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Analyses of Cocondensation of Melamine and Urea through Formaldehyde with Carbon 13 Nuclear Magnetic Resonance Spectroscopy[*1]

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炭素13核磁気共鳴スペクトル法によるメラミン/ユリアホルムアルデヒドの共縮合反応の解析[*1]

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種々の条件で合成したユリア，メラミン，メラミン・ユリア共縮合樹脂の解析をC-13 NMRによって行い，メラミンとユリアがメチレン結合やジメチレンエーチル結合によって共縮合することが判定できるかどうかを検討した。ユリア樹脂とメラミン樹脂のメチレン結合の炭素によるシグナルは，分離して観察でき，共縮合系のメチレン結合の炭素シグナルと分離して出現することが推定された。ジメチレンエーテル結合による炭素シグナルは，ユリア樹脂とメラミン樹脂で0.9 ppm離れて出現し，共縮合樹脂のそれが両者の中間に出現することが確認された。

The ^{13}C-NMR (carbon 13 nuclear magnetic resonance) spectra of urea-formaldehyde (UF) resins, melamine-formaldehyde (MF) resins, and melamine-urea-formaldehyde (MUF) cocondensed resins synthesized under various conditions were taken with a frequency of 75 MHz. The main purpose was to investigate whether or not the occurrences of cocondensation between melamine and urea through the formations of methylene or dimethylene ether linkages could be identified. The signals due to carbons of methylene linkages of UF resins were distinguishable from those of MF resins. The signals due to carbons of cocondensed methylene linkages ($-NH-\underline{C}H_2-NH-$), in which both nitrogen atoms are secondary, were suggested to be identifiable separately from those due to UF and MF resins. The corresponding carbons of dimethylene ether linkages of UF and MF resins could be identified clearly by the difference of their chemical shifts of 0.9 ppm. The carbon signals due to cocondensed dimethylene ether linkages were found to appear at the chemical shifts between those due to UF and MF resins.

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

1. INTRODUCTION

It is well known that the incorporation of melamine into urea-formaldehyde (UF) resins upgrades the performance and controlling formaldehyde emissions of UF resins bonded products, and melamine-urea-formaldehyde (MUF) cocondensed resins have been applied widely to the manufacturing of plywood, particle board, and laminated wood. However, the

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reaction mechanism of the cocondensation of melamine and urea with formaldehyde has not been explained clearly, although many researchers have made efforts to determine the occurrence of the cocondensation.

In earlier work, a strong resemblance unexpectedly was observed between the ^{13}C-NMR (carbon 13 nuclear magnetic resonance) spectra of aqueous melamine-formaldehyde (MF) resin and UF resin in the magnetic field of 40-100 ppm where all of the combined methylene carbons afford signals, and it was found that the chemical shift of each carbon of MF resin was superimposed on those of UF resin.[1] Furthermore, it also was confirmed that the spectrum of MUF resin was indistinguishable from those of UF and MF resins in the same magnetic field.

This research initially focuses on basic studies of the reaction between melamine and urea with formaldehyde to determine the effect of reaction conditions on cocondensation and the chemical structures of MUF resins. In this paper, preliminary observations are made of ^{13}C-NMR spectra of UF, MF, and MUF resins re-investigated with a 75 MHz apparatus.

2. EXPERIMENT

2.1 Preparation of UF resins

UF, MUF, and MF resins were synthesized from commercial urea, melamine, and 37% formalin, respectively. Two kinds of UF resins (UF-1 and UF-2) were synthesized by the second addition of urea to the resin initially prepared with a molar ratio of F/U=3 at pH 4.75. The final molar ratios of the two resins were F/U=1.4 and 1.7, respectively. Each resin was neutralized in the final stage. The resin (UF-3) of a molar ratio of F/U=3.0 was synthesized at pH 1.0 according to the common method for preparing UF-concentrate. Two kinds of UF resins, UF-4 and UF-5, were commercial resins supplied by Mitsuitoatsu Chemical Company.

