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^{13}C CP/MAS NMR Study of the Structural Dependence of Urea–Formaldehyde Resins on Formaldehyde-to-Urea Molar Ratios at Different Urea Concentrations and pH Values

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ABSTRACT: Urea–formaldehyde (UF) resins prepared at room temperature from reaction mixtures with four different formaldehyde-to-urea molar ratios (1.00, 1.50, 2.00, and 3.00), three different urea concentrations, and six pH values (1, 3, 5, 7, 9, and 12) were investigated by ^{13}C CP/MAS NMR spectroscopy of 50.3 MHz. The quantitation aspect of obtaining ^{13}C CP/MAS NMR spectra at spinning rates of about 6.5 kHz was examined. The resins prepared under acidic conditions range from a very simple structure to complicated ones, the details depending on the urea concentration, pH value, and formaldehyde-to-urea molar ratio, whereas samples prepared under neutral or basic conditions mainly consist of methylolureas and/or structures with dimethylene ether connections between two urea units. The structural variations that occur in UF resins as the formaldehyde-to-urea molar ratio, concentration, and pH value are varied are discussed in terms of structural trends in these systematically synthesized UF resin systems.

Introduction

Urea–formaldehyde (UF) resins[1] have been widely used as binders in various wood products. The reaction between formaldehyde and urea and the structures of the resins formed have been investigated by various methods.[2] Among these methods, liquid-state ^{1}H NMR spectroscopy[3-9] provides some direct and useful information. Liquid-state ^{13}C NMR studies[10-17] have so far provided the most complete information on the reactions and structures of UF resins that can be dissolved in suitable solvents. However, limitations in the solubility of UF resins, especially cured resins, often preclude the use of liquid-state analytical tools. Therefore, the structures of insoluble fractions and the nature of the curing process of UF resins, which are very important issues concerning the performance characteristics of UF resins, are out of the range of applicability of liquid-state spectroscopy. The reaction conditions that lead to *soluble* UF resins are very limited. Hence, UF resins prepared by a large range of reaction conditions cannot be studied by liquid-state analytical techniques, such as ^{13}C NMR spectroscopy.

The curing process in UF resins has been studied by Raman[18] and IR[19] spectroscopies, differential thermal analysis (DTA),[20] and X-ray diffraction.[21] However, the information obtained by these methods on the curing process and especially on the structures of the UF resins in later stages of curing has been limited in chemical structural detail. The high-resolution solid-state ^{13}C NMR technique that consists of the combination of cross polarization[22] with high-power ^{1}H decoupling and magic-angle spinning[23] (^{13}C CP/MAS)[24] is a powerful technique for overcoming the "conventional" liquid-state limitation of ^{13}C NMR spectroscopy. The high-resolution solid-state ^{13}C NMR approach eliminates structural uncertainties associated with employing the dissolution process together with liquid-sample techniques; therefore, it provides an ideal tool for studying the curing process and the detailed structures of UF resins, as evidenced in the previous work of this laboratory.[25] The UF resin system has also been studied by ^{15}N CP/MAS NMR spectroscopy,[26] although the information obtained by this approach has been less detailed than that provided by ^{13}C CP/MAS experiments in the particular samples studied. In the present paper, we describe a detailed ^{13}C CP/MAS NMR study of chemical structure in UF resin systems.

Urea has four N–H sites available for interaction with formaldehyde, which in turn has two atomic sites available in the carbonyl group for interaction; therefore, the reaction products between urea and formaldehyde can range from the very simple one, monomethylolurea, $H_2NC(O)NHCH_2OH$, to very complicated, widely cross-linked three-dimensional products. The factors[1] that affect the composition of products include the concentrations of the main reaction components (formaldehyde and urea), pH, temperature, duration of reaction, and the identities and concentrations of any other relevant substances (e.g., catalysts) present in the reaction mixtures. In a complicated UF resin system, a large variety of functional groups can coexist with each other and the composition in a reaction mixture presumably can be changed by varying the parameters mentioned above.

Studies of the structures of UF resin systems in the past had been largely fragmentary, and a more systematic approach seemed to be warranted. In this paper, we focus on the effects of urea concentration, formaldehyde-to-urea molar ratio, and pH on the structures of UF resins. Most of the reactions were carried out at room temperature (23 ± 2 °C), except for a few cases in which the control of temperature was difficult within the short time period of a rapidly exothermeric reaction. The curing of UF resins was carried out over a wide range of temperatures, from room temperature to about 150 °C. Ambient-, medium-, or high-temperature curing are known to produce resins with different properties,[1b] and we intend to employ ^{13}C CP/MAS NMR spectroscopy for investigating the causes of these differences. This room-temperature study is the first step toward that goal. Furthermore, the end use of UF resins is typically at room temperature; therefore, the possibility of further interactions within UF resins at room temperature, including curing and degradation, should be well-understood in order to provide improved UF resin service.

