Cocondensation of Urea with Methylolphenols in Acidic Conditions

BUNICHIRO TOMITA[1]* and **CHUNG-YUN HSE**[2]

Division of Chemistry of Polymer Materials, Department of Forest Products, Faculty of Agriculture, The University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113, Japan, [2]USDA Forest Service, Southern Forest Experiment Station, 2500 Shreveport Highway, Pineville, Louisiana 71360

SYNOPSIS

The reactions of urea with methylolphenols under acidic conditions were investigated using 2- and 4-hydroxybenzyl alcohol and crude 2,4,6-trimethylophenol as model compounds. The reaction products were analyzed with ^{13}C-NMR spectroscopy and GPC. From the reaction of urea with 4-hydroxybenzyl alcohol, the formations of 4-hydroxybenzylurea, *N,N'*-bis(4-hydroxybenzyl)urea, and tris(4-hydroxybenzyl)urea were confirmed and the formations of *N,N*-bis(4-hydroxybenzyl)urea and tetrakis(4-hydroxybenzyl)urea were suggested. From the reaction of urea and 2-hydroxybenzyl alcohol, 2-hydroxybenzylurea and *N,N'*-bis(2-hydroxybenzyl)urea were identified. Further, the alternative copolymer of urea and phenol could be synthesized by the reaction of urea with 2,4,6-trimethylolphenol. It was also found that the cocondensation between *p*-methylol group and urea prevails against the self-condensation of the methylolphenol even at the low pH below 3.0, and that *p*-methylol group has the stronger reactivity to urea than *o*-methylol group. © 1992 John Wiley & Sons, Inc.

Keywords: urea • phenol • formaldehyde • cocondensation • hydroxybenzylurea

INTRODUCTION

Polymers of phenol or urea with formaldehyde have dominated such areas as the wood adhesives and molding plastics for many years. Phenolic resins (PF) have demonstrated proven performance in producing exterior quality composites while low-cost urea–formaldehyde resins (UF) have performed well in interior application. Nevertheless, the potential scarcity and high cost of phenolic resins together with concerns about rather low durability and formaldehyde emission from UF resins have stimulated efforts to develop a new resin system.

Recently, so-called "phenol–formaldehyde–urea cocondensed resins," which are generally made only by mechanical blending of UF resin and alkaline type PF resins (resol), have been used as adhesives for the manufacturing of wood products. However, since these resins are cured with ammonium chloride which will react with free formaldehyde in the resins to produce an acidic state gradually, the curing of UF resin is considered to precede that of resol. Therefore the effective cocondensation cannot be expected between them. In order to develop practical uses it is necessary to introduce cocondensation between phenol and urea at the time of resin preparation. In our earlier work,[1,2] the occurrence of cocondensation of phenol and urea/melamine by formaldehyde was determined with ^{13}C-NMR spectroscopy and it was concluded that a synthetic method of reacting methylolphenols with an excessive amount of urea under acidic condition is effective. Nevertheless, the information is still needed on the effects of various conditions on the acidic cocondensation of phenol and urea.

The purpose of this article is, therefore, focused on elucidation of the chemical reactions of various methylolphenols with urea under acidic states to establish the effective cocondensation method and optimum reaction conditions. Three kinds of methylolphenols—4-hydroxybenzyl alcohol (*p*-methy-

---

* To whom all correspondence should be addressed.

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 30, 1615–1624 (1992)

lolphenol, PMP), 2-hydroxybenzyl alcohol (*o*-methylolphenol, OMP) and 2,4,6-trimethylolphenol (TMP)—were used as model compounds to react with urea.

EXPERIMENTAL

Reaction of Urea with 4-Hydroxybenzyl Alcohol and 2-Hydroxybenzyl Alcohol

Industrial grade urea and reagent grade 2- and 4-hydroxybenzyl alcohols (Aldrich Chemical Company, Inc.) were used. Several reactions were performed by changing the molar ratio of hydroxybenzyl alcohol to urea as well as the pH. In the case of the equimolar reaction (PMP/U = 1 or OMP/U = 1), e.g., each hydroxybenzyl alcohol (20.7 g) and urea (10.0 g) were dissolved into 20 mL of warmed water, and the mixture was adjusted to the desired pH levels by using 50% H_2SO_4 or AcOH and 1 *N* NaOH. The mixture was put in Erlenmeyer flask equipped with condenser, and maintained at 85°C with magnetic stirring. The pH was adjusted during reaction, and the sample was taken every 10 min in the early stage and freeze-dried. Sometimes oily products began to separate from water and precipitate after cooling. The precipitates were washed with water and dried. The kinds of experiments are listed in Table I.

Synthesis of Sodium 2,4,6-Trimethylolphenate

Sodium hydroxide (8.0 g, 0.2 mol) was dissolved in 20 mL of water and 8.8 g (0.2 mol) of phenol added according to Freeman.[3] After cooling to room temperature, 48.8 g (0.6 mol) of 37% formalin was added to the solution, which was allowed to stand at room temperature for 1 week. The solution was poured into 500 mL of isopropyl alcohol. The white precipitates formed were filtered off, washed with isopropyl alcohol, and dried in a vacuum. ^{13}C-NMR spectra of the precipitates both in alkaline solution and acidified solution showed the trimethylolphenol (sodium salt) as the main product.