2.2 Preparation of MUF resins

Three kinds of MUF resins were synthesized in two steps: (1) melamine, urea, and formalin were mixed in their target molar ratios, separately, and reacted at 80°C at pH 4.75; (2) the mixtures were adjusted to pH 7.7 and reacted at 80°C for a certain time. The molar ratios of MUF-1, MUF-2, and MUF-3 were 3/1/0.35, 3/1/0.35 and 3/1/0.5, respectively.

2.3 Preparation of MF resins

Aqueous melamine resins (MF-1 and MF-2) were synthesized with the molar ratio of F/M=3 by two steps: (1) melamine was added to formalin, whose pH previously was adjusted at 9.0, and methylolation was performed at 80°C for 15 min; (2) condensation was performed at the same temperature for the target reaction times after correcting the pH to 6.4-6.6. Then the reaction mixtures were cooled and their pHs were adjusted to the range of 8.0-9.0.

2.4 ^{13}C-NMR Measurement

Fourier transform ^{13}C-NMR spectra were obtained on an AC-P 300 spectrometer (Bruker) at a frequency of 75 MHz and a pulse delay of 4 sec with inverse proton decoupling. Each aqueous resin was diluted directly with DMSO-d_6, and was used as a NMR sample. The chemical shifts were calculated by defining a ^{13}C chemical shift of DMSO-d_6 as 39.7-39.8 ppm or by that of internal methanol as 44.9 ppm.

3. RESULTS AND DISCUSSION

3.1 Review of ^{13}C-NMR study on UF, MUF, and MF resins

The structures of UF resins have been analyzed with ^{13}C-NMR spectroscopy by many workers,[2-5] and the structures of MUF cocondensed resins have been compared with those of UF resins and MF resins in an earlier work.[1] Figure 1 shows a comparison of ^{13}C-NMR spectra (measured with a frequency of 25 MHz) between UF and MUF resins, from earlier results. It can be seen that all the carbons due to combined formaldehydes gave broad signals. For example, Signal e attributed to the methylene carbon ($-HN-\underline{C}H_2-NH-$) of UF resins was broad in Figure 1, and its chemical shift was superimposable with that of the corresponding carbons of MUF cocondensed resin. It was concluded that the cocondensed methylene carbons of MUF resins cannot be distinguished from the methylene carbons of UF and MF resins. Moreover, it was found that each chemical shift of the corresponding carbon of the combined formaldehyde, including a dimethylene ether linkage, is superimposable among the three resins. Therefore, the occurrences of a cocondensed methylene linkage and a dimethylene ether linkage could not be judged by the measurements at a frequency of 25 MHz.

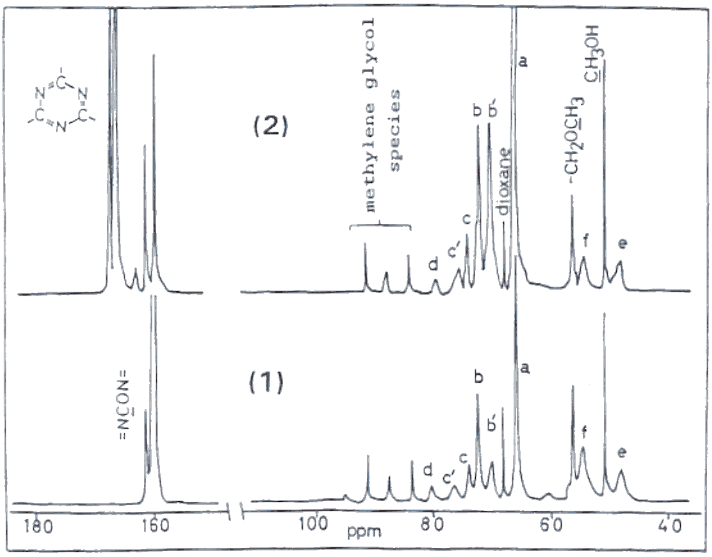

Fig. ^{13}C-NMR spectra (25 MHz) of (1) urea resin and (2) commercial melamine-urea resin in water solution.

