

# <sup>13</sup>C-NMR Study on the Structure of Phenol-Urea-Formaldehyde Resins Prepared by Methylolureas and Phenol

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**ABSTRACT:** Phenol-urea-formaldehyde (PUF) resins were synthesized by reacting mixture of methylolureas (MMU), phenol, and formaldehyde. The structure of PUF cocondensed resins at different stages of reaction were analyzed by liquid <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy. The liquid <sup>13</sup>C-NMR analysis indicated that methylolureas had the dominant content in MMU with the reaction between urea and formaldehyde under the alkaline condition. The PUF cocondensed resins had no free formaldehyde. methylolureas were well incorporated into

the cocondensed resins by reacting with phenolic units to form cocondensed methylene bridges. The second formaldehyde influenced the further reaction and the structure of the PUF resins. The resins with the prepared method of PUFB possessed relatively high degree of polymerization and low proportion of unreacted methylol groups. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2195–2202, 2009

**Key words:** phenol-urea-formaldehyde; resins; methylolureas; structure; <sup>13</sup>C-NMR analysis

## INTRODUCTION

Thermosetting phenol-formaldehyde (PF) resins have been greatly used as wood adhesives for many decades. PF resins have an excellent performance in producing exterior quality wood products such as laminated wood, particleboard, and oriented strand-board.<sup>1</sup> However, the main problems of PF resins are their much slower curing rate and higher cost when compared with other formaldehyde-type resins.<sup>2–5</sup> Urea-formaldehyde (UF) resins possess advantages of fast curing time and low price.<sup>6,7</sup> To utilize advantages of PF resins and UF resins, many attempts have been made to prepare phenol-urea-formaldehyde (PUF) cocondensed resins for reducing the cost and curing time of PF resins. PUF resins are usually synthesized by direct cocondensation of phenol, urea, and formaldehyde under alkaline conditions. The low-condensation PF resins coreacting with up to 42% molar urea during resin preparation can yield PUF resins under alkaline conditions.<sup>8</sup> The PUF resins can be also obtained by the use of very high viscosity and high condensation level PF resins drowned in urea added at the end of the reaction to decrease their viscosity.<sup>9</sup> Recent decade years, some

new methods have appeared to synthesize PUF resins. Under acidic condition, a different synthesis method was used for preparing PUF cocondensed resins with the reaction of phenol and UF-concentrates, which were a series of UF resins synthesized by changing the F/U molar ratio and the reaction pH value.<sup>10</sup> The resol PUF cocondensed resins displayed almost the same curing behaviors and heat resistance as a commercial PF resol.<sup>11</sup> A resol-type PUF resin was prepared by the reaction of a mixture of trimethylolphenols with urea under acid conditions,<sup>12</sup> which had a great heat resistance after completion of the reaction.<sup>13</sup>

In general, the structure, composition, and characteristics of PUF resins are significantly influenced by synthesis condition including reaction temperature, pH value, reaction time, and synthesis method.<sup>14–16</sup> Some researches have shown that the pH value has significant effects on the structure, reaction rate constant, and curing behavior of the resins.<sup>10,17–20</sup> However, the forming processes of the structure of PUF resins at different stages of reaction are not completely comprehended. Hence, it is necessary to make clear that how different synthesis conditions influence the forming processes of the structure of PUF cocondensed resins. Liquid <sup>13</sup>C nuclear magnetic resonance (NMR) has been used for investigating and analyzing detailed structure, composition, and chemical shift assignments of PUF cocondensed resins.<sup>8,21–23</sup> Especially, the <sup>13</sup>C-NMR chemical shifts of cocondensed groups

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between phenolic ring and urea units were exactly identified in recent work.<sup>24</sup>

In this article, two new types of synthesis methods were used to prepare the PUF cocondensed resins. To better understand the changes of the structure and composition for PUF resins in the process of preparation, and investigate the effect of different synthesis methods on the structure of PUF resins, liquid <sup>13</sup>C-NMR was employed to identify and quantify the structural features.

## EXPERIMENT

### Materials

In the following experiments, formaldehyde aqueous solution (37%), solid phenol, and solid urea were of industrial grade respectively from Xilong Chemical Industries, Beijing Chemical Industries, and Zhongán Chemical Industries, China. Formic acid (HCOOH) and all the other chemicals used were of AR grade from Beijing Chemical Industries, China.