Reaction of Urea with 2,4,6-Trimethylolphenol

Sodium 2,4,6-trimethylolphenate was dissolved in water (20–30%, w/w), and acidified to pH 5.0 by H_2SO_4 and AcOH. After adding a calculated amount of urea, the pHs of the solutions were adjusted to the target levels. Other reaction conditions were the same as the reaction of urea with *o*- or *p*-methylolphenol.

Gel Permeation Chromatography, Infrared Spectroscopy and ^{13}C-NMR Measurements

Each dried sample was dissolved into dimethylformamide (DMF) and analyzed by a liquid Chromatograph ALC/GPC with R-401 Differential Refractometer (Waters Associates). One Shodex GPC-AD-2002 column (Showa Denklo Co., Ltd.) was kept at 60°C in a constant temperature bath. The flow rate of DMF was 3.0 mL/min. The preparative GPC was performed under the same conditions.

Table I. Experimental Conditions of the Reaction of Methylolphenols and Urea[a]

Starting Compound	Molar Ratio Methylolphenol/Urea	pH[b]	Remarks
p-Methylolphenol	4.0	2.0	Precipitated
	2.0	2.0	Precipitated
	1.0	2.0	Precipitated
	1.0	3.0 (AcOH)	Crystallized
	1.0	4.0	Crystallized
	1.0	7.0	Crystallized
	0.5	2.0	Crystallized
	0.2	2.0	Crystallized
o-Methylolphenol	1.0	3.0 (AcOH)	Solution
	0.5	2.0	Precipitated
	0.2	2.0	Precipitated
Trimethylolphenol	0.33	2.0	Precipitated
	0.1	2.0	Solution
	0.05	2.0	Solution

[a] Reaction temperature: 85°C.

[b] The pH was adjusted by 50% H_2SO_4 unless otherwise cited.

IR spectra were taken with a 1420 Ratio Recording Infrared Spectroscopy (Perkin-Elmer) after casting the acetone solutions of samples on NaCl cell and drying in a vacuum.

NMR spectra were obtained in pyridine-d_5 or D_2O solution with a FT-80A NMR spectrometer (Varian) at a frequency of 20.0 MHz with the complete decoupling of proton. Chemical shifts were calculated by defining the center of three signals of pyridine-d_5 that appeared in the upper magnetic field at 123.6 ppm, while by defining internal methanol at 50.0 ppm in D_2O solution.

RESULTS AND DISCUSSION

Reaction of Urea with 4-Hydroxybenzyl Alcohol

Identification of Products

The isolation of the reactants from urea and 4-hydroxybenzyl alcohol by gel permeation chromatography was found to vary depending on differences in reaction pH and molar ratio (PMP/U), as shown in Figures 1 and 2. The three peaks were observed at a low molecular-weight region except for the reactants at the higher molar ratio of PMP/U = 2.0. These three peaks were well isolated with the preparative GPC. Figure 3 shows each gel permeation chromatogram after the preparative GPC. The products from peaks 1 and 2 were crystallized, respectively, while that from peak 3 was an amorphous solid. Their IR spectra were similar with that of the

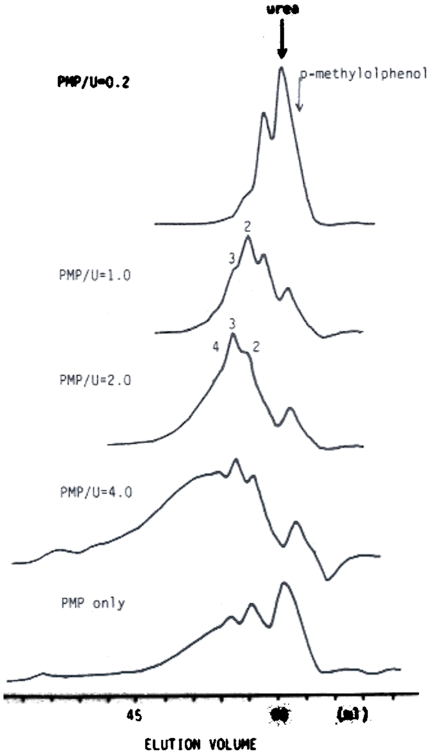


Figure 2. Gel permeation chromatograms of the reactants from p-methylolphenol and urea at various molar ratios (PMP/U). Reaction condition: 85°C, pH 2.0, 30 min.

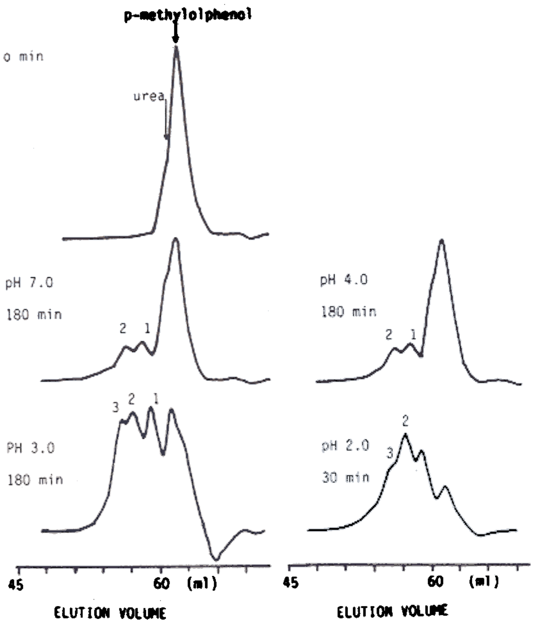


Figure 1. Gel permeation chromatograms of the reactant from urea and p-methylolphenol at the molar ratio of PMP/U = 1 under various pH levels. Reaction temperature: 85°C.

