

Analysis on Cocondensation of Melamine and Urea through Carbon 13 Enriched Formaldehyde with Carbon 13 Nuclear Magnetic Resonance Spectroscopy*¹

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炭素13をエンリッチしたホルムアルデヒドによる メラミンとユリアの共縮合反応の炭素13核磁気 共鳴スペクトル法による解析*¹

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C-13をラベルしたホルムアルデヒドを用いてメラミンとユリアのホルムアルデヒドによる中性下における共縮合反応を検討した。DMSO-d₆溶液に水が存在すると¹³C-NMRスペクトルの化学シフトが低地場にシフトすることが分り、前報の化学シフトを訂正した。メラミンのメチロール基はユリアの第一級アミノ基との共縮合によるメチレン結合を生成しやすく、メラミンのジメチレンエーテル結合生成による自己縮合に優先する。トリメチロールメラミンとジメチロールユリアの反応では、メチレン結合よりジメチレンエーテル結合の生成による共縮合が優先した。また、ユリアのメチロール基もメラミンの第一級アミノ基とメチレン結合により共縮合した。さらに、メラミン、ユリア、ホルムアルデヒドの3者を同時に反応させた系では、ジメチレンエーテル結合による自己縮合と共縮合がメチレン結合によるそれらに優先することが判明した。

The urea-formaldehyde (UF) resins, melamine-formaldehyde (MF) resins, and melamine-urea-formaldehyde (MUF) cocondensed resins were synthesized using the labeling method with ¹³C enriched formaldehyde under neutral conditions and their ¹³C-NMR (nuclear magnetic resonance) spectra were analyzed. The remarkable down-field shifts by 1.2 to 2.7 ppm of the corresponding signals of UF and MUF resins were recognized by the addition of water to the DMSO-d₆ solution of NMR samples. According to the results, the chemical shifts were corrected by measurements of DMSO-d₆ solution free of water. The formation of cocondensed methylene linkages was induced mainly by the reaction of methylol groups of melamine and primary amino groups of urea residue, and that of cocondensed dimethylene ether linkages was apt to take place in the case of a shortage of primary amino groups of urea residue. In the reaction of methylolurea and dimethylolmelamine, methylol groups of urea residue also were found to react with the primary amino group of methylolmelamine to form cocondensed methylene linkages.

Keywords: melamine/urea, formaldehyde, cocondensation, C-13 NMR, C-13 enriched formaldehyde.

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1. INTRODUCTION

In the work for the previous paper,¹⁾ whether or not the occurrences of cocondensation between melamine and urea through the formation of the methylene linkage could be identified was investigated with ¹³C-NMR (carbon 13 nuclear magnetic resonance)

spectroscopy. The chemical shifts of two kinds of cocondensed methylene carbons were calculated using those of self-condensed methylene carbons of urea-formaldehyde (UF) and melamine-formaldehyde (MF) resins with additivity relationship, and the presences of the signals corresponding to the calculated chemical shifts were suggested strongly in the spectra of melamine-urea-formaldehyde (MUF) cocondensed resins.

It also was investigated whether occurrences of the cocondensation between melamine and urea through the formation of a dimethylene ether linkage could be identified. As a result, the signals due to cocondensed methylene carbons of a dimethylene ether linkage were recognized clearly between the signals of the self-condensed dimethylene ether linkage of UF and MF resins.

Although the occurrences of cocondensation through the formation of methylene or dimethylene ether linkages were identified, more precise information about the cocondensed structures was still needed. In general, signals of these resins synthesized from industrial formaldehyde were quite small in intensity and broad in their ^{13}C -NMR spectra because of great viscosity of the sample. Therefore, it was considered that a more precise analysis of cocondensed methylene carbons would be possible if ^{13}C enriched formaldehyde was used when the resins were synthesized.

In the work for this paper, three kinds of resins, UF, MF, and MUF, were synthesized using ^{13}C enriched formaldehyde (isotope formaldehyde), and the occurrences of cocondensation were analyzed from their NMR spectra. Several reactions using ^{13}C enriched formaldehyde also were analyzed to determine the driving force to introduce the cocondensation through the formation of methylene or dimethylene ether linkage into the melamine-urea resin system.