In the present study, urea and formalin were used as the organic starting materials. *N,N'*-dimethylolurea and paraformaldehyde can provide similar chemical functionalities (as a source of methylols and various linkages) to that of 37% formalin in the syntheses of UF resins; the

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structural consequences of using these two reactants as starting materials are described separately.[27]

Experimental Section

1. **Samples.** Reactions between 37% formalin (Fischer Scientific, certified ACS, containing 8% methanol and 55% water) and urea (Mallinckrodt, analytical grade) were carried out at six different pH values (1, 3, 5, 7, 9, and 12) and four different formaldehyde-to-urea (F/U) molar ratios 1.00/1.00, 1.50/1.00, 2.00/1.00, and 3.00/1.00. The desired pH values were attained by employing aqueous phosphoric acid or sodium hydroxide solutions. Buffer solutions were not used in order to avoid the possible involvements of the conjugate acid-base species of a buffer. However, the pH values were monitored during the course of reaction; trends with pH change were easy to follow. The common UF curing agents, ammonium chloride and ammonia, were avoided in the present study because of the possible formation of very complicated UF resin networks with these agents.[12,28] In addition, the involvement of ammonium chloride can cause a drop in the pH value substantially during the course of reaction.

The formaldehyde/urea/water (F/U/W) molar ratios employed for the reaction mixtures studied at six different pH's were 1.00/1.00/2.48, 1.00/1.00/12.5, 1.00/1.00/105, 1.50/1.00/3.72, 1.50/1.00/20.3, 1.50/1.00/105, 2.00/1.00/4.96, 2.00/1.00/25.0, 2.00/1.00/107, 3.00/1.00/7.44, 3.00/1.00/23.6, and 3.00/1.00/105. (One more F/U/W molar ratio, 2.00/1.00/44.6, at pH 3, and one more F/U/W molar ratio, 2.00/1.00/175, at pH 5, were also employed to synthesize UF resins.) All the reactions were started at room temperature (23 ± 2 °C) without any control of reaction temperature thereafter; pertinent details of temperature changes during the reaction are described in the Results and Discussion.

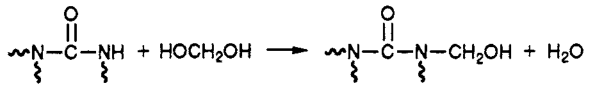
Except for a few cases noted explicitly in the text below, the reaction conditions were maintained for 12 h; after the 12-h period, the resulting reaction mixtures were subjected to the specific treatments described here and in the Results and Discussion. If there was any separable liquid in a reaction mixture, it was removed and the remaining precipitate portion, without neutralization, was spread out on a watch glass for drying. The liquid portions were not investigated systematically in this study; however, some of the liquid portions were vacuum dried at −5 °C to produce solid samples suitable for ^{13}C CP/MAS studies, as described in the Results and Discussion. In some cases, the reaction mixture remained a clear solution even after 12 h of reaction; such mixtures were vacuum dried at −5 °C to produce solid samples for ^{13}C CP/MAS studies. As mentioned in the Introduction, the end use of UF resins is at room temperature without neutralization to pH 7, corresponding closely to the post-reaction treatments used in the study reported here. The results of other treatments and their effects on the structures of the resulting UF resins will be described elsewhere.[28] Model compounds, methylenediurea ($NH_2C(O)NHCH_2NHC(O)NH_2$), and dimethylolurea dimethyl ether ($CH_3OCH_2NHC(O)NHCH_2OCH_3$), were synthesized by the procedures described by Ludlam.[29]

2. **NMR Measurements.** ^{13}C CP/MAS NMR spectra were obtained at 50.3 MHz on a home-modified Nicolet NT-200 spectrometer. At this field of 4.7 T, the nuclear electric quadrupole effect[30-36] of ^{14}N is sufficiently quenched to render enough ^{13}C resolution of adjacent carbons for accurate peak assignments and intensities. Most spectra were obtained with a 1-ms contact time and a 1-s repetition time, except for some variable-contact-time experiments described in the Results and Discussion. Spectra of resins were also taken with the interrupted-decoupling (dipolar-dephasing) CP/MAS technique[37] with a 50-μs interrupted-decoupling period. Peak positions were determined relative to liquid tetramethylsilane (TMS) by sample substitution. Peak intensities (integrated areas) were determined by deconvoluting the spectra. Although for some severely overlapping peaks there are substantial uncertainties associated with deconvolution, useful trends can nevertheless be extracted for each series of UF resin samples.

For all of the UF resin samples studied, MAS speeds of about 6.5 kHz provide spectra with spinning sidebands outside the centerband region of resin signals. For some sticky resin samples there was a tendency in long-term 6.5-kHz MAS experiments for the sample to push out the cap of the spinner. For such cases the samples were spun at about 3.2 kHz or at two different spinning rates near 3.2 kHz to avoid ambiguity of spinning sidebands. For some samples on which CP/MAS experiments were carried out at 6.5 kHz, CP/MAS experiments were also carried out at 3.2 kHz to study the possible effects of spinning rates on the spectra.[38]

Results and Discussion

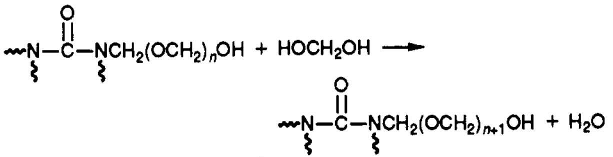
1. **Overview of Reaction Mechanisms.** The first step leading to formation of a UF polymer is believed to be the methylolation of the amide group of urea:



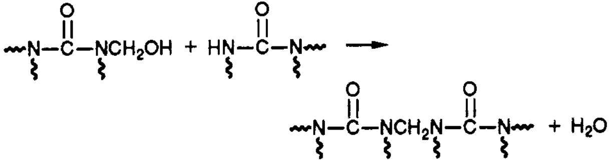
$$\sim\underset{\wr}{N}-\overset{O}{\overset{\|}{C}}-\underset{\wr}{N}H + HOCH_2OH \longrightarrow \sim\underset{\wr}{N}-\overset{O}{\overset{\|}{C}}-\underset{\wr}{N}-CH_2OH + H_2O \qquad (1)$$