Note Signal assignments are common to the two resins: (a) $-NH\underline{C}H_2OH$, (b) $-N(CH_2-)\underline{C}H_2OH$, (b') $-NH\underline{C}H_2O\underline{C}H_2NH-$ and $-NH\underline{C}H_2OCH_2OH$, (c) $-NH\underline{C}H_2OCH_3$, (c') $-N(CH_2-)\underline{C}H_2OCH_2NH-$, $-N(CH_2-)\underline{C}H_2O\underline{C}H_2N(CH_2-)-$, and $-N(CH_2-)\underline{C}H_2O-CH_2OH$, (d) $-N(CH_2-)\underline{C}H_2OCH_3$, (e) $-NH\underline{C}H_2NH-$, (f) $-N(CH_2-)\underline{C}H_2NH-$, (g) $-N(CH_2-)\underline{C}H_2N(CH_2-)-$.

3.2 ^{13}C-NMR analyses of methylene linkages of UF and MF resins

The ^{13}C-NMR spectra of five kinds of UF resins, three kinds of MUF resins, and two kinds of MF resins were obtained with a frequency of 75 MHz, and their spectra of methylene regions between 45 and 55 ppm are shown in Fig. 2. Table 1 summarizes the results of assignments of chemical shifts for the ten kinds of resins. Although the chemical shifts were determined using internal DMSO-d_6 or methanol, their calculated values could not be employed always for direct comparisons because of setting errors when defining the chemical shift of the standard.

In Fig. 2 three signals (a, b, and c) are recognized as UF resins, whereas the spectrum at 25 MHz gave only one broad signal in this region as shown in Fig. 1. The signals appearing in this region already were assigned to methylene carbons of $-NH-\underline{C}H_2-NH-$, where both

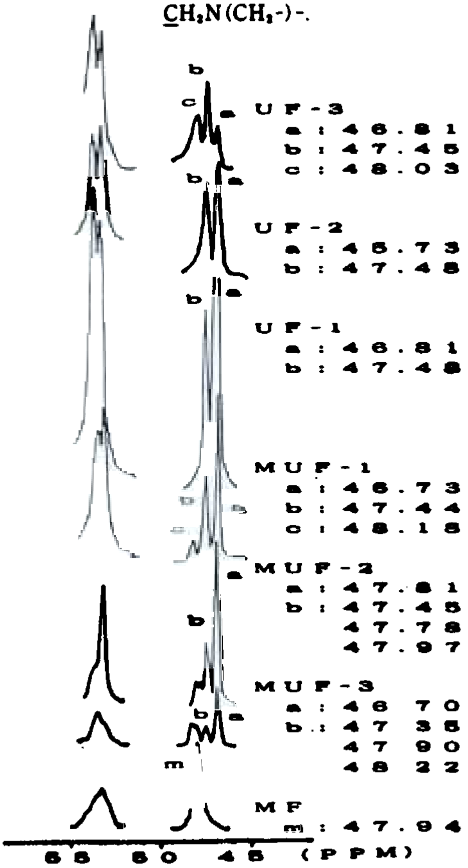

Fig. 2 Comparison of ^{13}C-NMR spectra (75 MHz) in the regions of methylene linkages of urea resins (UF), melamine resins (MF), and melamine-urea resins (MUF).

Table 1 ¹³C Chemical shifts of urea resins, melamine resins, and melamine-urea resins.

