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Synthesis of Phenol-Urea-Formaldehyde Cocondensed Resins from UF-Concentrate and Phenol

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Keywords

Phenol
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Formaldehyde
Cocondensed resins
Resol
C-13 NMR
Structure
GPC

Summary

A new synthetic method to obtain phenol-urea-formaldehyde cocondensed resins was developed by reacting phenol with "UF-concentrate", which is a kind of urea-formaldehyde (UF) resin prepared with a high molar ratio of formaldehyde to urea (F/U) such as above 2.5. The products were analyzed with ^{13}C-NMR spectroscopy and gel permeation chromatography. The ratio of cocondensation and the amount of phenol incorporated into cocondensed resins were found to increase, when the UF-concentrates were prepared under alkaline conditions. It was also found that resol-type cocondensed resins can be synthesized by alkaline treatments of the cocondensed resins which were once prepared under acidic conditions.

Introduction

Phenol- and urea-formaldehyde resins have dominated such areas as the wood adhesives and molding plastic for many years. Phenolic resins (PF) have demonstrated proven performance in producing exterior quality compositions while low-cost urea-formaldehyde resins (UF) have performed well in interior application. Recently, so-called "phenol-formaldehyde-urea resins", which are generally made only by mechanical blending of UF resin and alkaline type PF resins, have been used as adhesives for the manufacturing of wood products. In order to develop practical uses of these resins, it is necessary to introduce cocondensation between phenol and urea at the time of resin preparation.

Our recent work has resulted in isolation of basic cocondensation products of methylolphenols and urea, and succeeded to synthesize an alternating copolymer of urea and phenol through the formation of methylene linkage from the reaction of urea and 2,4,6-trimethylolphenol (Tomita and Hse 1992). Further, the cocondensed resins, containing a small amount of self-condensed units between phenols through methylene or benzylether linkage, have also been synthesized from the reaction of urea and the mixture of methylolphenols (Tomita and Hse 1993). These resins have been named "Resin I".

During the course of the investigation a new method to produce cocondensed resins was discovered. The new method was quite different from the reactions mentioned above (Resin I). The new cocondensed resins named "Resin II" are obtained by reacting phenol with a so-called "UF-concentrate", which is a kind of urea-formaldehyde resin prepared with the higher molar ratio of formaldehyde to urea (F/U) such as above 2.5 under acidic conditions.

It was also found that a resol-type cocondensed resin named "Resin II-2" can be easily synthesized by reacting the cocondensed resins under alkaline conditions as the second step. This paper will discuss the synthesis and structure of these new cocondesed resins.

Experimental

Preparation of UF-concentrate

The calculated amount of 37% formalin (i.e., 973 g or 12 mol in the case of F/U = 3.0) was adjusted at the target level of pH by 50% sulfuric acid or 10% sodium hydroxide, and maintained at 55 °C. Then urea (i.e.,240 g or 4 mol in the case of F/U = 3.0) was added gradually with constant stirring for 15 minutes as follows: addition of urea was equally divided in 15 parts, and each part was added every one minute. After addition of urea, the solution was heated at 80 °C for 60 minutes, and then allowed to stand at room temperature. Several UF-concentrates were synthesized by changing the F/U molar ratio and the reaction pH.

Synthesis of cocondensed resins (Resin II and Resin II-1)

UF-concentrate was adjusted at the target pH level between 2.0 and 4.5, and then phenol was added. The amounts of phenol added were determined by the molar ratio of F/U/P. For example, when the UF-concentrate prepared with F/U = 3.0 (973 g of 37% formalin and 240 g of urea) was used, 418 g of 90% phenol (4 mol) was added at room temperature with stirring. The mixture was adjusted again at the target pH, and maintained at 90 °C for a certain time. Several samples were prepared by changing the pH and reaction time. The resins thus obtained were called "Resin II". When the reaction was performed under a strongly acidic condition for a long reaction time, oily precipitates were produced, which were named as "Resin II-1".

Synthesis of resol-type cocondensed resins (Resin II-2)

The Resin II, including Resin II-1, was generally soluble in alkaline conditions. It was adjusted at pH 9.0–10.5 with sodium hydroxide at room temperature, and heated at 90 °C for 30 minutes with constant stirring. Several samples were prepared by changing the alkaline condition. After these treatments, the resol-type cocondensed resin was obtained, and named "Resin II-2".