2. EXPERIMENT

2.1 Preparation of urea-formaldehyde resins (UI2)

A 20% isotope formalin (ICN Biochemical Inc. 99% ^{13}C enriched, 300 mg, 2.0 mmol) was placed in a small flask with a stirrer and diluted with 0.7 g of water. After its pH was adjusted to 9.80 with 1N NaOH, urea (60 mg, 1 mmol) was added, and then the mixture was heated at 80°C for 30 min with stirring. The pH of the

mixture was adjusted to 4.50 with 1N HCl after cooling to room temperature, and it was heated at 80°C for 100 min. Then the mixture was cooled to room temperature and its pH was adjusted to 7.70.

2.2 Preparation of melamine-formaldehyde resin (MI3)

MF resin (MI3) of the molar ratio of F/M=3.0 was synthesized. After the mixture of 20% isotope formalin (360 mg, 2.4 mmol) and water (500 mg) was adjusted to pH 8.2 with 1N NaOH, melamine (100 mg, 0.8 mmol) was added. After the mixture was heated at 83°C for 3 min, melamine was dissolved, and then its pH was adjusted to 6.7. After heating at 80°C for 30 min, the reaction mixture was cooled to room temperature.

2.3 Preparation of MUF cocondensed resin (MI3-U)

A 20% isotope formalin (450 mg, 3.0 mmol) was placed in a small flask with a stirrer and diluted with 0.7 g of water. After its pH was adjusted to 8.9 with 1N NaOH, 126 mg of melamine (1.0 mmol) was added. The mixture was heated at 80°C min with stirring. Melamine was dissolved completely after heating 15 min, and then urea (120 mg, 2 mmol) was added. The pH of the mixture was determined as being 6.7. After the mixture was heated at 80°C for 30 min, the solution became cloudy, and it then was freeze-dried.

2.4 Preparation of the resin (MI3-FUF) from methylolmelamine and dimethylolurea

A mixture of 20% isotope formalin (200 mg, 1.33 mmol) and water (500 mg) was adjusted to pH 9.3, and then melamine (56 mg, 0.44 mmol) was added. After heating the mixture at 80°C for 10 min, melamine was dissolved completely, and it was cooled to room temperature. Dimethylolurea (52 mg, 0.44 mmol) was added, and the pH of the mixture was adjusted to 6.7. It began to be cloudy after heating for 30 min, and then it was cooled to room temperature.

2.5 Preparation of the resin (UI2-M2) from methylolurea and dimethylolmelamine

The pH of the mixture of isotope formalin (310 mg, 2.07 mmol) and water (500 mg) was adjusted to pH 9.0. To mixture was added urea (60 mg, 1.0 mmol), and it was heated at 80°C for 30 min. After cooling to room temperature, dimethylolmelamine (92 mg, 0.5 mmol) was added. After the dissolving of dimethylolmelamine by heating at 80°C for 5 min, the pH was

adjusted to 6.5. The mixture was heated at 80°C for 30 min, and its pH was adjusted twice at 6.5. After 30 min, it became cloudy, and then it was cooled to room temperature.

2.6 Preparation of the resin (MIUI5)

To a mixture of 99% ^{13}C enriched paraformaldehyde (INC Biochemicals, Inc., 75 mg, 2.5 mmol) and water (800 mg) a few drops of 1N NaOH solution was added, and heated to 80°C. After 5 min, paraformaldehyde was dissolved completely, and the pH of the mixture was determined to be 9.6. Melamine (63 mg, 0.5 mmol) and urea (30 mg, 0.5 mmol) were added, and heated at 80°C. Melamine was dissolved after heating for 10 min, and the pH of the mixture was determined as to be 9.8. After adjusted its pH to 6.2, it was heated at 80°C for 30 min, and then it began to form precipitates.

2.7 ^{13}C -NMR measurement

All the samples were dissolved in $\text{DMSO}-d_6$ after freeze-drying, and their ^{13}C -NMR spectra were obtained on a AC-300 spectrometer (Bruker) at a frequency of 75 MHz by complete decoupling of protons using 5 mm sample tubes. Numbers of accumulation times were 512 to 2,560. The chemical shifts were calculated by defining a center of the signals due to $\text{DMSO}-d_6$ as 39.5 ppm.