Structures	UF-1	UF-2	UF-3	UF-4	UF-5	MUF-1	MUF-2	MUF-3	MF-1	MF-2
DMSO-d6	39.65	39.70	39.70	39.70	38.99	39.31	39.82	39.69	39.84	39.67
[illegible]	46.81 47.48	46.73 47.48	46.81 47.45 [illegible]	47.00	47.00	46.73 47.44 [illegible]	46.81 47.45 47.78	46.70 47.35 47.90	47.94	47.78
$\underline{C}H_2OH$	49.89	49.81	49.88	49.89	49.86	49.90	49.91	49.87	49.83	49.91
$-N(CH_2-)-\underline{C}H_2-NH-$	53.43 53.72			53.60	53.65	53.10 53.50	53.24	53.15 53.54	53.27	53.40
$-N(CH_2)-\underline{C}H_2-N(CH_2-)-$	59.86					59.62				
[illegible]							70.18	69.37 69.52 69.87	69.96	70.20
$-NH-\underline{C}H_2OCH_2OH$			68.18			69.31	69.40		68.87	68.80
$-N(CH_2-)-\underline{C}H_2OH$	70.89 71.31	70.64 70.81 71.24	70.84 71.37	71.10	71.09	70.56 71.28	70.84 70.96 71.27	70.56	70.79	70.40
$-NH-\underline{C}H_2OCH_3$	73.06	72.97	72.55 73.04 73.43	73.10 73.24	73.09	73.14	73.09	73.05 73.38	73.31	73.55
$-N(CH_2-)-\underline{C}H_2OCH_2-N-$	75.38				75.50	74.86 75.51	75.09			74.90
$-N(CH_2-)-\underline{C}H_2OCH_3$	79.25	78.92	78.72 79.09 79.58		78.70	78.74 79.10	78.00 79.00	77.20 77.50	78.63	
$HO\underline{C}H_2OH$	82.96	82.90	83.00	82.90	82.93	83.07	83.04	83.76	82.97	83.00

adjacent amine groups are secondary. Therefore, these splittings should be derived from the effect of substitution at the delta-position, that is, substitution to amine groups at the other side of the urea residue.

The following structures can be considered for the environments of the methylene carbons discussed:

$H_2N-CO-NH-\underline{C}H_2-NH-CO-NH_2$ [0],

$H_2N-CO-NH-\underline{C}H_2-NH-CO-NH(CH_2-)$ [I],

$(-CH_2)HN-CO-NH-\underline{C}H_2-NH-CO-NH(CH_2-)$ [II]

$H_2N-CO-NH-\underline{C}H_2-NH-CO-N(CH_2-)_2$ [II′]

$(-CH_2)HN-CO-NH-\underline{C}H_2-NH-CO-N(CH_2-)_2$ [III],

and $(-CH_2)_2N-CO-NH-\underline{C}H_2-NH-CO-N(CH_2-)_2$ [IV].

Although the above five structures were considered for the methylene linkage discussed, only three signals could be recognized in Fig. 2. It was reported by Stothers that the substitution effect of a carbon atom at the delta-position is a slight down-field shift by 0.3 ppm, and that to the epsilon-position is negligible.⁸⁾ It also was reported that the chemical shift of a methylene carbon due to dimethylenetriurea is less by 0.4 ppm than that of methylenediurea.⁵⁾ On the other hand, the difference of chemical shift between Signals a and b is 0.7 ppm, and that between Signals b and c is also 0.7 ppm. Therefore, the assignment of these three signals cannot be attained completely at this time because five structures can be considered. However, if the presences of Structure [0], that is, methylenediurea, and Structure [I] in practical resins are negligible, Signal a can be assigned safely to Structures [II] or [II′], and Signal b to [III] as well as Signal c to [IV].

In Fig. 2 the relative intensity of Signal a is very strong in UF-1 synthesized with the smaller molar ratio of F/U = 1.4, which is considered to have few branching structures, and it decreased with the increasing synthetic molar ratio as observed in UF-2 (F/U = 1.7) and UF-3 (F/U = 3.0). Signal c is recognized in UF-3, whereas it is not observed in UF-1 and UF-2. The UF-3 must have many branchings at delta-positions because it was synthesized with the large molar ratio of F/U = 3.0. More precise investigations using model compounds and resins will be necessary to determine the chemical shift of each structure.

The signal observed at 50-55 ppm in Fig. 2 already was assigned to the methylene carbons of $-NH-\underline{C}H_2-N(CH_2-)-$ where one of the adjacent nitrogen atoms is tertiary.[2,3,5] A precise assignment of this region also is necessary.