^{13}C-NMR measurement

The ^{13}C-NMR spectra of UF-concentrates were measured after dilution with deuterium oxide. The Resin II and Resin II-2 were freeze-dried after neutralization, and dissolved in pyridine-d_5. The Resin II-1 was separated from the water layer, dried in vacuum after washing several times with water, and then dissolved into pyridine-d_5. The quantitative spectra were obtained with FT-80A NMR spectrometer (Varian) or AC-P 300 NMR spectrometer (Bruker) at a pulse delay of 4–10 minutes with the gated decoupling of proton. The chemical shifts were determined by defining the center of three signals of pyridine-d_5 that appeared in the upper magnetic field at 123.6 ppm, while defining internal methanol at 50.0 ppm in D_2O solution. Quantitative date were based on integral values of each peak.

Gel permeation chromatography

Each freeze-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-KD-802 column (Showa Denko Co. Ltd.) was kept at 60 °C in a constant temperature bath. The flow rate of DMF was 1.0 mL/min.

Results and Discussion

Synthesis of UF-concentrate

The ^{13}C-NMR spectrum of the UF-concentrate, which was synthesized with the high molar ratio of F/U = 3.5 under pH 3.0 is shown in Figure 1, in which each signal was easily assigned according to the reported values of chemical shift for urea-formaldehyde resins (de Breet *et al.* 1977; Tomita and Hatono 1978). The signals at around 80–90 ppm due to methylene glycol species indicated the presence of a large amount of free formaldehyde. The signals due to the carbons of all combined formaldehyde appeared at the magnetic field between 45 and 80 ppm, while the carbonyl carbons of urea residues appeared between 150 and 160 ppm. The small signal at around 155 ppm was assigned to the carbonyl carbons of uron ring, the formation of which might be derived from strongly acidic condition (Tomita and Hatono 1978). From the spectrum the quantity of each combined formaldehyde could be normalized and represented as the F/U ratio to the quantity of urea residue by using their integral values.

Four kinds of UF-concentrates were synthesized by changing the molar ratio and reaction pH. They were stored at room temperature for almost one year after synthesizing, and then their ^{13}C-NMR spectra were measured. Table 1 shows the results of quantitative determination of their compositions. It is obvious that the amounts of total combined formaldehyde and chemical composition were similar among the four resins although the synthetic molar ratio of F/U or reaction pH was different. Further, it should be noted that their chemical compositions did not change greatly after storage for one year under strongly acidic conditions. Only the content of free formaldehyde was changed by the difference of synthetic molar ratio. It could be judged from the data that further reaction can not proceed any more even in strongly acidic condition once addition of formaldehyde to urea attains a certain level (F/U = 2.0–2.2). From these results the method to synthesize the cocondensed resins from UF-concentrates and phe-