3. RESULTS AND DISCUSSION

3.1 Correction of Chemical Shifts

During the course of this work, discrepancies of

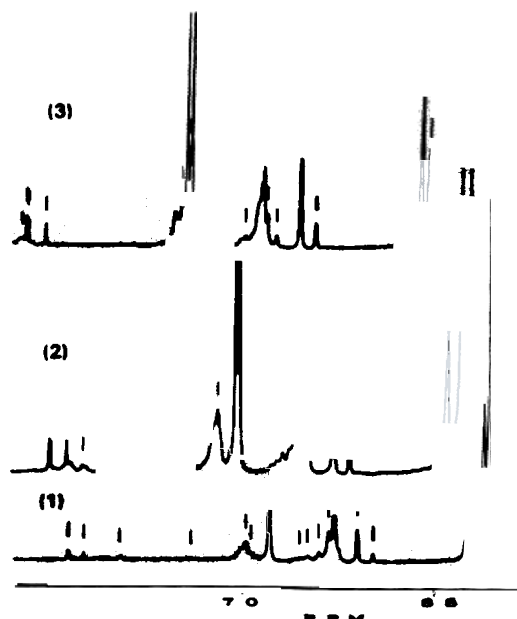


Fig. 1 Effects of the addition of water to $\text{DMSO}-d_6$ solution on chemical shifts of carbons of UF resin (UI2).

Note Water contents: (1) 0%, (2) 20%, (3) 50%.

Table 1 Changing of ^{13}C chemical shifts for the various methylene carbons for UF resin by the presence of water in a $\text{DMSO}-d_6$ solution.

Structures of Methylene carbon	Chemical shifts (ppm) ^{a)}			Shift values ^{b)} (ppm)
	Contents of water			
	0 %	10%	50%	
-NH-CH ₂ -NH-	45.45	46.16	47.18	1.73
	45.57	—	47.32	1.75
	46.17	46.82	47.73	1.56
-NH-CH ₂ -N(CH ₂ -)-	51.80	52.53	53.65	1.85
	51.91	52.66	53.84	1.91
	52.21	53.06	54.08	1.87
-NH-CH ₂ OH				
-NH(CH ₂ -)-CH ₂ OH				
N-CH ₂ -O-CH ₂ -NH-				
C=O				
HO-CH ₂ -OH	82.02	82.45	83.08	1.06

^{a)} Chemical shifts were calculated by defining $\text{DMSO}-d_6$ as 39.5 ppm. ^{b)} Shift values were based on the difference of chemical shifts between those for 0% and 50%.

chemical shifts have been observed sometimes for the corresponding carbons of UF and MF resins. The UF resin (UI2) was diluted to two levels of concentration, 20 and 50%, with water. Figure 1 shows one of the examples for spectral changing by the presence of water in a DMSO- d_6 solution. The down-field shifts of the corresponding signals are recognizable. These results are summarized in Table 1. The same tendencies also were observed for the NMR spectra of MF resin (MI3) and MUF cocondensed resin (MI3-U). The samples for NMR measurements had been prepared either by diluting the water solutions of the

resins with DMSO- d_6 or by dissolving the freeze-dried resins with the same solvent. The presence of strong intermolecular hydrogen bonds can be considered between the protons of the resins and DMSO- d_6 , because the solvent is one of the strong dipolar aprotic solvents. The values of down-field shifts for the carbons of methylene linkages were 1.56 to 1.75 for $-\text{NH}-\underline{\text{CH}_2}-\text{NH}-$ and 1.85 to 1.91 for $-\text{NH}-\underline{\text{CH}_2}-\text{N}(\text{CH}_2-)-$. And those for the carbons of methylol groups were 1.27 to 1.45 for $-\text{NH}-\underline{\text{CH}_2}\text{OH}$, and 2.10 to 2.11 for $-\text{N}(\text{CH}_2-)-\underline{\text{CH}_2}\text{OH}$. Furthermore, remarkable down-field shifts by 2.38–2.76 were recognized for

Table 2. ^{13}C Chemical shifts of methylene carbons for UF resin, MF resin, and MUF cocondensed resins in DMSO- d_6 solutions.