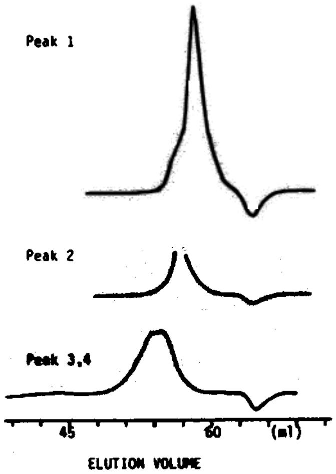


Figure 3. Gel permeation chromatograms of isolates by preparative GPC.

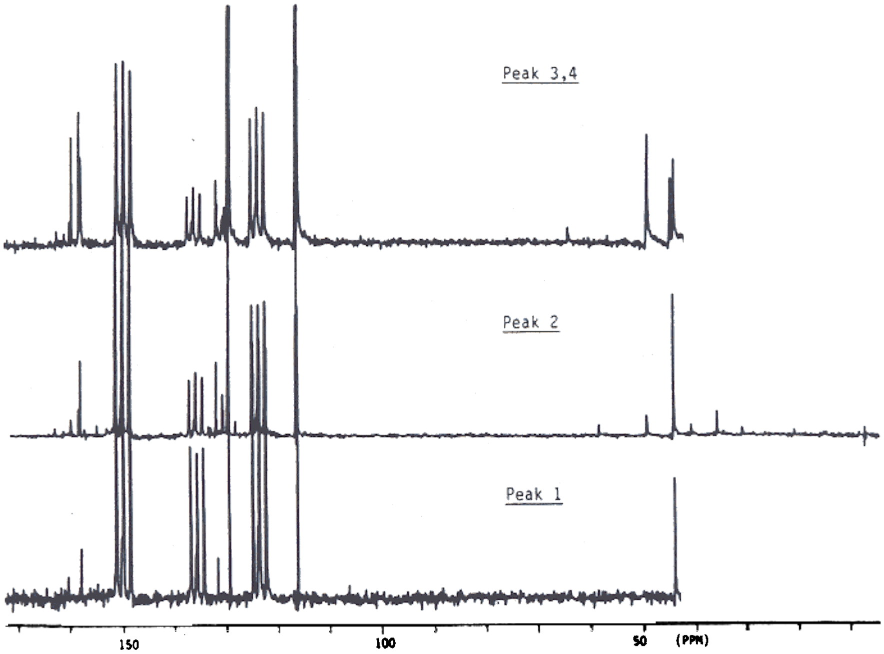


Figure 4. ^{13}C-NMR spectra of isolates by preparative GPC in pyridine-d_5

self-condensates of 4-hydroxybenzyl alcohol. However, strong absorptions between 1640 and 1650 cm^{-1} strongly suggested the presence of amide group.

Figure 4 shows their ^{13}C-NMR spectra measured in pyridine-d_5 solution. The chemical shifts of methylene carbon due to the cocondensation between urea and *p*- or *o*-methylolphenol have been determined with the model experiments.[1,2] The peak 1 was easily identified as 4-hydroxybenzylurea by the appearance of the signal of the cocondensed methylene carbon at 44.2 ppm. Furthermore, the signal at 160.4 ppm indicated the presence of the carbonyl carbon of the monosubstituted urea residue. The substitution of the aliphatic group to urea residue was reported to cause a downfield shift of the carbonyl carbons from urea itself (162.5 ppm in pyridine-d_5).[4,5]

The NMR spectrum of the peak 2 shows also the strong signal at 44.3 ppm as well as the small signals due to the self-condensation of 4-hydroxybenzyl alcohol (35.9 ppm) and other impurities. The structure of *N,N'*-bis(hydroxybenzyl)urea was strongly suggested. In the case of urea–formaldehyde adducts, the chemical shifts of methylene carbons of *N,N'*-dimethylolurea (65.3 ppm) was quite similar with that of monomethylolurea (65.0 ppm).[4] It had been concluded that the chemical shift of the carbon of methylol group is not greatly affected by the second substitution to the other amide group of urea residues. As this result was considered applicable to the substitution of hydroxybenzyl carbon, the signal at 44.3 ppm was assigned to the methylene carbon of *N,N'*-bis(4-hydroxybenzyl)urea. Further the signal at 159.7 ppm indicated the carbonyl carbon of *N,N'*-disubstituted urea residue, because the second substitution causes the downfield shift. Therefore it was concluded that the main component of the peak 2 is *N,N'*-bis(hydroxybenzyl)urea.

The isolates of the peak 3 contained *N,N'*-bis(4-

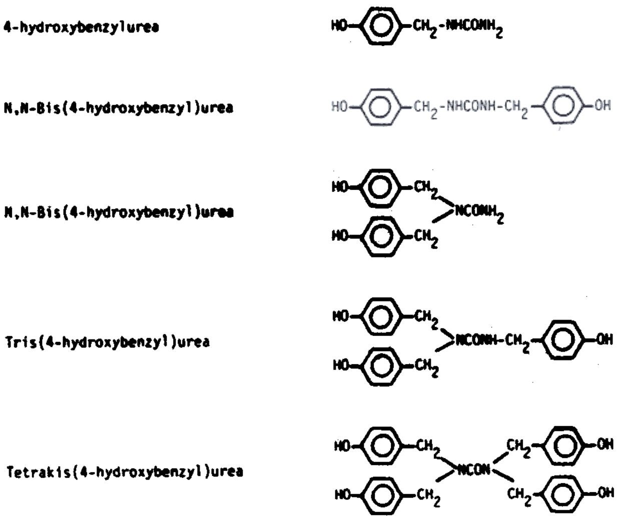


Figure 5. Structures of derivatives from the reaction of 4-hydroxybenzyl alcohol with urea in acidic condition.

