with every urea unit having one side branch and the minimum value would be zero with all urea units having no branch, i.e., linear polymer chain struc-

tures suggested in the early period of UF resin development.<sup>29</sup>

Furthermore, the number of total polymer chain branches was compared with the values of terminal hydroxymethyl groups for samples of the d- and b-series (Table II). For heat-treated Resin Samples 2.40d, 2.10d, and 1.80d, the Type I hydroxymethyl groups bonded to polymeric UF components are not measurable, but it is reasonable to first assume that the values would be the same as those of corresponding a-series resin samples, i.e., values obtained before adding the second urea. The sum value of Type I, Iii, and one half of Type II hydroxymethyl group values reflect the number of polymer chain ends and its shortage against the number of polymer branches obtained from the methylene and methylene-ether group value above is assignable to free amide terminal groups. The free amide group terminal branch values thus obtained were 0.027 for Sample 2.40d, 0.068 for Sample 2.10d, and 0.091 for Sample 1.80d, increasing, as expected, as the  $F/U_1$  ratio decreased. These values should be viewed as the minimum values due to the assumption made that the Type I hydroxymethyl group values of heat-treated d-series resins are the same as those of the a-series, which are the maximum values. Thus, the results show that fresh industrial UF resins made with relatively long cooling times after the addition of the second urea would have free amide groups as polymer chain branch ends at varying levels depending on the  $F/U_1$  ratio as well as the cooling temperature/time history as indicated an earlier report.<sup>1</sup>

Furthermore, the various polymer structures of untreated b-series resin samples were obtained by comparing with d-series samples. First, the level of Type II/Iii hydroxymethyl groups that migrated to the second urea in the heat treatments was obtained from <sup>13</sup>C NMR data, and the values were proportionated into Type II and Iii hydroxymethyl group values by assigning the averages of the decreasing/increasing values of methylene/methylene-ether group levels among different types in the heat treatments to the Type Iii hydroxymethyl group levels, as discussed above. The balance amount was assigned to Type I hydroxymethyl groups. These Type II and Iii hydroxymethyl group values were then combined with Type I and II/Iii hydroxymethyl group and free amide group values of d-series samples to obtain the total number of polymer branches of b-series samples. In order to avoid a double counting, however, the summation was made after the



**Figure 6** A schematic polymer chain structure of Resin Sample 2.10 based on  $^{13}\text{C}$  NMR results as a 12.5-mer UF polymer molecule having 7.5 polymer chain end groups. The end groups are to be capped with 4.0 Type I and 2.0 Type II, and 1.0 Type Iii, hydroxymethyl groups and a 0.5 free amide group.

free amide group value of d-series samples was adjusted down by the migrated Type II hydroxymethyl group values. The obtained total number of side-chain branches, which includes Type III hydroxymethyl groups, similarly decreased as the  $F/U_1$  mole ratio decreased: 0.493 for resin Sample 2.40b, 0.444 for resin Sample 2.10b, and 0.363 for resin Sample 1.80b (Table II). The latter two values included some free amide terminal group values, indicating that freshly made UF resins even if the second urea is added at room temperature could harbor free amide groups on polymeric resin molecules when lower  $F/U_1$  mole ratios were used. It is also interesting to see that resin Sample 1.80b showed the lowest level of Type II/III hydroxymethyl groups and the highest level of free amide groups. Although originated from the low  $F/U$  ratio used in resin synthesis, these polymer molecular structure differences appear to be responsible for the unusual rheological and storage behaviors observed earlier. The results of the calculation are illustrated in Figure 6 for Sample 2.10b, with slightly adjusted values for ease of drawing, as a 12.50-mer with 7.50 polymer chain terminal groups that include four Type I, two Type II, and one Type III hydroxymethyl groups and 0.50 free amide group. And, for resin Sample 2.10d, all hydroxymethyl groups are reduced and free amide groups are increased.

One uncertainty included in the polymer branching calculation is the level of Type III hydroxymethyl groups in the heat-treated d-series resin samples, for which the values were assumed to be negligible. This assumption was made from the following consideration: if a part of the residual Type II/III groups is to be assigned to Type III

hydroxymethyl groups in samples of the d-series, the calculated free amide group level needs to be decreased by the same amount: for example, in Sample 2.40d, if only about 10% of Type II/III hydroxymethyl groups value is assumed to be that of Type III hydroxymethyl groups, the free amide group needs to go to zero. This low level of free amide groups appears contradictory considering the heat treatment experienced in the presence of an excess free amide groups of the second urea. Thus, the assumption appears reasonable, but in the future it will be useful to obtain the resolution of Type II/III peaks using more advanced  $^{13}\text{C}$  NMR techniques.