This methylolation reaction is catalyzed[1] by both acids and bases. The heat of reaction is about −5 kcal/mol[39] (of $-CH_2OH$ formed) for both the formation of monomethylolurea ($NH_2C(O)NHCH_2OH$) and *N,N′*-dimethylolurea ($HOCH_2NHC(O)NHCH_2OH$). The methylolation reaction is reversible, which partly explains the liberation of formaldehyde from UF resin products.[40] The effect of the presence of methanol in the reaction mixture is a marked decrease in the reaction rate of methylolation;[41] however, this retardation works in both directions of eq 1.

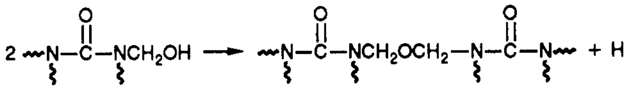
Methylol groups can undergo the following reactions,[1] in addition to the reverse reaction of eq 1:



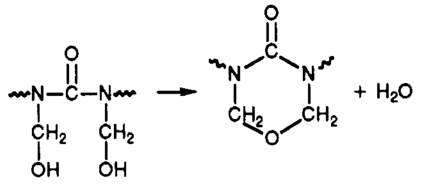
$$\sim\underset{\wr}{N}-\overset{O}{\overset{\|}{C}}-\underset{\wr}{N}CH_2(OCH_2)_nOH + HOCH_2OH \longrightarrow \sim\underset{\wr}{N}-\overset{O}{\overset{\|}{C}}-\underset{\wr}{N}CH_2(OCH_2)_{n+1}OH + H_2O \qquad (2)$$



$$\sim\underset{\wr}{N}-\overset{O}{\overset{\|}{C}}-\underset{\wr}{N}CH_2OH + H\underset{\wr}{N}-\overset{O}{\overset{\|}{C}}-\underset{\wr}{N}\sim \longrightarrow \sim\underset{\wr}{N}-\overset{O}{\overset{\|}{C}}-\underset{\wr}{N}CH_2\underset{\wr}{N}-\overset{O}{\overset{\|}{C}}-\underset{\wr}{N}\sim + H_2O \qquad (3)$$



$$2\sim\underset{\wr}{N}-\overset{O}{\overset{\|}{C}}-\underset{\wr}{N}CH_2OH \longrightarrow \sim\underset{\wr}{N}-\overset{O}{\overset{\|}{C}}-\underset{\wr}{N}CH_2OCH_2-\underset{\wr}{N}-\overset{O}{\overset{\|}{C}}-\underset{\wr}{N}\sim + H_2O \qquad (4)$$



(5)

The formation of methylene linkages according to eq 3 is catalyzed by acids, but not bases.[1] The formation of uron expressed in eq 5 has been confirmed by liquid-state ^{13}C NMR studies.[12-14]

2. **Overview of Thermal, pH, and Solubility Behaviors.** The solubility of *N,N′*-dimethylolurea in neutral or alkaline aqueous solution is about 12 g/100 g at room temperature; therefore, the appearance of cloudiness in a reaction mixture of formalin and urea without added water at pH 7 and 9 roughly indicates the formation of *N,N′*-dimethylolurea in excess of this solubility limit. For the reaction between 37% formalin and urea without added water at pH 12, the appearance of cloudiness takes about 10 min for the four F/U molar ratios, 1.00, 1.50, 2.00, and 3.00. It takes more than 90 min for cloudiness to appear in samples prepared with the same four F/U molar ratios

at pH = 9 and more than 5 h for samples prepared from 37% formalin and urea with F/U molar ratios of 1.00, 1.50, and 2.00 at pH 7. A sample prepared at pH 7 from 37% formalin and urea with a F/U molar ratio of 3.00 remained a clear solution even after 12 h of reaction. For the reaction between 37% formalin, urea, and added water with F/U/W molar ratios of 1.00/1.00/12.5, 1.50/1.00/20.3, 2.00/1.00/25.0, and 3.00/1.00/23.6, the appearance of cloudiness at pH 12 occurs after about 2 h, whereas all the reaction mixtures with these molar ratios at pH 9 and pH 7 are still clear solutions after 12 h of reaction. All the reaction mixtures with F/U/W molar ratios of 1.00/1.00/105, 1.50/1.00/105, 2.00/1.00/107, and 3.00/1.00/105 at the three pH values, 7, 9, and 12, are clear solutions after 12 h of reaction, as expected, because all the methylolureas that may be formed should dissolve at these concentrations, as long as there are few, if any, linkages formed between urea units. Such linkage formation at pH 7 and 9 presumably proceeds very slowly at room temperature, if it happens at all, as indicated by the ^{13}C CP/MAS results discussed in a later part of this article.

The times at which cloudiness appears indicate qualitatively that the expected rates of formation of methylol groups are higher at pH 9 and lower at pH 7 for the two pH values, 7 and 9, and that the rates of formation of methylols are reduced by dilution. The reaction between 37% formalin and urea at pH 12 at four different F/U molar ratios of 1.00, 1.50, 2.00, and 3.00 without any added water is noticeably exothermic. The highest temperature attained in these reaction mixtures was 34 °C; however, the reaction temperature quickly and spontaneously returned to room temperature without any external action.