Table II. Aliphatic ^{13}C Chemical Shifts (ppm) of Hydroxybenzylureas Obtained from the Reaction of Urea and Methylolphenols[a]

Compound	Methylene Carbon: Monosubstituted to Nitrogen	Methylene Carbon: Disubstituted to to Nitrogen	Carbonyl Carbon of Urea Residue
4-Hydroxybenzyl alcohol	64.7		
4-Hydroxybenzylurea	44.2		160.4
N,*N*^{1}-bis(4-hydroxybenzyl)urea	44.3		159.7
N,*N*-bis(4-hydroxyenzyl)urea		49.1	160.0
Tris(4-hydroxybenzyl)urea	44.7	49.2	159.3
Tetrakis(4-hydroxybenzyl)urea		(49.2)	(159.3)
2-Hydroxybenzyl alcohol	61.1		
2-Hydroxybenzylurea	40.6		161.3
N,*N*^{1}-bis(2-hydroxybenzyl)urea	40.6		160.6
N,*N*-bis(2-hydroxybenzyl)urea	(46.4)		Unknown
Tris(2-hydroxybenzyl)urea	(46.4)		Unknown

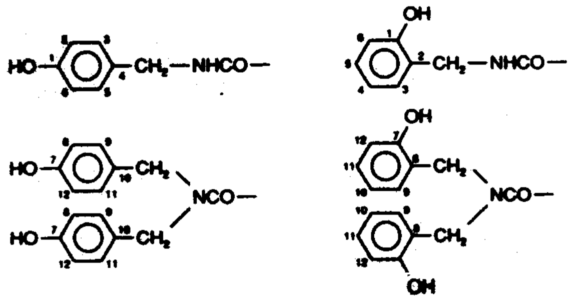
[a] The value in parenthesis is estimated.

hydroxybenzyl)urea as impurity as shown in the upper spectrum of Figure 4. The new signal at 49.2 ppm was observed. It has been determined that the calculated chemical shift of the disubstituted methylene carbon to the same nitrogen atom is 50.3 ppm in the derivatives from 4-hydroxybenzyl alcohol and

Table III. Aromatic ^{13}C Chemical Shifts (ppm) of Hydroxybenzylureas Obtained from the Reaction of Urea and Methylolphenols[a]

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12
4-Hydroxybenzyl alcohol	157.3	115.8	129.1	134.0	129.1	115.8						
4-Hydroxybenzyurea	157.9	116.3	129.5	131.8	129.5	116.3						
N,*N*^{1}-bis(4-hydroxybenzyl)urea	158.0	116.3	129.5	131.8	129.5	116.3						
N,*N*-bis(4-hydroxybenzyl)urea							158.3	116.5	129.6	131.7	129.6	116.5
Tris(4-hydroxybenzyl)urea	157.5	116.0	129.0	131.5	129.0	116.0	157.9	116.3	129.2	131.5	129.2	116.3
Tetrakis(4-hydroxybenzyl)urea												
2-Hydroxybenzyl alcohol	156.1	128.0	129.3	120.3	129.4	116.4						
2-Hydroxybenzylurea	156.2	128.5	130.0	120.3	129.8	116.6						
N,*N*^{1}-bis(2-hydroxybenzyl)urea												
Tris(2-hydroxybenzyl)urea												

[a] Numbering of carbon is as follows:



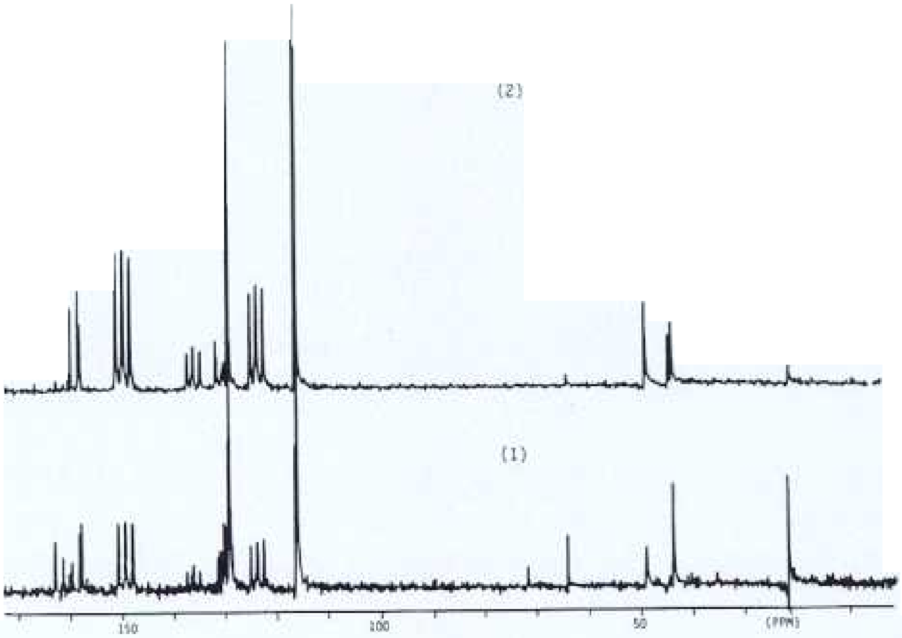


Figure 6. ^{13}C-NMR spectra of (1) the whole reactant and (2) crystal part from *p*-methylolphenol and urea. Reaction condition: PMP/U = 1.0, pH 3.0 (AcOH), 85°C, 5 h.

urea.[1,2] This chemical shift was almost identical with that observed in the present spectrum. Further, this signal was accompanied with that at 44.7 ppm which was assigned to the monosubstituted methylene carbon, as well as with the signal of the carbonyl carbon at 159.3 ppm. From this fact, it was concluded that the main component of the peak 3 was tris(4-hydroxybenzyl)urea.