### Synthesis of a mixture of methylolureas

Formaldehyde (1.2M) was charged into a stirred reactor and adjusted to pH value between 7.5 and 8.0 with 30% sodium hydroxide aqueous solution. After stirring for 5 min, 0.75M of urea was gradually added over a period of 10 min. Subsequently, the reaction mixture was then heated to 90°C within 40 min and maintained at this temperature for 40 min. The reaction product was then slowly cooled to 35°C, named as mixture of methylolureas (MMU). In the process of synthesis, the pH value of reaction mixture was constantly kept unchanged.

### Preparation of PUF cocondensed resins

The PUF cocondensed resins were prepared by using phenol, formaldehyde, and MMU as reactants. Two types of PUF resins, which were prepared with different synthesis methods, namely by adjusting the addition order of the MMU during the reaction, were respectively marked PUFA and PUFB.

The PUFA and PUFB resins were synthesized with the same molar ratio as follows: formaldehyde/phenol/urea (F/P/U) = 3.3/1/1, the first formaldehyde/phenol (F1/P) = 1.5, and the second formaldehyde/phenol (F2/P) = 0.23.

### Preparation of PUFA resin

The calculated amounts of MMU, phenol, 40% sodium hydroxide aqueous solution, and catalyzer A were charged into a stirred reactor. The reaction mixture were then heated to 70°C over a period of 20 min and maintained at this temperature for 10

min. After that, F1 was added into the reaction system and the temperature was then increased to 90°C within 20 min. The reaction mixture was kept at 90°C for about 35 min and a sample named PUFA1 was obtained. Subsequently, F2, the rest amounts of 40% sodium hydroxide aqueous solution, and some water were added into the reaction system, and then the temperature was set back to 85°C. The reaction was continued at 85°C until the resin reached a viscosity (measured at 20°C) of between 0.2 and 0.3 Pa s, and the final resin (PUFA) was obtained.

### Preparation of PUFB resin

The calculated amounts of phenol, F1, 40% sodium hydroxide aqueous solution, and catalyzer A were mixed in a stirred reactor. The reaction mixture was then heated to 70°C over a period of 20 min. Subsequently, the calculated amount of MMU was added into the reaction system and the temperature was gradually increased to 90°C within 25 min. The reaction mixture was then maintained at 90°C for about 35 min, and after that the sample named PUFB1 was obtained. Subsequently, F2, the rest amounts of 40% sodium hydroxide aqueous solution, and some water were added into the reactor. The reaction temperature was then increased to 85°C and kept at this temperature until the resin reached a viscosity (measured at 25°C) of between 0.2 and 0.3 Pa s, and the final resin (PUFB) was obtained. The characteristics of PUFA and PUFB resins were pH = 10 ± 0.1, solid content = 55 ± 1%.

### Liquid <sup>13</sup>C-NMR measurement

Liquid <sup>13</sup>C-NMR spectra were acquired with a Bruker DPX-300 FT-NMR spectrometer at a frequency of 75.47 MHz. All the spectra were run with a relaxation delay of 8 s over 800 scans. The chemical shifts of each spectrum were accurate to 0.1 ppm and all the samples were directly used for <sup>13</sup>C-NMR tests.

## RESULTS AND DISCUSSION

### Structure analysis of MMU

The <sup>13</sup>C-NMR spectrum of the MMU is shown in Figure 1. The results of structural assignments and the quantitative value from <sup>13</sup>C-NMR spectra are summarized in Tables I and II.<sup>25–27</sup>

The chemical shifts at 65.0, 71.4, and 159.9 ppm were respectively assigned to bridge link (–NH–CH<sub>2</sub>OH), (–N(CH<sub>2</sub>OH)<sub>2</sub>), and trimethylol of urea units. The chemical shifts from 159 to 163 ppm were assigned to the carbonyl group of various urea