The pH values of the reaction mixtures were adjusted to the desired values after mixing the formalin and urea, and the pH value was found to remain almost invariant over 12 h of reaction for the cases in which the pH value was set initially at 12 and 7. For some of the cases initially at pH 9, a pH drop to 8.5 was observed after 12 h of reaction.

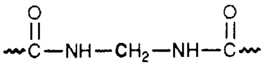
The appearance of cloudiness in the reaction mixtures obtained under acidic conditions can be attributed to the formation of methylol groups or the formation of linkages between urea units, as described in eqs 3 and 4. The ^{13}C CP/MAS results described below indicate that these linkages consist mainly of methylene linkages. Although it may be difficult to attribute the cause of cloudiness unambiguously in this manner for the concentrated reaction mixtures, it is more straightforward to attribute the appearance of cloudiness to the formation of linkages in the reaction mixtures with F/U/W molar ratios of 1.00/1.00/105, 1.50/1.00/105, 2.00/1.00/107, and 3.00/1.00/105, because the mono- and dimethylolureas without linkages to other urea units are soluble at these concentrations. The times of appearance of cloudiness in the reaction mixtures of these four F/U/W molar ratios are about 2 min at pH 1, 80 min at pH 3, and 6 h at pH 5. In each case the temperature during the 12 h of reaction period did not deviate significantly from room temperature (23 ± 2 °C). These rough measures of the time of appearance of cloudiness agree (qualitatively) with the idea of acid-catalyzed formation of methylene linkage according to eq 3.[1,27]

The reaction between 37% formalin and urea without added water at pH = 1 and at four different F/U molar ratios usually occurs vigorously, with the temperature rapidly rising to about 75 °C, and the whole reaction mixture becomes solidified within 2 min. (An exception to this solidification behavior is the case with the F/U molar ratio of 3.00/1.00.) It takes longer, about 10–20 min, for the sample to solidify at pH 3. More than 1 h is required before the appearance of cloudiness, and with no appreciable temperature change, for the cases at pH 5. Over a 12-h reaction period under acidic conditions for the *concentrated* reaction mixtures, i.e., 37% formalin and urea without any added water, pH changes were observed, e.g., from pH 5 to pH 4, or from pH 3 to pH 2.5. For the more dilute reaction mixtures, the pH changes are minor over a 12-h reaction period. For UF samples prepared under acidic conditions, the subsequent hydrolysis at 100 °C[42] resulted in pH increases, the extent of the observed pH increase depending on details of the procedure.

3. Chemical Shift Summary. For the convenience of the reader, there follows here a summary of ^{13}C NMR chemical shifts of some possible or likely structural fragments in urea–formaldehyde resins. The chemical shift values are based on liquid-state ^{13}C NMR results of model compounds and soluble urea–formaldehyde resins,[10–17] ^{13}C CP/MAS NMR studies on *N,N'*-dimethylolurea and UF resins,[25] and ^{13}C CP/MAS NMR studies of the model compounds, dimethylolurea dimethyl ether and methylenediurea. Due to the extensive chemical shift dispersion associated with amorphous solids, as discussed later, the chemical shifts are expressed here to the nearest ppm. Values are given in ppm to lower shielding than TMS. The carbon position having the indicated chemical shift is shown in boldface type.

A. $>N—CH_2—N<$ methylene linkages:

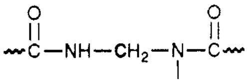
(1) connecting two secondary amides:



$\sim C(=O)—NH—CH_2—NH—C(=O)\sim$

(I) 47 ppm

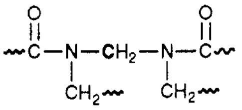
(2) connecting a secondary amide and a tertiary amide:



$\sim C(=O)—NH—CH_2—N(CH_2\sim)—C(=O)\sim$

(II) 54 ppm

(3) connecting two tertiary amides:

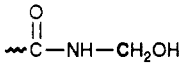


$\sim C(=O)—N(CH_2\sim)—CH_2—N(CH_2\sim)—C(=O)\sim$

(III) 60 ppm

B. $>N—CH_2OH$ methylol groups:

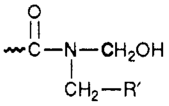
(1) attached to a secondary amide:



$\sim C(=O)—NH—CH_2OH$

(IV) 65 ppm

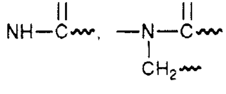
(2) single methylol group attached to a tertiary amide:



$\sim C(=O)—N(CH_2—R')—CH_2OH$

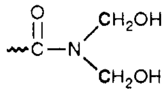
(Va) 72 ppm

where R′ is



$NH—C(=O)\sim$, $—N(CH_2\sim)—C(=O)\sim$, or $OCH_2\sim$

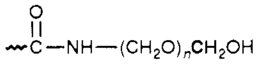
(3) *N,N*-dimethylol groups:



$\sim C(=O)—N(CH_2OH)_2$

(Vb) 72 ppm

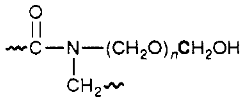
C. $-OCH_2OH$ groups of hemiformals:



$\sim C(=O)—NH—(CH_2O)_nCH_2OH$

(VIa) 87 ppm

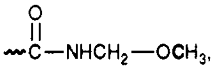
or



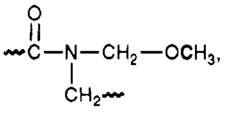
$\sim C(=O)—N(CH_2\sim)—(CH_2O)_nCH_2OH$