In the middle spectrum of Figure 4, the small signal corresponding to the disubstituted methylene carbons is observed at 49.1 ppm. This signal, however, was not accompanied with the signal due to the monosubstituted benzyl carbon of tris(4-hydroxybenzyl)urea. Therefore, the presence of *N,N*-bis(4-hydroxybenzyl)urea was strongly suggested in the peak 2.

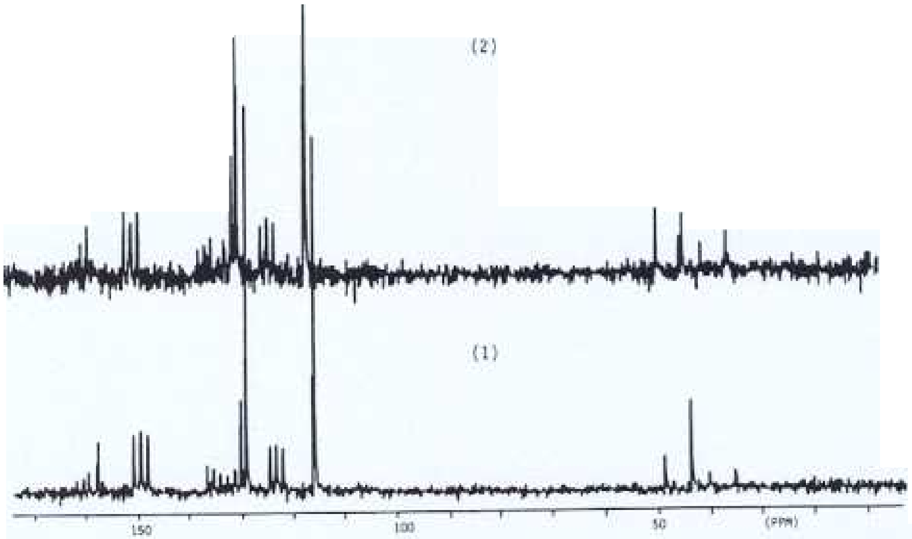


Figure 7. ^{13}C-NMR spectra of the reactants from *p*-methylolphenol and urea under pH 2.0 at 85°C for 30 min: (1) PMP/U = 1.0, (2) PMP/U = 2.0.

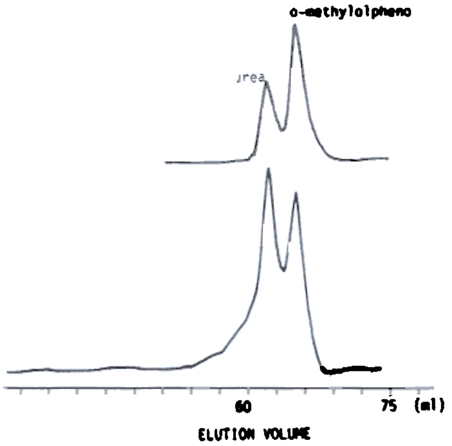


Figure 8. Gel permeation chromatograms of the mixture of urea and *o*-methylolphenol before (1) and after (2) reaction for 400 min under pH 3.0 (AcOH) at 85°C. Molar ratio: OMP/U = 1.

Figure 5 shows the structures of derivatives from the reaction of 4-hydroxybenzyl alcohol with urea in acidic condition.

The results of assignments on these derivatives are listed in Tables II and III including those of aromatic carbons. It is extremely interesting that the formation of these hydroxybenzylureas were recognized in the reaction of urea and *p*-methylolphenol under acidic condition, and that the cocondensation prevailed against the self-condensation of methylolphenol.

Effect of pH and Molar Ratio on Cocondensation

Figure 1 shows the effects of the pH on the reaction of 4-hydroxybenzyl alcohol with urea at the molar ratio of PMP/U = 1. It is obvious that the stronger acidic condition made the reaction time shorter to produce condensates. In the state under pH 2.0, the oily reactant began to separate from the water layer within 10 min, and it was important that the products mainly consisted of hydroxybenzylurea. Figure 6 shows the NMR spectrum of the whole reactant under pH 3 (AcOH), in which the self-condensation of 4-hydroxybenzyl alcohol was entirely negligible because of the absence of the methylene signals at 35.9 ppm (*o,p*-linkage) and 40.5 ppm (*p,p*-linkage).