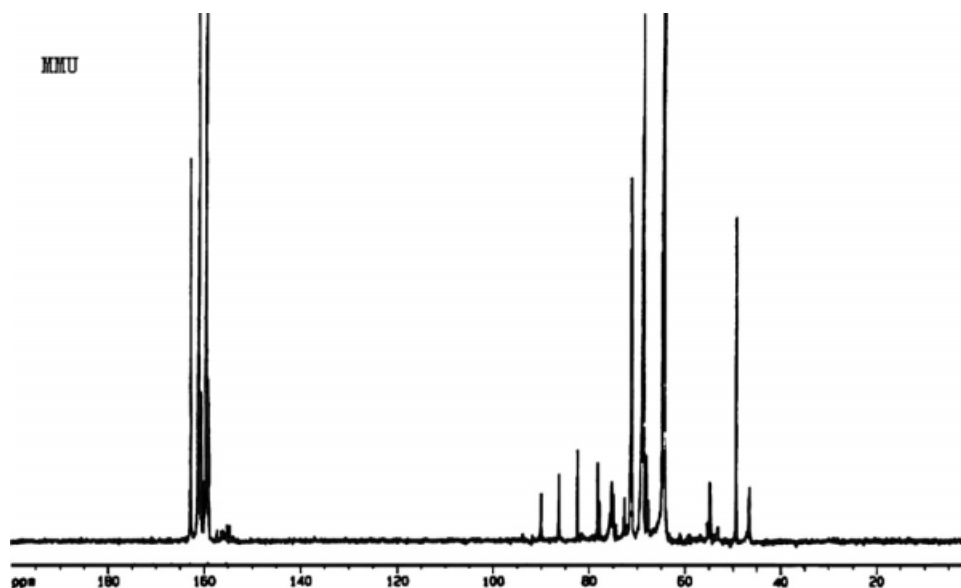


Figure 1 <sup>13</sup>C-NMR spectra of the mixture of methylolureas.

residues including free urea, monosubstituted, disubstituted, and trisubstituted ureas.

In general, the methylenes between urea units are scarcely formed in the process of synthesis under the alkaline condition.<sup>28</sup> However, the chemical shift between 53 and 54 ppm that was attributed to methylene between urea units was clearly found in the spectra of MMU. It was also noted that there was a comparatively big peak at 69–70 ppm, which indicated that methylene ether was formed between methylolureas during the reaction. It could be also known from Table II that the quantitative value of methylene ether was almost similar to that of function group ( $-\text{N}(\text{CH}_2\text{OH})_2$ ), and that the amounts of total methylolureas were substantially much higher than any other functional groups. This indicated that methylolureas were the main product during reaction between urea and formaldehyde under the alkaline condition. Therefore, it was concluded from the statements above that methylolureas had the highest proportion when compared with other groups in MMU, which can react with phenolic methylols.<sup>8</sup>

TABLE I  
Chemical Shifts Assignments of <sup>13</sup>C-NMR  
of Methylolureas

Group assignment	Chemical shift (ppm)
Carbonyl C=O	159–162
Free urea	162
Monosubstituted urea	160–161
Di- and trisubstituted urea	159–160
$\text{HOCH}_2\text{NHCON}(\text{CH}_2\text{OH})_2$	159.2–159.7
$-\text{N}(\text{CH}_2\text{OH})_2$	71.6–72.8
$-\text{NH}-\text{CH}_2-\text{O}-\text{CH}_2-\text{NH}-$	69–70
$-\text{NH}-\text{CH}_2\text{OH}$	65–66
$-\text{HN}-\text{CH}_2-\text{N}(\text{CH}_2-)$	53–54

### Structure analysis of PUF resins

The spectra of the PUF resins with the different synthesis methods are shown in Figures 2 and 3. The structural assignments of chemical shifts are summarized in Table III according to published information.<sup>8,13,14,16,17,19,23,28–31</sup>

Figure 2 shows the spectra of PUFA1 and PUFB1 resins respectively obtained during the synthesis of PUFA and PUFB resins before the addition of the second sodium hydroxide and formaldehyde. It can be seen from Figure 2 that some new peaks appear in the PUFA1 and PUFB1 when compared with the Figure 1, resulted from the complicated reaction followed by self-condensation and cocondensation of methylolphenols, phenol, methylolureas, and formaldehyde. The chemical shifts at 34.6–39.3 ppm, 68.2–69.0 ppm, and 72.3–72.6 ppm were respectively assigned to the methylene between phenols, methylene ether between urea units, and dimethylol of urea units. The resonances in the chemical shift range of 48.1–50.2 ppm represented methanol which existed in the formaldehyde solution as a stabilizer.<sup>17</sup> The peak of group ( $\text{CH}_3-\text{O}-\text{CH}_2\text{OH}$ ) appeared at around 56.5 ppm.

TABLE II  
<sup>13</sup>C-NMR Analysis of Structure of Methylolureas

Structure	Quantitative value
$-\text{N}(\text{CH}_2\text{OH})_2^a$	0.22
$-\text{NH}-\text{CH}_2-\text{O}-\text{CH}_2-\text{NH}-$	0.24
$-\text{NH}-\text{CH}_2\text{OH}^b$	1.45
$-\text{HN}-\text{CH}_2-\text{N}(\text{CH}_2-)$	0.04
Carbonyl C=O	1.00
Total amount of methylolureas	1.67