(VIb) 87 ppm

D. Methoxy groups of methylene methyl ethers:

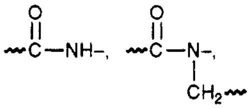

$\sim\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{NHCH_2{-}OCH_3}$,

(VIIa) 55 ppm


$\sim\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\underset{\underset{\mathrm{CH_2}\sim}{|}}{\mathrm{N}}-\mathrm{CH_2{-}OCH_3}$, or $\mathrm{R''(OCH_2)_{\mathit{n}}OCH_3}$

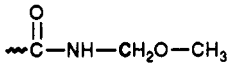
(VIIb) 55 ppm (VIIc) 55 ppm

where R″ is H–,

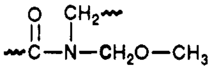

$\sim\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{NH}-$, $\sim\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\underset{\underset{\mathrm{CH_2}\sim}{|}}{\mathrm{N}}-$,

or $\mathrm{H_3C}-$

E. >N—CH2OCH3 methylene ether groups:


$\sim\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{NH{-}CH_2O{-}CH_3}$ or

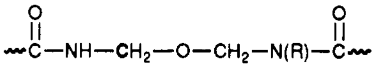
(VIII) 73 ppm


$\sim\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\overset{\overset{\mathrm{CH_2}\sim}{|}}{\mathrm{N}}-\mathrm{CH_2O{-}CH_3}$

(IX) 80 ppm

F. >N—CH2OCH2—N< dimethylene ether groups:

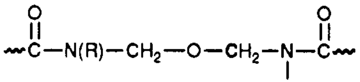
(1) attached to secondary amide(s):


$\sim\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{NH{-}CH_2{-}O{-}CH_2{-}N(R)}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\sim$

(X) 69 ppm

where R is H or $-\mathrm{CH_2}\sim$

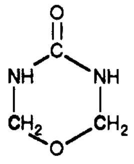
(2) attached to tertiary amide(s):


$\sim\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{N(R){-}CH_2{-}O{-}CH_2}-\underset{\underset{\mathrm{CH_2}\sim}{|}}{\mathrm{N}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\sim$

where R is H or $-\mathrm{CH_2}\sim$

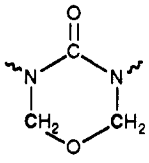
(XI) 76 ppm

(3) in unsubstituted uron:



(XII) 75 ppm

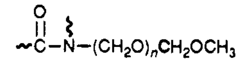
(4) in disubstituted urons:



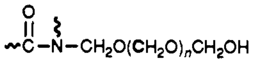
(XIII) 79 ppm

G. Methylene glycol, poly(oxymethylene glycols) and hemiformals, and their methyl ethers:

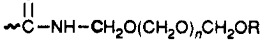
$\mathrm{HOCH_2OH}$	$\mathrm{HOCH_2{-}O{-}CH_2OH}$	$\mathrm{HOCH_2O(CH_2O)_{\mathit{n}}CH_2OH}$
(XIV) 83 ppm	(XV) 87 ppm	(XVIa) 87 ppm
$\mathrm{HOCH_2OCH_3}$	$\mathrm{H(CH_2O)_{\mathit{n}}CH_2OCH_3}$	$\mathrm{HOCH_2O(CH_2O)_{\mathit{n}}CH_2OH}$
(XVII) 91 ppm	(XVIIIa) 94 ppm	(XVIb) 88–92 ppm


$\sim\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\overset{\wr}{\mathrm{N}}-\mathrm{(CH_2O)_{\mathit{n}}CH_2OCH_3}$

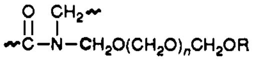
(XVIIIb) 94 ppm


$\sim\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\overset{\wr}{\mathrm{N}}-\mathrm{CH_2O(CH_2O)_{\mathit{n}}CH_2OH}$

(XVIc) 88–92 ppm


$\sim\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{NH{-}CH_2O(CH_2O)_{\mathit{n}}CH_2OR}$

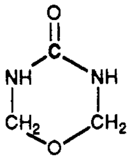
(XVId) 69 ppm
(R = H or $\mathrm{CH_3}$)


$\sim\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\overset{\overset{\mathrm{CH_2}\sim}{|}}{\mathrm{N}}-\mathrm{CH_2O(CH_2O)_{\mathit{n}}CH_2OR}$

(XVIe) 76 ppm
(R = H or $\mathrm{CH_3}$)

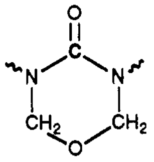
H. >N—C(O)—N< carbonyl groups:

(1) in unsubstituted uron:



(XIX) 157 ppm

(2) in disubstituted urons:



(XX) 156 ppm

(3) various other N-attached carbonyls: 155–169 ppm

4. Overview of ^{13}C NMR Properties. Before addressing details of the ^{13}C CP/MAS NMR analysis of UF resins, we present some useful guidelines for these analyses. In most cases, the signals corresponding to carbonyl carbons appear at about 160 ppm without any fine structure. Therefore, in contrast to the liquid-state ^{13}C NMR case,[10–17] the spectral region around 160 ppm does not usually provide a good diagnostic tool for the determination of environments around various carbonyl groups. Figure 1 shows some of the exceptions to this general statement. Figure 1a is the ^{13}C CP/MAS spectrum of a UF resin prepared from a mixture with a F/U/W molar ratio of 1.50/1.00/3.72 at pH 9. For Figure 1 and subsequent figures the pH value of the reaction mixture is represented in parentheses, e.g., 1.50/1.00/3.72 (9) for Figure 1a. This spectrum looks almost identical to the ^{13}C CP/MAS NMR spectrum of *N,N′*-dimethylolurea.[25] The splittings seen in the signals at about 160 and 65 ppm are due to the residual quadrupolar effect of ^{14}N on the ^{13}C spectra via the ^{14}N–^{13}C dipolar interaction; this effect has been studied from the theoretical as well as experimental points of view.[30–36] Figure 1b shows the analogous ^{14}N quadrupolar effect on the ^{13}C CP/MAS spectrum of the model compound, methylenediurea. The spectrum of dimethylolurea dimethyl ether (not shown here) has a similar splitting. The splitting due to the ^{14}N quadrupolar effect typically can be observed only in the spectra of simple systems, such as *N,N′*-dimethylolurea, methylenediurea, and dimethylolurea dimethyl ether. In a complex polymer, such as a UF resin, the chemical shift dispersion due to heterogeneity in chain length, cross-linking, and conformation enhances the line width to such an extent that the splittings are eclipsed.

Figure 1c shows the ^{13}C CP/MAS NMR spectrum of a UF resin prepared from a mixture with a F/U/W molar ratio of 3.00/1.00/105 at pH 1, room temperature, and 12 h of reaction. The solid sample was obtained by vacuum drying the entire reaction mixture at −5 °C for 30 h. This case is an apparent example of the existence of disubstituted urons (XIII, 79 ppm; XX, 156 ppm). The peak around 156 ppm[12–14] is attributed to the carbonyl groups of disubstituted urons (XX); usually it is accompanied by a peak with twicee its intensity at about 79 ppm,[12–14] which is attributed to the dimethylene ether linkages (XIII) in the rings of disubstituted urons. The unsubstituted uron has ^{13}C NMR signals at about 157 ppm[12–14] for the carbonyl carbon (XIX) and 75 ppm[12–14] for the dimethylene ether $\mathrm{CH_2}$ carbons (XII). In the discussion below, these patterns prove to be helpful for establishing the existence of urons in some UF resins.

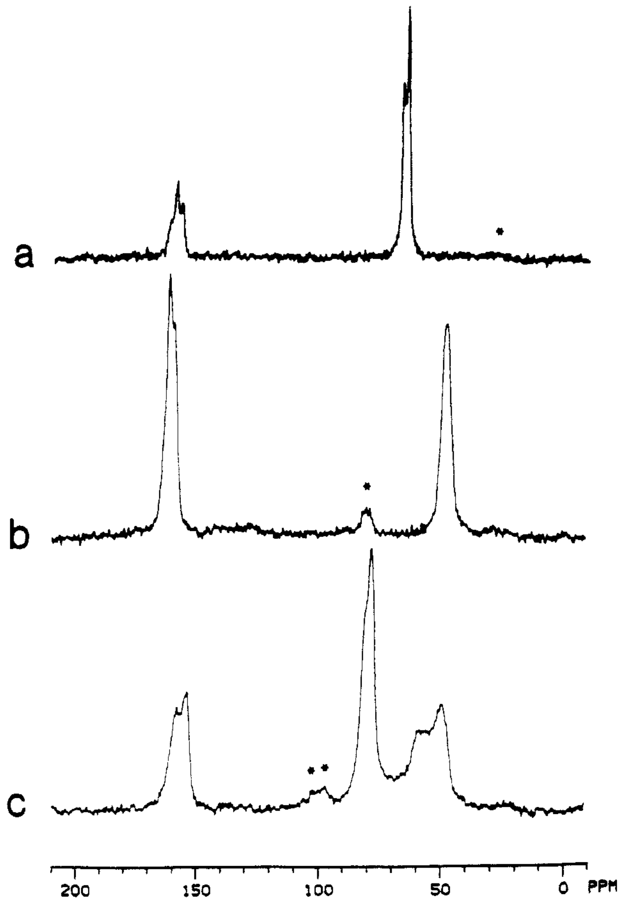


Figure 1. 50.3-MHz ^{13}C CP/MAS NMR spectra of three UF resin samples: (a) sample prepared at pH 9 from a mixture with a F/U molar ratio of 1.50 from 37% formalin and urea without adding water; (b) methylenediurea; (c) sample obtained by vacuum drying of the entire reaction mixture with a F/U/W molar ratio of 3.00/1.00/105 after 12 h of reaction at pH 1. Contact time = 1 ms; repetition time = 1 s. Spinning sidebands are indicated by asterisks.