Signal m at 47.9 ppm in MF-1 of Fig. 2 safely was assigned to the methylene carbons of $-NH-\underline{C}H_2-NH-$ between triazine rings. As the methylene carbons have triazine rings at the beta-position, its chemical shifts will not be varied as much as UF resins, and a broad singlet will be observed. It should be noted that Signal m of MF resin can be distinguishable from the Signals a, b, and c of UF resin.

3.3 ^{13}C-NMR analysis of MUF cocondensed methylene linkage

The cocondensed methylene carbons, which have two adjacent secondary nitrogen atoms, between urea residue and triazine rings can be represented as follows:

triazine ring$-NH-\underline{C}H_2-NH-CO-NH_2$ [X],
triazine ring$-NH-\underline{C}H_2-NH-CO-NH-CH_2-$ [Y], and
triazine ring$-NH-\underline{C}H_2-NH-CO-N(CH_2-)_2$ [Z].

The presence of Structure [X] was considered to be almost absent in practical resins. The chemical shift of the carbon in Structure [Y] can be calculated by using those of Signal a due to Structure [II] and Signal m in Fig. 2 with an additional relationship as follows:

$$(a+m)/2 = (46.8+47.9)/2 = 47.35$$

Therefore, the cocondensed methylene carbon will give a new signal around 47.35 ppm. However, this signal will overlap with Signal b due to the self-condensed methylene carbon. Therefore, the occurrence of cocondensation represented as Structure [Y] cannot be identified only by the presence of this signal with the coexistence with the self-condensed methylene carbon among the urea residue. However, the presence of this kind of cocondensed methylene structure was suggested strongly by a greater relative intensity of Signal b in MUF-3.

The chemical shift of the methylene carbons of Structure [Z] also can be calculated by using those of Signal c due to Structure [IV] and Signal m as follows:

$$(c+m)/2 = (48.2+47.9)/2 = 48.05.$$

Therefore, this kind of cocondensed methylene carbon will give a new signal between Signals m and c, whose presence is suggested strongly in MUF-2 and MUF-3 as shown in Fig. 2.

As mentioned above, the assignment of cocondensed methylene carbons between melamine and urea should be performed carefully because all of the chemical shifts are close to each other.

The signals observed at 50-55 ppm in the spectra of MUF-1, MUF-2, and MUF-3 in Fig. 2 must be derived from the methylene carbons of $-NH-\underline{C}H_2-N(CH_2-)-$ in which one of the adjacent nitrogen atoms is tertiary.[1] These signals may be due to the cocondensed carbons of triazine ring$-NH-\underline{C}H_2-N(CH_2-)-$ or triazine ring$-N(CH_2-)-\underline{C}H_2-NH-CO-$ as well as being due to the self-condensed methylene carbons. Therefore, investigations on this magnetic field will be required to determine the occurrence of the cocondensation.

3.4 Dimethylene ether linkages of UF, MF, and MUF resins

It has been reported by Breet and his co-workers that the chemical shifts for the carbons of dimethylene ether linkages of $-NH-CH_2-O-CH_2-NH-$ were 70.9 and 69.9 ppm for UF and MF resins, respectively.[2] In earlier works they were 69.4 and 69.7 ppm, respectively.[1,5] Assignments for this region are too complicated, because the signals of both carbons due to dimethylene ether linkages and hemiacetalized methylol groups coexist and overlap each other. However, these chemical shifts could be identified in the spectra of UF-4 and UF-5. Because the signals due to acetal methylene of $-NH-CH_2-O-CH_2OH$ was not recognized at the chemical shifts about 85 ppm as shown in Table 1, its presence could be excluded.[1,2,5] As a result, the signal at 69.1 ppm safely was assigned to the carbon of $-NH-\underline{C}H_2-O-$