$$\text{Total amount of methylolureas} = a + b$$

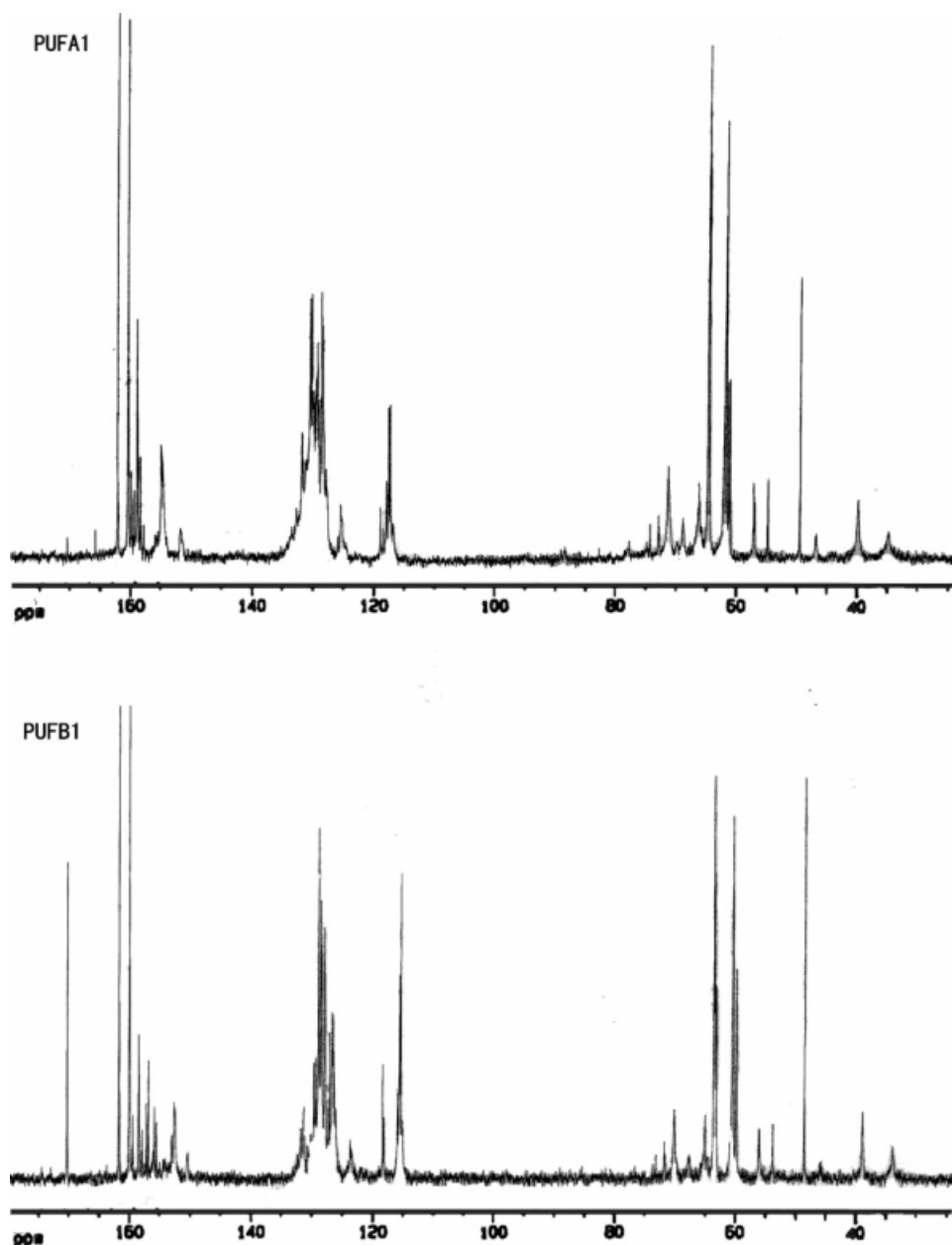


Figure 2  $^{13}\text{C}$ -NMR spectra of the PUFA1 and PUFB1 resins.

The chemical shifts of cocondensed methylene groups between phenolic ring and methylolureas appeared at 46.4–46.7 ppm and 54.1–54.8 ppm, according to recent research.<sup>24</sup> There were no peaks at around 80–90 ppm which were assigned to free formaldehyde in the spectra of all PUF resins.<sup>10</sup> This indicated that the synthesis method by the reaction of phenol, formaldehyde, and mixture of MMUs was able to make the addition formaldehyde fully react with phenol or methylolureas, when compared with other synthesis processes.<sup>8,20</sup>