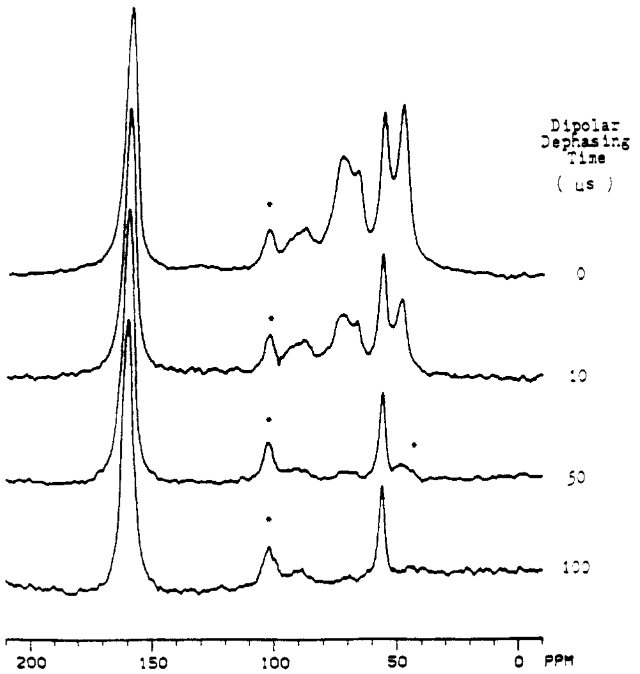


Figure 2. 50.3-MHz ^{13}C CP/MAS NMR spectra of a UF resin sample prepared at pH 5 from a mixture with a F/U molar ratio of 2.00 from 37% formalin and urea without adding water. Contact time = 1 ms; repetition time = 1 s; dipolar dephasing time (interrupted decoupling periods) as shown. Spinning sidebands are indicated by asterisks.

Figure 2 shows the interrupted-decoupling ^{13}C CP/MAS NMR spectra obtained on a UF resin prepared at pH 5 from a mixture with a F/U/W molar ratio of 2.00/1.00/4.96. The spectra were obtained with interrupted-decoupling periods of 0, 10, 50, and 100 μs, a 1-ms contact time, and a 1-s repetition time. During the interrupted-decoupling period, ^1H–^{13}C dipolar interactions cause dephasing of the ^{13}C magnetization vectors; the weaker the dipolar interactions, the less the dephasing. Therefore, the magnetization of a ^{13}C nucleus without one or more directly attached protons or a ^{13}C nucleus attached to protons in a rapidly rotating moiety, such as $-CH_3$, can survive an interrupted-decoupling period of 50 μs quite well. Judging from Figure 2, the peak around 160 ppm and a portion of the 55 ppm peak (about 54% ± 5%) survive the interrupted decoupling much better than other peaks, whereas the peak at about 47 ppm and another portion of the 55 ppm peak (about 46% ± 5%) do not survive the interrupted-decoupling period. By using this interrupted-decoupling approach, one can estimate that roughly 54% of the 55 ppm peak in Figure 2a is due to the methoxy groups (VII) of methylene methyl ether ($-CH_2OCH_3$) moieties, which result from the reaction of methanol in the 37% formalin with methylol groups formed by the methyloylation of urea units. When this type of ether moiety is attached to a secondary amide group, the $^{13}CH_2$ resonance of the $-CH_2OCH_3$ group appears at 73 ppm in the spectrum. Therefore, we assert that most of the intensity around 73 ppm in Figure 2 is due to the CH_2 of methylene ethers (VIII). As expected, the spectrum (not shown here) of the model compound, dimethylolurea dimethyl ether, shows similar interrupted-decoupling behaviors of peaks at about 160 and 55 ppm. Part (about 46%) of the 55 ppm peak in Figure 2a is attributed to the methylene linkage (II) connecting one secondary amide and one tertiary amide at each end, which is a relatively immobile moiety; and the dipolar interactions between the ^{13}C nucleus and its two direct-bonded protons are strong enough to render quick dephasing of the corresponding ^{13}C magnetization during the 50-μs interrupted-decoupling period, as shown in Figure 2c. The same dephasing behavior during the interrupted-decoupling period is displayed by the methylene linkage of the model compound, methylenediurea (spectrum not shown). This kind of structure dependence of the interrupted-decoupling behavior is applied in this paper to distinguish methoxy groups (VII) of methylene methyl ethers from methylene linkages (II) that connect secondary amide and tertiary amide groups; both species VII and II have roughly the same chemical shift around 55 ppm in the ^{13}C CP/MAS NMR spectrum.

In ^{13}C CP/MAS NMR spectra, an individual peak intensity depends not only on the relative concentration of the corresponding type of carbon environment but also on the ^1H–^{13}C cross-polarization efficiency. In order to obtain meaningful relative intensity comparisons *within* a given spectrum and trends for the spectra of a set of samples, the ^1H–^{13}C cross-polarization efficiency should be known for each individual peak in each spectrum. The ^1H–^{13}C cross-polarization efficiency depends on the duration of cross polarization (contact time, τ), the ^1H–^{13}C cross-polarization rate constant, T_{CH}^{-1}, which depends on the strength of the ^1H–^{13}C and ^1H–^1H dipolar interactions, and $T_{1\rho}^H$ (the rotating-frame spin–lattice relaxation time for the proton set that transfers polarization to the given ^{13}C magnetization component). With 1.1% natural abundance for ^{13}C and the rather high-density ^1H milieu of the urea–formaldehyde resin samples, and under a Hartmann–Hahn match[43] condition, the cross-polarized ^{13}C NMR magnetization $I(\tau)$ can be described by eq 6,[44]