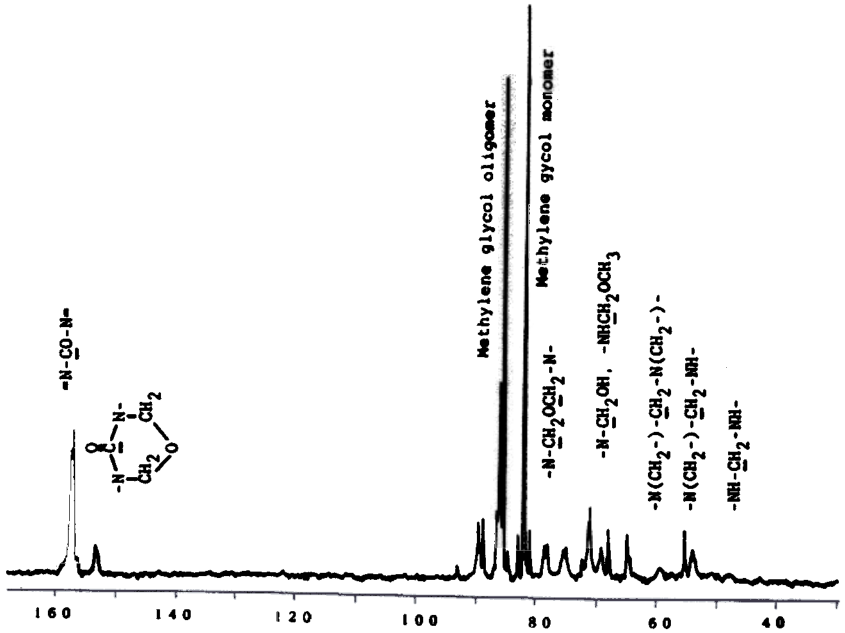

Fig. 1. ^{13}C-NMR spectrum (20 MHz) of UF-concentrate prepared at pH 3.0 with the molar ratio of F/U = 3.5 in D_2O solution.

Table 1. 13C-NMR analysis of structure of UF-concentrates stored for one year after synthesis

Structure	Synthetic condition (pH and molar ratio) pH 1.0 F/U = 3	pH 1.0 F/U = 4	pH 4.8 F/U = 3	pH 4.8 F/U = 4
Methylene linkage	0.63	0.56	0.53	0.66
Dimethylene ether linkage	0.52	0.48	0.44	0.70
Methylol group	0.93	0.94	0.87	0.67
Methylated methylol group	0.10	0.10	0.05	0.00
Free formaldehyde	0.92	2.15	1.22	2.14
Combined formaldehyde	2.20	2.10	2.10	2.00
Total formaldehyde	3.10	4.20	3.10	4.10
Urea residue	1.00	1.00	1.00	1.00
(uron ring)	(0.25)	(0.15)		-

Note: The quantitative values are represented by the molar ratio of F/U.

nol was considered to be effective. It is considered in this method that the self-condensations of UF resins will not take place any more, while cocondensation between methylol groups of UF-concentrate and phenol or self-condensation between phenols will dominate the reaction.

Synthesis and structure of cocondensed resins

Figure 2 shows the ^{13}C-NMR spectrum of a whole product (Resin II) from the reaction of UF-concentrate and phenol under strongly acidic conditions, in which the signals due to cocondensed methylene carbons are clearly observed at around 44 ppm besides those due to free formaldehyde and unreacted phenol (Tomita and Matsuzaki 1985; Tomita and Hse 1992). A longer reaction time resulted in formation of oily precipitates (Resin II-1), which had larger amounts of cocondensed methylene linkage than self-condensations between urea residues or phenolic rings, as shown in Table 2, where chemical

Table 2. ^{13}C-NMR analysis of cocondensed resin synthesized from UF-concentrate and phenol

Structure		Percentage (%) of formaldehyde Resin II-1	Resin II-2
Methylene linkage			
cocondensation	Ph–CH$_2$–N=	66	25
self-condensation	Ph–CH$_2$–Ph	4	9
self-condensation	=N–CH$_2$–N=	3	12
Dimethylene ether linkage			
self-condensation	=N–CH$_2$OCH$_2$–N=	25	6
cocondensation	Ph–CH$_2$OCH$_2$–N=	0	3
Methylol group			
urea residue	=N–CH$_2$OH	2	3
phenol ring	Ph–CH$_2$OH	0	42
Total formaldehyde		100	100

Note: Both resins were synthesized with the molar ratio of F/P/U = 3/1/1. Resin II-1 was the oily precipitate and Resin II-2 was the resol-type resin obtained from Resin I.