In the Figures 2 and 3, some remarkable peaks at 61.2, 64.0, and 160.0–162.2 ppm appeared in the four resins. The signal at around 171.0 ppm in the PUFB1 and PUFB resins were assigned to the carbonyl car-

bon of formic acid, the formation of which might be due to the oxidation of formaldehyde,<sup>27</sup> however, this peak was not found in the PUFA1 and PUFA resins at all. The peaks at 61.2 and 64.0 ppm were assigned to the phenol methylol groups (*o*-Ph-CH<sub>2</sub>OH and *p*-Ph-CH<sub>2</sub>OH), substituting the hydrogen of the phenolic ring at *ortho* and *para* position. The chemical shifts from 160.0 to 162.0 ppm were attributed to the carbons of the substituted carbonyl groups including various hydroxybenzyl ureas, and the signal at 162.0–163.0 ppm was always associated with free urea. Besides, some overlapping peaks appeared prominently at 124.0–131.0 ppm, which were assigned to the aromatic carbons according to some reports.<sup>17,20,31</sup>

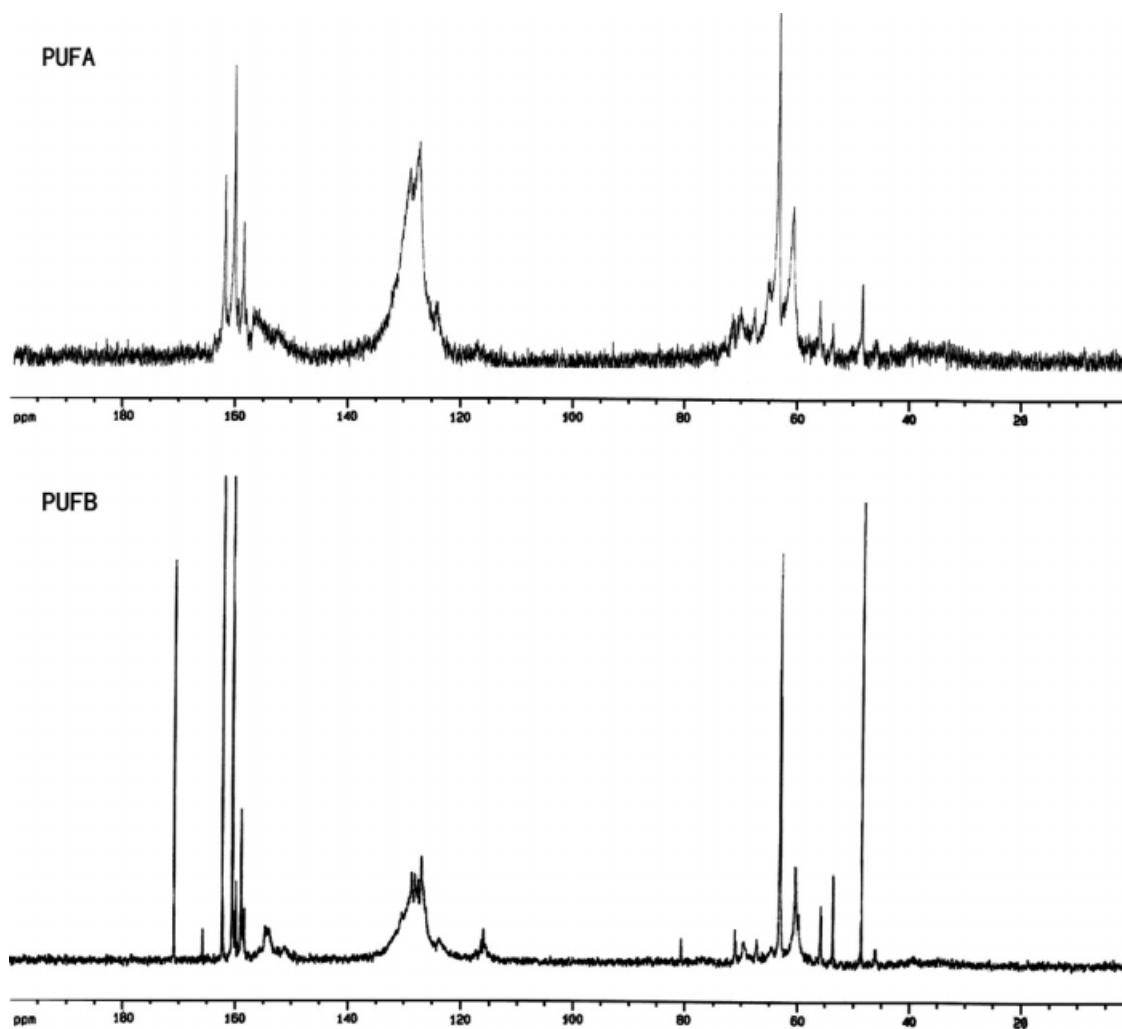


Figure 3 <sup>13</sup>C-NMR spectra of the PUFA and PUFB resins.