Figure 2 shows the changes of gel permeation chromatograms of the reactants by the different molar ratio (PMP/U) at the same pH (2.0) and reaction time (30 min). When the molar ratio was below 1.0, only the three peaks identified in the previous section could be recognized. On the other hand, the high molecular-weight part began to be observed in the chromatograms of the reactant at the molar ratio of 2.0 and 4.0. Their GPC patterns, however, were different from that of the novolak synthesized from 4-hydroxybenzyl alcohol at the same condition. Figure 7 shows the NMR spectra of the reactants at PMP/U = 1 and 2, the latter of which the signals due to the self-condensation of 4-hydroxybenzyl alcohol can be observed at around 35 and 40 ppm as well as those due to the cocondensation at around 44 and 49 ppm. Every 4-hydroxybenzylurea shown in Figure 5 has the free *o*-position to react with the other molecule. Therefore the formation of the condensates involving both of the cocondensation and the self-condensation was considered at the higher molar ratio of PMP/U, and the structures in which one urea residue has several novolak-type substituents were proposed.

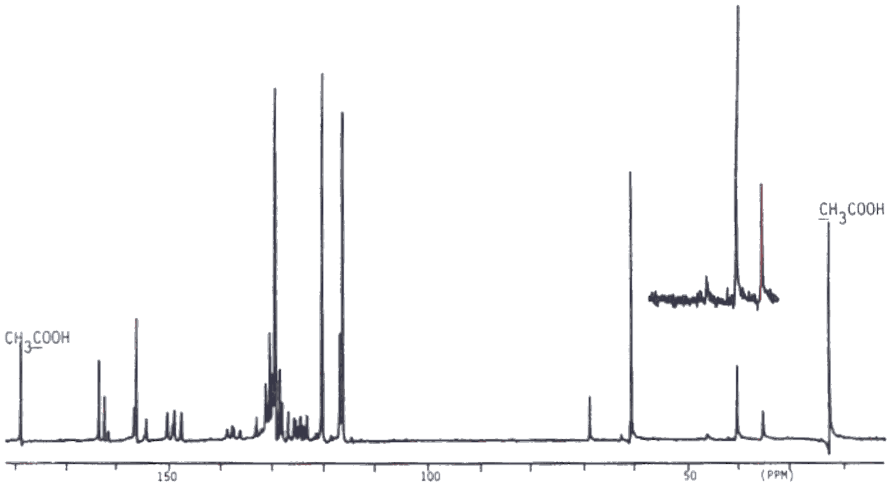


Figure 9. ^{13}C-NMR spectrum of the reactant from urea and *o*-methylolphenol under pH 3.0 (AcOH) at 85°C for 400 min.

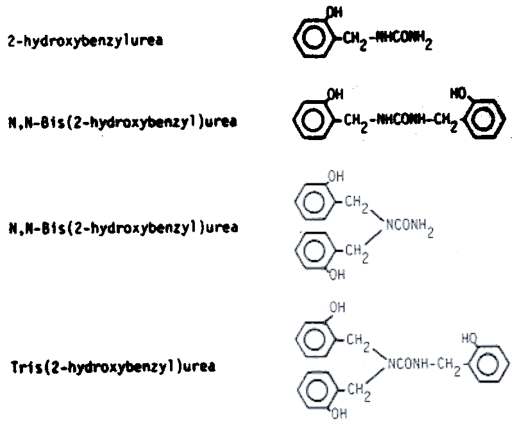


Figure 10. Structures of 2-hydroxybenzylureas.

Reaction of Urea with 2-Hydroxybenzyl Alcohol

Identification of Products

Figure 8 shows the changes of gel permeation chromatogram on the equimolar reaction of urea and 2-hydroxybenzyl alcohol under pH 3.0 (AcOH) at 85°C. Though a large amount of urea still remained unreacted after reacting 400 min, a considerable consumption of 2-hydroxybenzyl alcohol was recognized, and the ^{13}C-NMR spectrum of the reactant showed three signals at 35.8, 40.6, and 46.4 ppm shown in Figure 9. The signal at 35.8 ppm was assigned to the carbon of *o,p*-methylene linkage of the self-condensed novolaks. Though the signal at 40.6 ppm might be assigned to the carbon of *p,p*-methylene linkage in phenolic resins, its formation was easily denied since the model compound had only *o*-methylol group. The chemical shift was identical with the value determined as methylene carbon of 2-hydroxybenzylurea in previous studies.[1,2] Moreover the signal at 161.3 ppm was assigned to the carbonyl carbon of 2-hydroxybenzylurea. The small signal at 160.3 ppm was assigned to the carbonyl carbon of *N,N'*-bis(2-hydroxybenzyl)urea in a similar manner as the assignment of *N,N'*-bis(4-hydroxybenzyl)urea. The methylene carbon of *N,N'*-bis(2-hydroxybenzyl)urea will be overlapped with that of 2-hydroxybenzylurea at 40.6 ppm. The small signal at 46.4 ppm implied the disubstituted methylene carbons to amide group of tris(2-hydroxybenzyl)urea or *N,N*-(2-hydroxylbenzyl)urea. The downfield shift by 5.8 ppm from the monosubstituted methylene carbon (40.6 ppm) was identical with that observed between tris(4-hydroxybenzyl)urea or *N,N*-bis(hydroxybenzyl)urea and 4-hydroxybenzylurea as shown in Table II.

Figure 10 shows the structures of 2-hydroxybenzylureas.