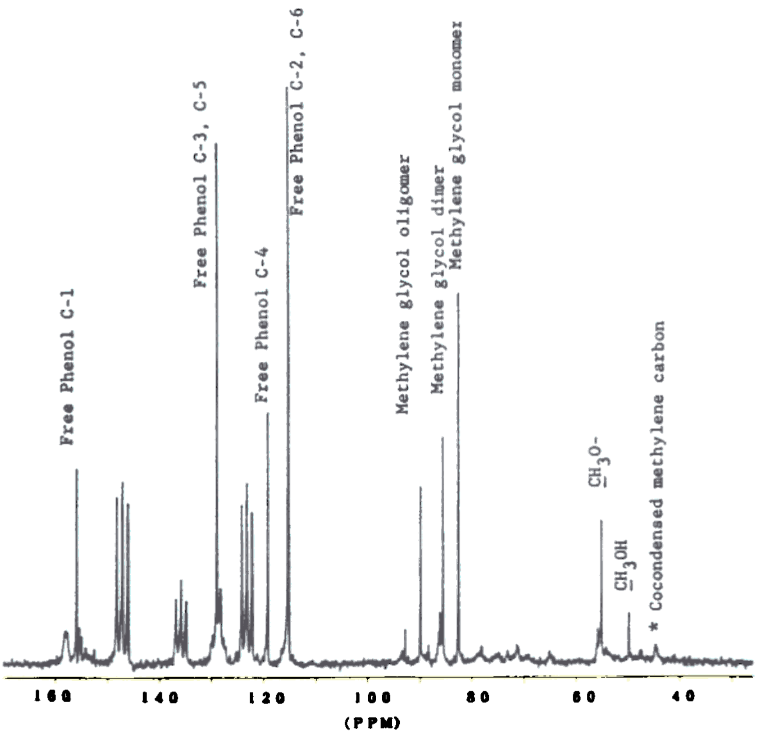

Fig. 2. ^{13}C-NMR spectrum (20 MHz) of phenol-urea-formaldehyde cocondensed resin (Resin II) with the molar ratio of F/U/P = 4.0/1/1 in pyridine-d_5 solution.

shift assignments and quantitative determination were referred to Tomita and Hse 1992. Since it was also shown in Figure 2 that Resin II had a large amount of phenol unreacted as well as free formaldehyde consisting of many kinds of methylene glycol species, the synthesis of resol-type cocondensed resins was attempted by treating under alkaline conditions. The resol-type cocondensed resin (Resin II-2) thus obtained was shown to contain large amounts of phenolic methylol group and methylene linkages in condensation as shown in Table 2, though it had self-condensed units between urea residues or phenolic nuclei to some extents as well as dimethylene ether linkages. It should be noted that this resin can be cured like resol, and that its synthetic method is quite simple for practical application.

Effects of synthetic condition on structure of UF-concentrate

The cocondensed resins (Resin II) and resol-type cocondensed resins (Resin II-2) always contained a considerable amount of self-condensed methylene between urea residues. Most of the self-condensation was considered to take place during the preparation of UF-concentrate. Therefore, if the condensation is reduced to a small extent when UF-concentrate is prepared, the final cocondensed resins will be rich in cocondensed units between urea residues and phenol nuclei. Efforts to find the most suitable condition were attempted by changing pH during the preparation of UF-concentrate while keeping the molar ratio constant at F/U = 3.5. UF-concentrates were generally synthesized by two steps; the first step involved divided additions of urea to formalin under a certain pH at 55 °C and the second step involved heating the mixture at 80 °C. Figures 3 and 4 show gel permeation chromatograms of freeze-dried samples of UF-concentrate prepared under different pH at 80 °C, and reflect the variation of molecular-weight distributions during different reaction times. The mixture obtained by the first reaction at the strongly acidic condition of pH 3.0 indicates a wide molecular-weight distribution as shown in Figure 3, which becomes wider as the reaction time increases. It was confirmed from results of reactions under various pH (pH 3.0, 4.8, 6.8, and 9.0) that decreasing acidity resulted in a narrow molecular-weight distribution and a low average molecular-weight. The UF-concentrates synthesized at the neutral condition of pH 6.8 and the alkaline condition of pH 9.0 seemed to especially contain methylolureas as main components as shown in Figure 4. The ^{13}C-NMR spectra of the same UF-concentrates as analyzed with GPC were also measured. The quantitative data were summarized in Table 3, where the amounts of each combined formaldehyde and free formaldehyde were based on the F/U molar ratio.

It is obvious from Table 3 that the UF-concentrate synthesized under the alkaline condition of pH 9.0 contained quite fewer condensed methylene linkages when compared with those under pH 3.0 and 4.8. Further, the amount of methylol groups increased as the reaction pH became higher, while free formaldehyde decreased. As a result, it was concluded that the alkaline condition was suitable to the synthesis of UF-concentrate used for preparation of the cocondensed resins.