Structures	Chemical shifts (ppm)		
	UF resin	MF resin	MUF resin
		47.04	
$-\text{NH}-\underline{\text{CH}_2}-\text{N}(\text{CH}_2-)-$	51.80 51.91 52.22	52.14	
$-\text{N}(\text{CH}_2-)-\underline{\text{CH}_2}-\text{N}(\text{CH}_2-)-$	59.16 59.55		
$\text{NH}-\underline{\text{CH}_2}\text{OH}$		65.70	
$\text{NH}(\text{CH}_2-)-\underline{\text{CH}_2}\text{OH}$		69.50	
$-\text{NH}-\underline{\text{CH}_2}-\text{O}-\text{CH}_2-\text{NH}-$		68.23	
$\text{N}(\text{CH}_2-)-\underline{\text{CH}_2}-\text{O}-\text{CH}_2-\text{N}-$	74.10 74.50	— about 75.0	
$-\text{NH}-\underline{\text{CH}_2}\text{OCH}_3$	77.09 77.58		
$\underline{\text{C}}=\text{O}$	157.36 157.69 158.58		157.61 158.90 160.42
Triazine $\underline{\text{C}}$			
$\underline{\text{CH}_2}\text{OH}$			

Note The mark (—) means that signals were not clear.

the carbonyl carbons of urea residues. These down-field shifts due to the addition of water were considered to be derived from the breaking hydrogen bonds between the solvent and the protons of the resins. According to these results, the chemical shifts of all methylene carbons were determined as shown in Table 2 by measuring the DMSO- d_6 solution free from water.

3.2 Analysis of cocondensed methylene linkage of MUF resin

Figure 2 shows ^{13}C -NMR spectra of UF, MF and MUF resins, which were synthesized with ^{13}C enriched formaldehyde. It is noted that the presences of the signals due to methyl carbons of methanol and methyl ethers are almost negligible in each spectrum, because the enriched formaldehyde contains only a small amount of methanol. Expanded spectra for the three

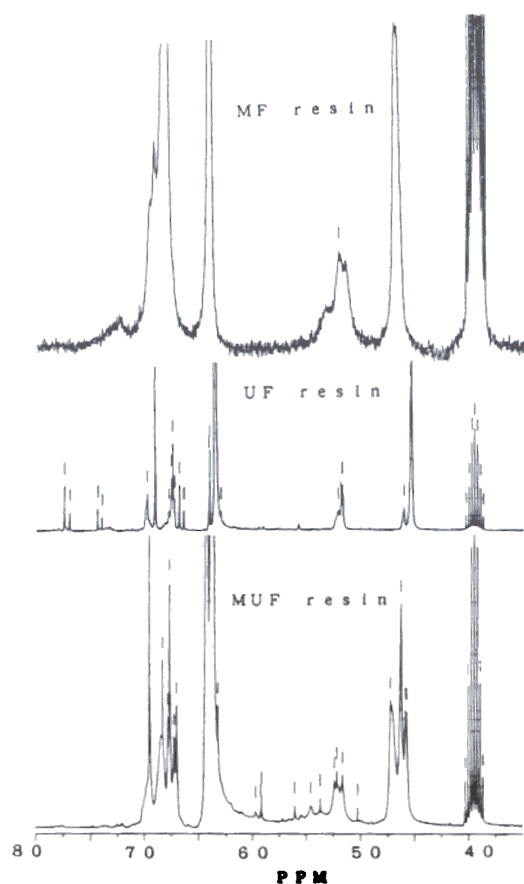


Fig. 2. Comparison of ^{13}C -NMR spectra among MF (MI3), UF (UI2), and MUF (MI3-U) resins in the magnetic fields of 40 to 80 ppm.

resins are compared in the magnetic field between 45 and 57.5 ppm in Fig. 3, where the signals due to carbons of methylene linkages appear. The signals which appeared in this magnetic field already were assigned to methylene carbons of $-\text{NH}-\text{CH}_2-\text{NH}-$, in which both of the adjacent amino groups are secondary because having hydrogen atoms.¹⁻³⁾ Furthermore, the splitting of the signals would be derived from the effect of the substitution at the delta-position, that is substitution to an amino group on the other side of the urea residue.

The chemical shifts of the signals that appeared in this region also are summarized for the three resins as shown in Table 2. There are good separations of methylene carbons between the UF and MF resins. The large closed signals at 45.33 and 45.45 ppm and the small one at 46.17 ppm in the spectrum of the UF resin appear separately from a broad signal at 47.04 ppm in the spectrum of the of MF resin.