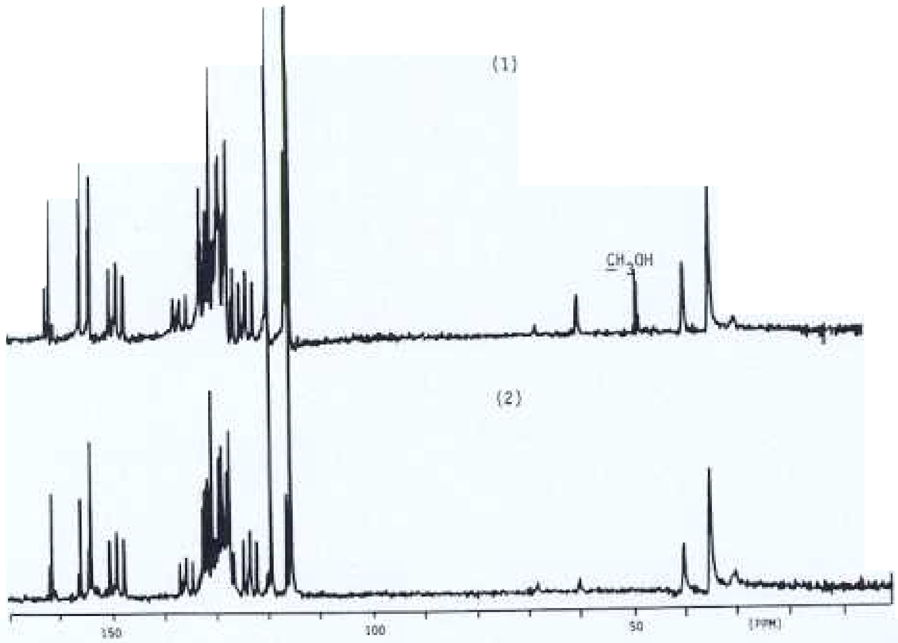


Figure 11. ^{13}C-NMR spectra of the precipitates from the reaction of urea and *o*-methylolphenol. Reaction condition: (1) OMP/U = 0.2, (2) OPM/U = 0.5, pH 2.0, 85°C, 30 min.

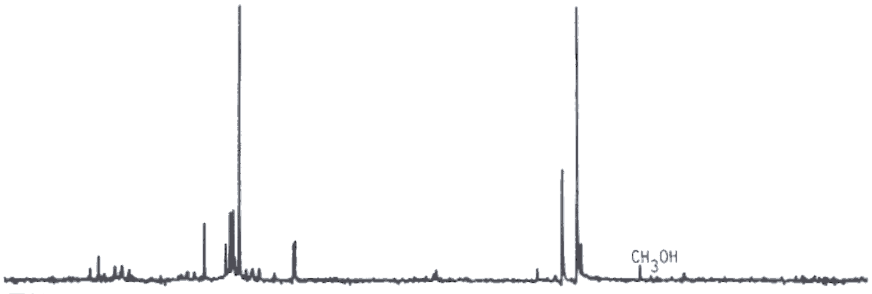


Figure 12. ^{13}C-NMR spectrum of crude 2,4,6-trimethylolphenol after acidification.

Effects of pH and Molar Ratio on Cocondensation

In Figure 9 the signal at 61.1 ppm was easily assigned to the unreacted methylol carbon of 2-hydroxybenzyl alcohol and that at 69 ppm was also assigned to the carbon of dimethylene ether linkage.[5,6] When compared with 4-hydroxybenzyl alcohol (Fig. 6), the cocondensation of 2-hydroxybenzyl alcohol and urea was confirmed to be slow at pH 3.0 (AcOH). Gel permeation chromatography on reactions of the molar ratios OMP/U = 0.2 or 0.5 at a strong acidic condition of pH 2.0 showed that 2-hydroxybenzyl alcohol was completely consumed after reacting from 30 min to form polymeric materials. Figure 11 shows the NMR spectra of the oily materials isolated from both reaction mixtures. The presences of the strong signal at 35.8 ppm due to the *o,p*-methylene carbon and that at around 30 ppm due to the *o,o*-methylene carbon indicated that the self-condensation of 2-hydroxybenzyl alcohol was the main reaction. The intensity of the cocondensed methylene carbon at 40.6 ppm was about half of the self-condensed methylene carbon. The formation of the cocondensed polymer, in which urea residue was grafted by a novolak type substituents, was suggested besides the coexistence of novolaks themselves.

Reaction of Urea with 2,4,6-Trimethylolphenol

According to Freeman,[3] sodium 2,4,6-trimethylolphenate was obtained and its water solution was used as 2,4,6-trimethylolphenol after acidification. Figure 12 shows the ^{13}C-NMR spectrum of the acidified solution, where the presence of self-condensates is almost negligible. Two large signals at 61.7 and 64.6 ppm were easily assigned to the carbons of *o*- and *p*-methylol groups of 2,4,6-trimethylolphenol, respectively.[5,6] The small signal at 61.5 ppm was assigned to the carbon of *o*-methylol group in 2,4-dimethylolphenol.[6] The presences of 2,6-dimethylolphenol and monomethylolphenols in the sample were denied by the NMR spectrum.