Effects of synthetic condition of UF-concentrate on structure of cocondensed resins

Several cocondensed resins were synthesized by reacting UF-concentrate with phenol under the pH 2.0 for 30 minutes. Three kinds of UF-concentrate differed in pH at preparation were reacted with phenol, where all final molar ratios were kept at F/U/P = 3.5/1/1.

Fig. 3. Gel permeation chromatograms of UF-concentrate during synthesis at pH 3.0 with the molar ratio of F/P/U = 3.5/1/1. Note: Reaction time: (1) 0 min, (2) 15 min, (3) 60 min.

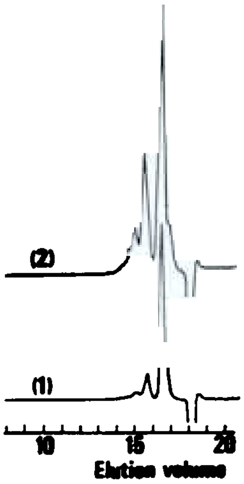

Fig. 4. Gel permeation chromatograms of UF-concentrate during synthesis at pH 9.0 with the molar ratio of F/P/U = 3.5/1/1. Note: Reaction time: (1) 0 min, (2) 30 min.

Table 3. ^{13}C-NMR analysis of structure for UF-concentrate differing in synthetic pH but with the same molar ratio of F/U = 3.5

	Reaction pH		
Structure	3.0		9.0
Methylene linkage	0.34	0.35	0.04
Dimethylene ether linkage	0.66	0.72	1.09
Methylol group	0.45	0.84	1.19
Methylated methylol group	0.14	0.17	0.21
Free formaldehyde	1.88	1.41	0.97
Combined formaldehyde	1.59	2.08	2.53
Total formaldehyde	3.47	3.49	3.50
Urea residue	1.00	1.00	1.00

Note: Quantitative vales are represented by the molar ratio of F/U.

Table 4. ^{13}C-MR analysis of methylene structure for cocondensed resins synthesized from three kinds of UF-concentrate differing in preparation pH but with the same molar ratio of F/P/U = 3.5/1/1

	Preparation pH of UF-concentrate		
Structure	3.0	4.8	9.0
Total self-condensed methylene linkage between urea residues	0.55	0.41	0.19
Total cocondensed methylene linkage between urea and phenol	0.44	0.54	0.62

Note: Quantitative values are represented by F/P or F/U.

The molecular-weight distributions of cocondensed resins were analyzed with GPC. Although the UF-concentrate prepared with the alkaline condition of pH 9.0 was used, the cocondensation seemed to proceed well, and the incorporation of phenol into resins was higher. The structures of these cocondensed resins were also analyzed with ^{13}C-NMR spectroscopy. Table 4 summarizes quantitative data for each structure (Tomita and Hse 1993). When compared among three pH levels in the preparation of UF-concentrate, the alkaline condition resulted in the highest amount (F/U = 0.62) of the cocondensed methylene linkage between urea residues and phenolic nuclei, while it had the lowest amount (F/U = 0.19) of self-condensed methylene linkage between urea residues. The presences of self-condensed methylene linkages between phenol nuclei and phenolic methylol groups were almost negligible. It was concluded that the UF-concentrate prepared under the alkaline state was desirable to obtain resins rich in the cocondensation at the second reaction.

Conclusion

It was found that UF-concentrates were quite stable even if allowed to stand under strongly acidic conditions for a long time such as more than one year. A new method to synthesize the cocondensed resins was attempted by reacting UF-concentrates with phenol under acidic conditions. It was concluded that the main reaction of UF-concentrate with phenol is the cocondensation between them. The cocondensation ratio and the amount of phenol incorporated into cocondensed resins were found to increase when the UF-concentrates were prepared under alkaline conditions. Since the cocondensed resins had a large amount of free formaldehyde and unreacted phenol, it was found that the resol-type cocondensed resins could be synthesized directly by alkaline treatments of the cocondensed resins, which were once prepared under acidic conditions.

It should be noted that resol-type cocondensed resins can be developed by a simple method. Since these resol-type resins can be considered for practical applications such as resol wood adhesives, further developments are encouraged.

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