The <sup>13</sup>C-NMR spectrum of PUFA and PUFB resins are shown in Figure 3. The spectra reveal the peaks similar to what described earlier in Figure 2. But the peak intensity of some function groups in Figure 3 presented some difference from those in Figure 2, such as the cocondensed methylene group between the phenolic ring and the urea units, methylol groups of urea and phenol, etc. The peak of trimethylolurea in MMU was not nearly found in the Figures 2 and 3, when compared with the spectra of Figure 1. This indicated that trimethylolurea was completely consumed by reacting with phenolic ring or other methylol units in the preparation of PUF resins. It was also of interest that the methylene group ( $-\text{N}(\text{CH}_2-)-\text{CH}_2-\text{N}(\text{CH}_2-)$ ) at around 60.4 ppm which did not appear in the Figure 1, was observed in the spectrum of the Figures 2 and 3. The reason for this could be much stronger alkaline in the preparation of PUF resins than MMU.

### Quantitative analysis of PUF resins

Total amount of the carbonyl carbons of the substituted ureas and free urea keeps unchanged in the process of MMU synthesis and PUF preparation, so the amounts of various function groups are quantified by using carbonyl groups as the internal standard. The quantitative results of MMU and PUF resins are shown in Tables II and IV, respectively.

It can be seen that both the PUFA and PUFB cocondensed resins contained plentiful amounts of methylol groups of phenolic ring and methylols of urea units. Those methylol groups endowed PUF resins with better water solubility and can react with active groups of wood to form chemical bond. Total amount of methylene of urea units in the PUFA (or PUFB) resin increased  $\sim 10$  times than that in the MMU when comparing Tables II and IV, which conformed that self-condensations of methylolureas also



**TABLE III**  
**<sup>13</sup>C-NMR Shifts and Group Assignments for PUF Resins**

Group assignment	Chemical shift (ppm)
Carbonyl C=O	160–163
Unreacted urea	163.0
Phenoxy Ar-COH	
Phenol	157–159
<i>para</i> -Substitution	155–158
<i>ortho</i> -Substitution	153–157
<i>ortho</i> - and <i>para</i> -Substitution	151–153
Methylol group	
<i>o</i> -Ph-CH <sub>2</sub> OH	61.1–61.5
<i>p</i> -Ph-CH <sub>2</sub> OH	64.5, 65.5
-NH-CH <sub>2</sub> OH	62.2, 63.7–65.2
-N(-CH <sub>2</sub> OH) <sub>2</sub>	72.7, 71.6–72.8
-N(CH <sub>2</sub> )-CH <sub>2</sub> OH	70.5–71.3
Cocondensed methylene group	
<i>p</i> -Ph-CH <sub>2</sub> -N(CH <sub>2</sub> -)CO-	49.2
<i>p</i> -Ph-CH <sub>2</sub> -NHCO-	44.2
<i>o</i> -Ph-CH <sub>2</sub> -N(CH <sub>2</sub> -)CO-	46.4
<i>o</i> -Ph-CH <sub>2</sub> -NHCO-	40.6
Methylene group between phenols	
<i>o,p</i> -Ph-CH-Ph	34.9
<i>p,p</i> -Ph-CH-Ph	39.7, 40.0
Methylene group between ureas	
-NH-CH <sub>2</sub> -N(CH <sub>2</sub> )-	54.5–54.8, 55.5
-N(CH <sub>2</sub> )-CH <sub>2</sub> -N(CH <sub>2</sub> )-	59.4, 59.8
Ether group between ureas	
-NH-CH <sub>2</sub> -O-CH <sub>2</sub> -NH-	69.0, 69.4
-N(CH <sub>2</sub> )-CH <sub>2</sub> -O-CH <sub>2</sub> -NH-	74–78
Benzylether group between phenols	
<i>o</i> -Ph-CH <sub>2</sub> -O-CH <sub>2</sub> -Ph	72, 71.6–72.8
<i>p</i> -Ph-CH <sub>2</sub> -O-CH <sub>2</sub> -Ph	69.1
Reactive formaldehyde adducts	80–100

took place in the synthesis of the PUF resins. Total amount of methylolureas decreased from 1.67 for MMU to 0.74 and 0.40 for PUFA and PUFB, respectively, and some amounts of cocondensed methylene groups appeared in the PUFA and PUFB resins. This suggested that methylolureas was well incorporated into the cocondensed resins by reacting with phenolic units to form cocondensed methylene bridges.