When the acidified solution was reacted with urea at the molar ratio of TMP/U = 0.33, the oily products began to separate from water layer after reacting under pH 2.0 at 85°C for 30 min. Its gel permeation chromatogram (Fig. 13) shows the formation of polymeric materials. In the ^{13}C-NMR spectrum (Fig. 14) three signals at 40.5, 44.3, and 49.2 ppm are observed as well as the signal of unreacted *o*-methylol groups at 61.5 ppm. Since the starting materials had quite few free positions available for reaction with a methylol group, the self-condensation by the methylene linkage was almost denied, which was also confirmed by the absence of the signal due to the *o,p*-linkage in the magnetic field of around 36 ppm. Therefore the signal at 40.5 ppm was safely assigned to the cocondensed methylene carbons between *o*-position and urea residue,

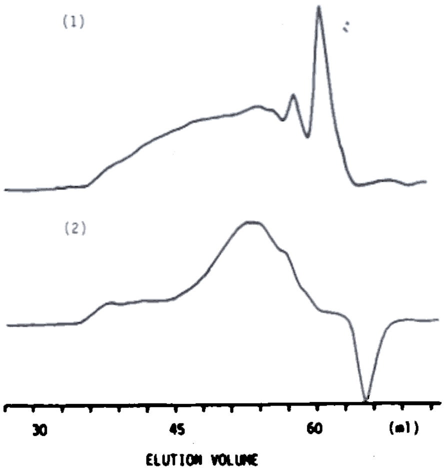


Figure 13. Gel permeation chromatograms of (1) the reactant from urea and trimethylolphenol and (2) oily precipitates. Reaction condition: TMP/U = 0.33, pH 2.0, 85°C, 30 min.

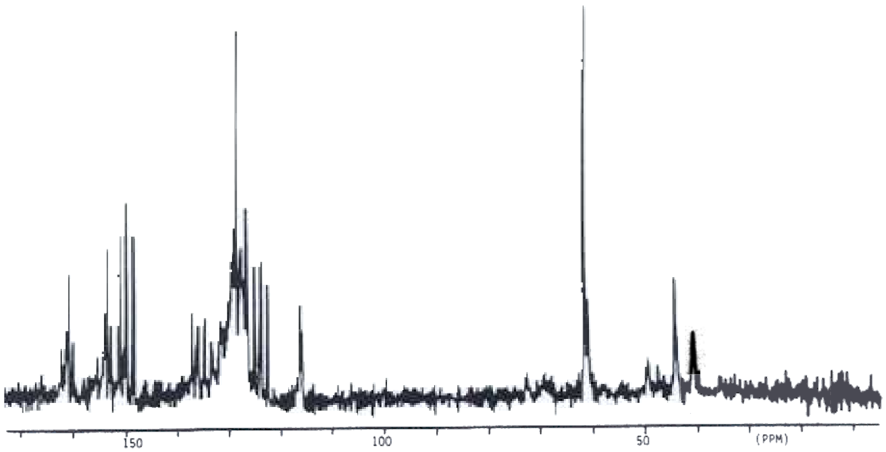


Figure 14. ^{13}C-NMR spectrum of the oily products from the reaction of urea and trimethylolphenol. Reaction condition: TMP/U = 0.33, pH 2.0, 85°C, 30 min.

and that at 44.3 ppm to those between *p*-position and urea residue. Further *N,N*-disubstituted methylene linkage was concluded to form mainly from *p*-methylol group because of the presence of the signal at 49.2 ppm. Therefore no self-condensation of phenols were recognized.

From these results it was proved that this polymer was the alternative copolymer of urea and phenol through methylene linkage like as the structure represented in Figure 15. It is particularly of significance that the alternative copolymer can be synthesized by the simple method under acidic condition.

CONCLUSION

The reaction of urea with methylolphenols under acidic conditions were investigated using 2- and 4-hydroxybenzyl alcohol and crude 2,4,6-trimethylolphenol as model compounds. Several new cocondensed compounds between urea and phenol through methylene linkage have been identified. Furthermore, it should be noted that the alternative copolymer could be synthesized from the reaction of 2,4,6-trimethylolphenol with urea. It was found that the cocondensation between *p*-methylol group and urea is faster than the self-condensation of *p*-methylol even at the low pH (< 3.0), and that *p*-methylol group has the stronger reactivity of urea than *o*-methylol group.

This is the first time that the cocondensation between urea and phenol through formaldehyde has been elucidated completely. We hope that these results will develop not only the new urea/formaldehyde/phenol resin system, but also the chemistry of the whole formaldehyde resins.

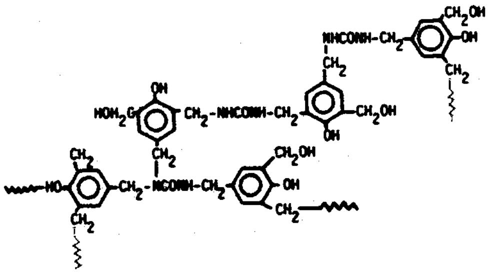


Figure 15. Structure for the alternative copolymer from urea and 2,4,6-trimethylolphenol.

This research was performed under the Research Agreement No. 19-87-076 between Faculty of Agriculture, The University of Tokyo and Southern Forest Experiment Station, USDA Forest Service.

REFERENCES AND NOTES

1. B. Tomita and T. Matsuzaki, *Ind. Eng. Chem. Proc. Res. Dev.*, **24**, 1 (1985).
2. B. Tomita and T. Matsuzaki, *ACS Polym. Prepr.*, **24**(2), 165 (1983).
3. J. H. Freeman, *J. Chem. Soc.*, 6257 (1952).
4. B. Tomita and S. Hotono, *J. Polym. Sci. Polym. Chem. Ed.*, **16**, 2509 (1978).
5. A. J. J. de Breet, W. Dankelman, W. G. B. Huysmans, and J. de Wit, *Angew. Makromol. Chem.*, **62**, 7 (1977).
6. H. Pasch, P. Goetzky, and H. Raubach, *Acta Polym.*, **32**(1), 14 (1981).

Received January 29, 1990
Accepted August 5, 1991