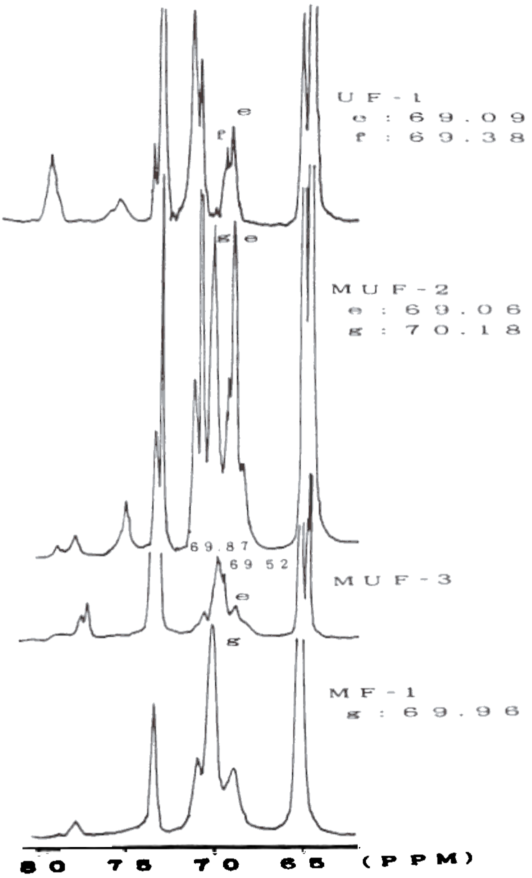

Fig. 3. Comparison of ^{13}C-NMR spectra (75 MHz) in the region of dimethylene ether linkages of urea resins (UF), melamine resins (MF), and melamine-urea resins (MUF).

CH_2-NH-. In the upper spectrum of Fig. 3 for UF-1, Signals e and f were assigned to these carbons. The same kind of methylene carbon appeared as Signal g in the bottom spectrum for melamine resin (MF-1). Furthermore, both of Signals e and g are recognized in the spectrum of MUF-2, which means that the formations of dimethylene ether linkages were dominated only by two type of self-condensations. On the other hand, the new signals at 69.87 and 69.52 ppm can be observed in the spectrum of MUF-3, whereas the relative intensities of Signals e and g are almost negligible. Therefore, it was confirmed that the cocondensation between melamine and urea takes place also trough the formation of dimethylene ether linkages. The broad signals at 75-77 ppm also were attributed to the dimethylene ether carbons of -NH (CH_2-)-$\underline{C}H_2$-O-CH_2-N< in every spectrum of Fig. 3. The analysis of this region may give more precise information about the cocondensations.

4. CONCLUSION

The ^{13}C-NMR spectra of UF resins, MF resins, and MUF cocondensed resins were measured with a frequency of 75 MHz. Their spectra at 45-50 ppm, where carbons of methylene linkages of -NH-$\underline{C}H_2$-NH- are observed, were re-investigated in detail. The chemical shifts of two kinds of cocondensed methylene carbons were calculated with additivity relationships using those of self-condensed methylene carbons of UF and MF resins. The presence of the signals corresponding to the calculated chemical shifts were suggested strongly in the spectra of MUF cocondensed resins.

Furthermore, their spectra at 65-70 ppm, where those of dimethylene ether linkages of -NH-$\underline{C}H_2$-O-CH_2-NH- are observed, also were re-investigated. As a result, the signals due to cocondensed methylene carbons of the dimethylene ether linkages were recognized clearly between the signals of self-condensed dimethylene ether linkages of UF and MF resins.

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REFERENCES

1) Tomita, B.; Ono, H.: *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 3205-3215 (1979).

2) Breet, A. J. J.; Dankelman, W.; Huysmans, W. G. B.; Wit, J.: *Angew. Makromol. Chem.*, **62**, 7-31 (1977).

3) Slonim, I. Y.; Alekseeva, S. G.; Urman, Ya. G.; Arshava, B. M.; Aksel'rod, A. Ya.: *Vysokomol. Soedin., Ser.*, **A 19**, 793-807 (1977).

4) Ebdon, J. B.; Heaton, P. E.: *Polymer*, **18**, 971-977 (1977).

5) Tomita, B.; Hatono, S.: *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 2,509-2,525 (1978).

6) Stothers, J. B.: "Carbon 13-NMR Spectroscopy," Academic Press, 1972.