#### Effects of synthetic methods on the structure of PUF resins

Both the sample PUFA1 and PUFB1 were the primary resins, which were prepared by the reaction of phenol, MMU, and the first formaldehyde under the alkaline condition with two methods. While the differences between them lied in the order of the material addition: PUFA1, the reaction of MMU and phenol were continued for a moment and then formaldehyde was added, however, PUFB1, after phenol reacting with formaldehyde for a moment, MMU was added.

It is clear from Table IV that the total content of each group in PUFA1 resin showed remarkable difference from that in PUFB1 resin, except the content of methylene group between phenols. The total

amount of methylol groups between phenols or methylol groups of urea units in PUFA1 resin was much larger than that in PUFB1 resin, however, the total amount of cocondensed methylene or self-condensed methylene group of urea units in PUFA1 presented lower than that in PUFB1. This indicated that phenolic methylols of the PUFB1 resin were consumed to form mainly the cocondensed methylene, and the chance for the self condensation of urea methylols in PUFB1 resins occurred larger than that in PUFA1 resin. The amounts of some groups were not greatly influenced by the prepared methods, such as the methylene bridges (*p,p*-Ph-CH-Ph or *o,p*-Ph-CH-Ph) and ether group between ureas. The data of Table IV also shows that the PUFB1 resin had almost twice amount of cocondensed methylene than PUFA1 resin. This result indicated that the PUFA prepared method did not largely favor the cocondensation reaction between phenol and methylolureas. In the PUFA1 or PUFB1 resin, the amount of methylol group (*o*-Ph-CH<sub>2</sub>OH) remained higher than that of methylol group (*p*-Ph-CH<sub>2</sub>OH), and the total amount of methylene bridges (*p,p*-Ph-CH-Ph) and cocondensed methylene (*p*-Ph-CH<sub>2</sub>-N(CH<sub>2</sub>-)CO-) presented comparatively higher than that of methylene links at *ortho* position. Therefore, it could be known that *para* methylol groups reacted more easily with other function groups such as methylol groups of urea units or methylol group (*o*-Ph-CH<sub>2</sub>OH). This result is compatible with the published result.<sup>17</sup>

The comparative analysis of the PUFA and PUFB showed similar results to that of the PUFA1 and PUFB1. The total cocondensed methylene of the PUFB resin had nearly similar proportion to the methylene groups of phenolic ring and urea units. Besides, in the PUFB resin, the bridge (*p*-Ph-CH<sub>2</sub>-N(CH<sub>2</sub>-)CO-) dominated in the cocondensed methylene bridges. However, this regulation was not remarkable in the PUFA resin. The results of the quantitative analysis also revealed that the PUFB resin had higher rate of condensation and degree of polymerization than PUFA resin. Furthermore, the amounts of phenolic methylol groups of the PUFB resin were considerably lower than those of the PUFA. It could be concluded from the above statements that the resins with the prepared methods of PUFB possessed relatively high degree of polymerization and low proportion of unreacted methylol groups, and that methylolureas were well incorporated into the cocondensed resins. Therefore, it was desirable from a structural point of view to study that how the crosslinking agents of the PUFB resin was formed with this prepared method. Previous research indicated that pH value significantly influences the structure and composition of PUF resins. Although both PUFA and PUFB resins had the

TABLE IV  
<sup>13</sup>C-NMR Quantitative Analysis of PUF Resins

Structure	Sample			
	PUFA1	PUFA	PUFB1	PUFB
Methylol group				
[1] <i>o</i> -Ph-CH <sub>2</sub> OH	0.97	0.95	0.88	0.70
[2] <i>p</i> -Ph-CH <sub>2</sub> OH	0.87	0.96	0.78	0.90
[3] -NH-CH <sub>2</sub> OH	0.27	0.38	0.18	0.13
[4] -N(-CH <sub>2</sub> OH) <sub>2</sub>	0.05	0.15	0.05	0.10
[5] -N(CH <sub>2</sub> )-CH <sub>2</sub> OH	0.32	0.21	0.26	0.17
Cocondensed methylene group				
[6] <i>p</i> -Ph-CH <sub>2</sub> -N(CH <sub>2</sub> )-CO-	0.13	0.18	0.27	0.33
[7] <i>o</i> -Ph-CH <sub>2</sub> -N(CH <sub>2</sub> )-CO-	0.05	0.12	0.06	0.09
Methylene group between phenols				
[8] <i>o,p</i> -Ph-CH-Ph	0.11	0.11	0.10	0.10
[9] <i>p,p</i> -Ph-CH-Ph	0.18	0.19	0.17	0.19
Methylene group between ureas				
[10] -NH-CH <sub>2</sub> -N(CH <sub>2</sub> )-	0.06	0.07	0.06	0.11
[11] -N(CH <sub>2</sub> )-CH <sub>2</sub> -N(CH <sub>2</sub> )-	0.19	0.25	0.28	0.29
Ether group between ureas				
[12] -NH-CH <sub>2</sub> -O-CH <sub>2</sub> -NH-	0.11	0.16	0.09	0.11
Carbonyl C=O	1.00	1.00	1.00	1.00
Total methylol group between phenols	1.84	1.91	1.66	1.60
Total methylol group between ureas	0.64	0.74	0.49	0.40
Total methylene group between phenols	0.29	0.30	0.27	0.29
Total methylene group between ureas	0.25	0.32	0.34	0.40
Total cocondensed methylene group	0.18	0.30	0.33	0.42
Rate of condensation, <i>R</i>	0.39	0.49	0.49	0.58
Degree of polymerization, <i>P</i>	1.64	1.96	1.96	2.38