It is obvious from Fig. 3 and Table 2 that the signal at 46.27 ppm in the MUF resin appears separately from those of UF and MF resins. Furthermore, a

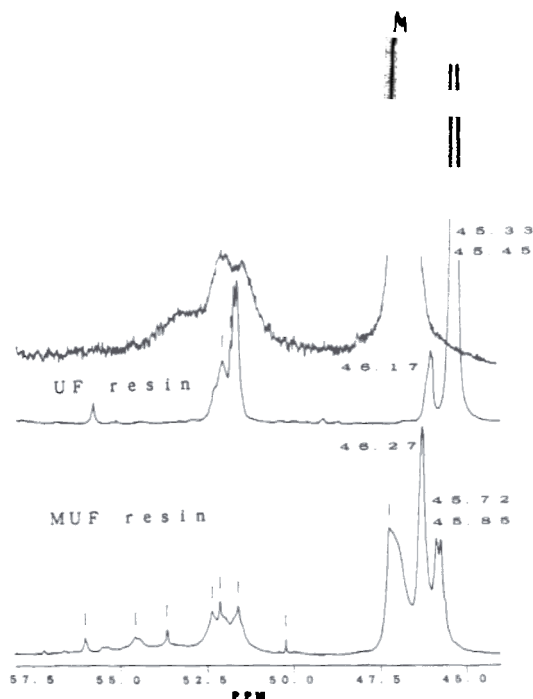
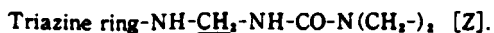
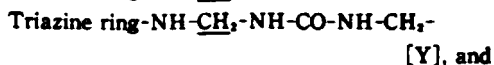
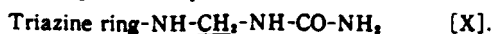


Fig. 3. Comparison of ^{13}C -NMR spectra among MF (MI3), UF (UI2), and MUF (MI3-U) resins in the magnetic fields of 45 to 57.5 ppm.

couple of signals appearing at 45.85 and 45.72 ppm in the MUF resin cannot be observed in the UF and MF resins. Therefore, it is concluded that these three signals at 46.27, 45.85, and 45.72 ppm are due to the carbons of the cocondensed methylene linkage between urea residue and triazine ring. Basic cocondensed methylene carbons, which have two adjacent secondary nitrogen atoms, between urea residue and triazine ring can be represented as follows:



The delta-position of the discussed carbons can be altered only in the adjacent urea residue in the structure of the cocondensed methylene linkages. Therefore, only three structures are considered for cocondensed methylene carbons having two secondary adjacent nitrogen atoms. Because the MUF cocondensed resins was synthesized by reacting urea with methylolmelamine which was prepared under the molar ratio of F/M=3/1, the formation of Structure [Z] is considered most unlikely. The substitution of carbon of the delta-position to the discussed carbon will cause the down-field shift by 0.3 ppm.^{4,9} As a result, the signals at 45.72 and 45.85 ppm of MUF cocondensed resin safely are assigned for the carbons of Structure [X], and that at 46.27 ppm for Structure [Y].

It can be concluded that the occurrence of the cocondensation is judged not only by comparison of chemical shifts, but also by that of signal patterns due to corresponding methylene carbons. As to the cocondensed dimethylene ether linkage of $\text{-NH-}\underline{\text{CH}_2}\text{-O-CH}_2\text{-NH-}$, it was found and reported in the previous paper that its carbon signal appears at the chemical shifts between those of self-condensed dimethylene ether linkages of UF and MF resins.¹¹

3.3 Reaction condition for the formation of cocondensation

The main focus on the formation of cocondensation here was whether or not the formation of a cocondensed methylene linkage is induced by the reaction of a methylol group of melamine with an amino group of urea or by that of a methylol group of urea with an amino group of melamine. It should be noted that the neutral condition was employed for all of the conden-

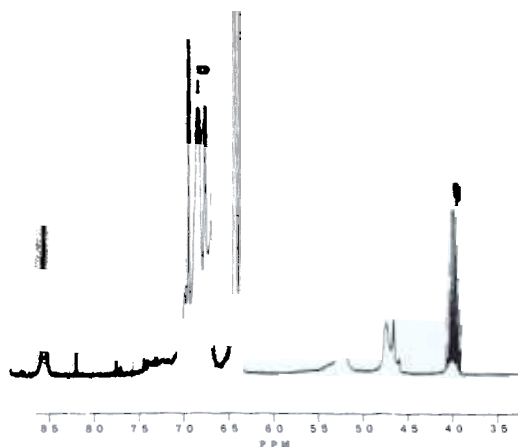
sation stages in the present work to prevent from the self-condensation of urea residues, and it is noted also that reactivities of methylol groups could be determined by the ^{13}C labeling method.