#### Resin Stability, Viscosity Changes, and Turbidity During Room Temperature Storage

The initial decreases and then increases in viscosity of samples of the b-series (with the second urea in) observed at room temperature on storage over a 50-day period [(Fig. 5(b))] were also different for different  $F/U_1$  mole ratio resins. The initial decrease in viscosity, a phenomenon similar to that observed in heat treatments, is relatable to the migration of hydroxymethyl groups from the polymeric UF resin components to the second urea. The initial viscosity decrease was highest for Sample 2.40 and lowest for Sample 1.80, which is ascribable to the different amounts of hydroxymethyl groups migrating to the second urea and the different amounts of the second urea. Overall, all three resins showed stable viscosity and remained clear for the first 21 days. Afterward, the viscosity of resins increased rela-

tively slowly for Samples 2.40 and 2.10 but more rapidly for Sample 1.80, reaching to an immobile stage at the end of the storage period. Details of the functional group changes occurring in this room temperature storage experiment will be reported later, but the viscosity increases appeared to be due to increases in the methylene–ether and methylene bonds even in the weakly alkaline pH<sup>2,30</sup>. Other factors such as agglomeration of resin molecules would also contribute to the viscosity increases, especially for Sample 1.80, which has the least amount of side-chain branches as well as the highest level of free amide groups on polymeric UF resin molecules. Furthermore, it was also noticed that the rate of viscosity increase was faster for smaller size storage samples (Gardener–Holdt tubes) in comparison to larger size samples (1/4 gallon containers). Although the underlying mechanism for this was unclear, the restricted mobility of polymers expedited the viscosity increasing process. Overall, it appeared that the different polymer chain structures of the three different resins examined played a major role in determining the resins' stability during the room temperature storage period. In practice, the viscosity stability of UF resins during transportation and storage is an important parameter because of the pumping and spraying operations needed to be carried out during board manufacture which interacts with the resins' thermosetting performance.

### Formaldehyde Emission

UF resins are known to exhibit varying ripening (storage) times after manufacture for optimum bonding efficiency or lowest formaldehyde emission. In this study Sample b-series resins (two-day storage), at an overall F/U ratio of 1.15, were examined to see any differences would result for different F/U<sub>1</sub> mole ratios used in resin syntheses. All laboratory PBs made in this study showed bending and internal bond strength values within normal values of ordinary laboratory boards allowing a comparison of the formaldehyde emission values of boards with respect to different resins. The 2-h desiccator formaldehyde emission level showed increases from Sample 2.40 (0.60 ppm) to Sample 2.10 (0.70 ppm) and slightly further to Sample 1.80 (0.72 ppm) (Table I). The differences in the formaldehyde emission observed were relatively small but they are still in the practically significant. Formaldehyde emission levels of PBs have been known to depend

primarily on the overall final F/U ratio used in the binder resin manufacturing and secondarily on the various hot pressing conditions.<sup>14,15</sup> Assuming the latter variables were kept constant, the differences in formaldehyde emission would arise from different polymer chain structures and related factors such as the monomeric/polymeric component ratios in the resins. Meanwhile, since the resins tested in this study were unaged ones, more definite differentiations would be possible in resins tested after ripening for various different time periods. Other detailed results from the room temperature storage experiment will be reported in a future publication.

### CONCLUSION

As the F/U<sub>1</sub> ratio used in the first step of resin synthesis decreased from 2.40 to 2.10 and to 1.80, <sup>13</sup>C NMR results of the UF resins indicated a decreasing number of side-chain branches and increasing number of free amide groups in the structure of polymeric UF resin molecules. Due to these polymer chain branching differences, the resultant UF resins, after the second urea is added to an overall F/U mole ratio of 1.15, gave rise to varying viscosity changes in stirring/heating treatments or in storing at room temperature as well as to varying formaldehyde emission levels of bonded PBs. A further characterization of the F/U<sub>1</sub> mole ratio effects in resin synthesis and various resin ripening modes in conjunction with evaluation of wood bonding efficiency and formaldehyde emission would be needed in order to systematically optimize the UF resin wood adhesive technology.

The author appreciates the financial support from the USDA NRI grant (97-35103-5051) and materials support from Georgia-Pacific Corporation, Louisville, MS. He also appreciates the help provided by Mr. Hui Wan in preparing PBs.

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