Total methylol group between phenols = [1] + [2]; total methylol group between ureas = [3] + [4] + [5]; total methylene group between phenols = [8] + [9]; total methylene group between ureas = [10] + [11]; total cocondensed methylene group = [6] + [7];  $R = ([c] + [d] + [e] + 0.5 [12]) / (p + u)$ ,  $p = 1$  and  $u = 1$  mol in the present work.  $P = 1 / (1 - R)$ .

same pH value, they had different structure and composition from each other. This indicated that synthesis method, or the addition order of the material, also had effect on the structure and composition of resins.

#### Effects of the second formaldehyde addition on structure of PUF resins

Although the chemical shifts of the PUF resins had not changed when the second formaldehyde was added, quantitative analysis of <sup>13</sup>C-NMR spectrum indicated that the composition of the cocondensed resins was indeed changed.

The second formaldehyde influenced the further reaction and the structure of the PUF resins. Both degree of polymerization and rate of condensation increased with the addition of the formaldehyde for both PUFA1 and PUFB1 resins. The amount of methylol group (*p*-Ph-CH<sub>2</sub>OH) of the PUFA resin increased when the second formaldehyde was added, however, the amount of group (*o*-Ph-CH<sub>2</sub>OH) almost remained unchanged. But for the PUFB resin, with the addition of second formaldehyde the amount of group (*p*-Ph-CH<sub>2</sub>OH)

increased, however, the amount of group (*o*-Ph-CH<sub>2</sub>OH) decreased. This was because the substitution occurred faster at the *para* positions than at the *ortho* positions, and the amount of group (*o*-Ph-CH<sub>2</sub>OH) in the PUFB resin was consumed more than that in the PUFA resin. Since the total amount of the methylene group of phenolic ring and the rate of condensation presented an increasing trend with the addition of the second formaldehyde, and the methylol group of phenol had slight increase in the PUFA resin, it was concluded that methylol groups of phenol consumed were mainly used to form the cocondensed methylene. With the second addition of formaldehyde, the methylol groups of phenol and methylol groups of urea units in the PUFB resin respectively decreased by 0.06 and 0.09, however, the methylene of phenols, methylene of ureas, and the cocondensed methylene group increased by 0.02, 0.06, and 0.09, respectively. This suggested that methylol groups of phenol and urea units chiefly participated in the self-condensation of urea methylol groups, and cocondensation between phenolic methylol groups and urea methylol groups after the second formaldehyde were added in terms of almost invariable ether group between ureas.

## CONCLUSIONS

MMUs were the main products in the reaction between urea and formaldehyde under the alkaline condition. In the synthesis of PUF resins, it was found that the synthesis method by the reaction of phenol, formaldehyde, and mixture of MMUs could be used for preparing cocondensed resin which had no free formaldehyde. Large amounts of MMUs were well converted into cocondensed methylene groups between phenols and urea units, and the methylene of self-condensation. The synthesis method, or the order of the material addition, had effect on the structure and composition of resins. However, the amounts of some groups (methylene between phenols, or ether group between ureas) were not greatly influenced by the method.

Both the PUFA and PUFB cocondensed resins contained plentiful amounts of methylol groups of phenols and urea units, which endowed the cocondensed resins with better water solubility and can react with active groups of wood to form chemical bond. It could be concluded that the resins with the prepared method of PUFB possessed relatively high degree of polymerization and low proportion of unreacted methylol groups, and that MMUs were well incorporated into the cocondensed resin. The second formaldehyde influenced the further reaction and the structure of the PUF resins. Methylol groups of phenol and urea units in the PUFB resin chiefly participated in the self-condensation of urea methylol groups, and cocondensation between phenolic methylol groups and urea methylol groups after the second formaldehyde were added in terms of almost invariable ether group between urea units.

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