3.4 Reaction of ^{13}C enriched methylolmelamine and urea (MI3-U)

The reaction of a methylolmelamine mixture (that is, synthesized with isotope formaldehyde of a molar ratio of F/M=3.0) and urea was investigated. The ^{13}C -NMR spectra of the cocondensed product are shown at the bottom of Figs. 1 and 2. In this reaction the mixture of methylolmelamine initially was synthesized, and then urea was reacted under almost the neutral condition of pH 6.5. Although methylation of urea took place with a small amount of free formaldehyde remaining in first stage, the neutral condition almost can exclude the formation of methylene linkages between urea residues. Therefore, the two signals at 45.45 and 45.57 ppm can be assigned to the carbons due to the cocondensed methylene linkages. The signals at about 68 ppm can be assigned safely to the carbons due to the self-condensed dimethylene ether linkages between triazine rings by comparison with the spectrum of melamine resin. It also is confirmed that the intensity of the signal due to the formation of dimethylene ether linkages between triazine rings was weak. Therefore, the reaction of the methylol group of melamine with urea will be due to the formation of both cocondensed methylene linkages as well as self-condensed methylene linkages.

3.5 Reaction of ^{13}C enriched methylolmelamine and dimethylolurea (MI3-FUF)

The ^{13}C -NMR spectrum of the reaction product (MI3-FUF) is shown in Fig. 4. In this reaction the ^{13}C labeling was performed on the mixture of methylolmelamine and, on the other hand, dimethylolurea was not enriched. Therefore, only the signals due to the reaction of methylol groups of methylolmelamine can be recognized. The signals due to the carbons of cocondensed methylene linkages and the self-condensed methylene linkages of melamine can be observed at 46.23 and 46.98 ppm, respectively. The methylene carbons of $\text{-N(CH}_2\text{)-}\underline{\text{CH}_2}\text{-NH-}$, where one adjacent nitrogen is tertiary, gave the signal at 51.92 ppm, and those due to dimethylene ether linkages of melamine gave the strong signal at 68.38



^{13}C -NMR spectrum of the reactant (MI3-FUF) of ^{13}C enriched methylolmelamine and dimethylolurea under neutral conditions. The signal CM is due to the cocondensed methylene carbons and the signal D is due to the dimethylene ether.

ppm, which include both self- and co-condensed ether linkages.

Because the spectrum displayed strong signals due to dimethylene ether linkages, it can be concluded that the formation of the ether linkages dominated the reaction under neutral conditions. In the cases of the syntheses of MI3, MI3-U, and MI3-FUF, all the molar ratios were constant at F/M=3.0. The methylation of melamine generally produces a wide distribution of many kinds of methylolmelamine.⁴⁾ Furthermore, this molar ratio will result in a large amount of secondary amino groups ($-\text{NH}-\text{CH}_2\text{OH}$), a small amount of tertiary amino groups ($-\text{N}(\text{CH}_2\text{OH})_2$), and a small amount of unreacted amino groups ($-\text{NH}_2$). The condensation due to the formation of methylene linkages is apt to take place with the reaction of the methylol group with the primary amino groups rather than the secondary amino groups. Therefore, the formation of methylene linkages was so slow that the formation of dimethylene ether linkages between methylol groups will prevail over those of methylene linkages.

3.6 Reaction of ^{13}C enriched methylolurea and dimethylolmelamine (UI2-M2)

Figure 5 shows the spectrum of the product (UI2-M2) from ^{13}C enriched methylolurea and dimethylolmelamine. The signals due to the self-condensed

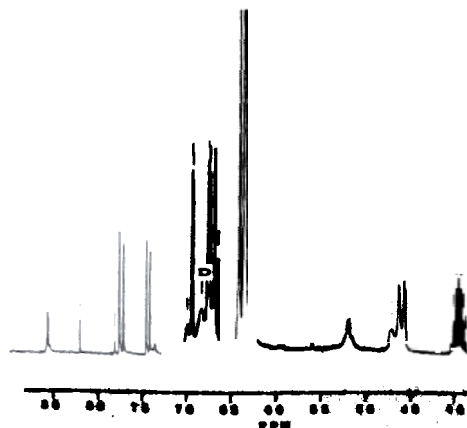


Fig. 5. ^{13}C -NMR spectrum of the reactant (UI2-M2) of ^{13}C -enriched methylolurea and dimethylolmelamine under neutral conditions.

Note The signals CM and D are the same as in Fig. 4.

methylene and dimethylene ether carbons for melamine are recognized at 46.98 and 68.37 ppm, which will be derived from the reaction of ^{13}C enriched formaldehyde remaining in the stage of methylation of urea with unlabeled dimethylolmelamine. The signal pattern in the magnetic field between 40 and 50 ppm corresponding to a methylene linkage is quite different from those of UF resins. The signals at 45.53, 45.66, and 46.24 ppm safely can be assigned to the carbons of cocondensed methylene linkages. It has been known also that dimethylolmelamine has a large amount of primary amino groups having wide distribution of methylol groups and amino groups.⁴⁾ As a result, it can be concluded that methylol groups of urea residue also react with the primary amino group of methylolmelamine to form cocondensed methylene linkages.

3.7 Reaction of the mixture of melamine and urea with ^{13}C enriched formaldehyde (M1UII5)

The mixture of melamine, urea, and ^{13}C enriched formaldehyde was reacted under the same neutral state. The NMR spectrum of the product is shown in Fig. 6. The neutral condition also will deny the formation of self-condensed methylene linkages between urea residues. Therefore, the signals at 45.00 and 45.16 ppm safely were assigned to the carbons of the cocondensed methylene linkages. The signals of the carbons due to both self-condensed methylene and

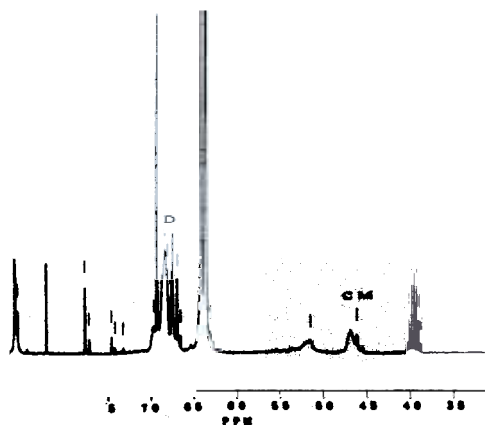


Fig. 6. ^{13}C -NMR spectrum of the reactant of urea, melamine, and ^{13}C enriched formaldehyde with the molar ratio of F/M/U=5/1/1 under neutral conditions (MIUI5).

Note The signals CM and D are the same as in Fig. 4.

dimethylene ether are observed at 46.70 and 68.35 ppm, respectively. It is noted that the spectrum in Fig. 6 closely resembles to that of Fig. 4, the spectrum of which was obtained from the reaction of ^{13}C enriched methylolmelamine and dimethylolurea. However, the broad signal at 68.35 may be attributed to the carbons of the cocondensed dimethylene ether linkage as well as to those of self-cocondensed dimethylene ether linkages.

It is concluded that the self-condensation by dimethylene ether of methylolmelamine prevails against the self- and co-condensation by methylene linkages under the conditions used in the present work.

4. CONCLUSION

The effective introduction of a cocondensed meth-

ylene linkage will be expected by the method in which methylolmelamine is reacted with urea itself or methylolureas having primary amino groups. The other method to introduce cocondensed methylene linkages can be considered as the reaction of methylol groups of urea with amino groups of melamine.

As to the carbons of methylene linkage, the signals observed at 50–55 ppm in the spectra are derived from the methylene carbons of $-\text{N}-\text{CH}_2-\text{N}(\text{CH}_2-)-$ in which one adjacent nitrogen atom is tertiary. However, precise analyses among the three resins can not be attained fully at the present time. Further investigation on this magnetic field will be made by changing the synthetic conditions of the resins.

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