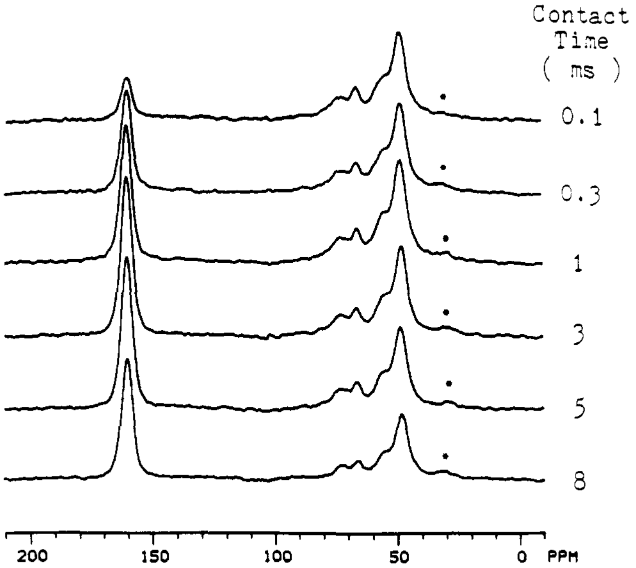


Figure 3. 50.3-MHz variable-contact-time ^{13}C CP/MAS NMR spectra of a UF resin sample prepared at pH 3 from a mixture with a F/U/W molar ratio of 2.00/1.00/25.0. Repetition time = 1 s; spinning rate = 6.6 kHz; contact times as shown. Spinning sidebands are indicated by asterisks.

where I^* is the ideal (full) cross-polarized ^{13}C

$$I(\tau) = \frac{I^*}{1-\lambda}(1 - e^{-(1-\lambda)\tau/T_{\mathrm{CH}}})e^{-\tau/T_{1\rho}^{\mathrm{H}}} \qquad (6)$$

$$\text{with } \lambda = T_{\mathrm{CH}}/T_{1\rho}^{\mathrm{H}}$$

magnetization—i.e., the value one would obtain if T_{CH} were infinitesimal and $T_{1\rho}^{\mathrm{H}}$ infinite.

By carrying out variable contact-time CP/MAS experiments in which several different contact times are employed, one can extract the parameters T_{CH} and $T_{1\rho}^{\mathrm{H}}$ for each individual peak in the spectrum at a given sample spinning rate by fitting the $I(\tau)$ data to eq 6. Figure 3 shows an example, the results of a variable-contact-time CP/MAS experiment on the UF sample prepared from a mixture with a F/U/W molar ratio of 2.00/1.00/25.0 at pH 3. From the T_{CH} and $T_{1\rho}^{\mathrm{H}}$ parameters derived from such plots, one can obtain the cross-polarization efficiency, $\sigma(\tau) = I(\tau)/I^*$, of each individual peak in the spectrum at a given contact time and sample spinning rate. Table I lists T_{CH}, $T_{1\rho}^{\mathrm{H}}$, and $\sigma(\tau)$ values for $\tau = 1$ ms for various peaks assigned to some likely structural fragments in seven UF resin samples investigated by variable-contact-time experiments. From Table I, we can see that the carbonyl carbons have much larger T_{CH} values and smaller 1-ms cross-polarization efficiencies than other, proton-bearing carbons; furthermore, the T_{CH} values of carbonyl carbons are considerably larger at a higher spinning rate for those two UF samples, 1.00/1.00/2.48 (12) and 3.00/1.00/23.6 (3), investigated at two different spinning rates. As shown in Table I, the maximum difference among the cross-polarization efficiencies for the proton-bearing carbons *within* a given spectrum is 3% in experiments with 1-ms contact times; however, the maximum difference between the cross-polarization efficiencies, $\sigma(1\ \mathrm{ms}) = I(1\ \mathrm{ms})/I^*$, for carbonyl carbons *and* proton-bearing carbons *within* a given spectrum is 12%; this difference appears in the spectrum of 3.00/1.00/23.6 (3) obtained with a spinning rate of 6.5 kHz.

In the present paper, we do not emphasize quantitative aspects of the ^{13}C CP/MAS analyses of carbonyl groups and rather mobile moieties, such as methoxy groups (VII, 55 ppm), short-chain poly(oxymethylene glycols) (87–92

Table I
T_{CH} Value, $T_{1\rho}^{\mathrm{H}}$, and σ (1 ms) for Some Likely Structural Fragments of Seven UF Resin Samples Investigated by Variable Contact-Time Experiments

											methylols						methylene linkages					
		carbonyls 155–169 ppm			poly(oxymethylene glycols) 87–92 ppm			dimethylene ether linkages XI, 76 ppm			V, 72 ppm			IV, 65 ppm			II, 54 ppm			I, 47 ppm		
sample[a]	spinning rate, kHz	T_{CH}, µs	$T_{1\rho}^{\mathrm{H}}$, ms	σ (1 ms)	T_{CH}, µs	$T_{1\rho}^{\mathrm{H}}$, ms	σ (1 ms)	T_{CH}, µs	$T_{1\rho}^{\mathrm{H}}$, ms	σ (1 ms)	T_{CH}, µs	$T_{1\rho}^{\mathrm{H}}$, ms	σ (1 ms)	T_{CH}, µs	$T_{1\rho}^{\mathrm{H}}$, ms	σ (1 ms)	T_{CH}, µs	$T_{1\rho}^{\mathrm{H}}$, ms	σ (1 ms)	T_{CH}, µs	$T_{1\rho}^{\mathrm{H}}$, ms	σ (1 ms)
1.00/1.00/2.48 (12)	3.5	275	7	0.88										95	7	0.88						
	6.1	410	7	0.83										115	7	0.88						
1.00/1.00/12.5 (5)	6.4	440	10	0.84										95	10	0.91	150	8	0.90	95	10	0.91
1.50/1.00/3.72 (3)	6.5	475	14	0.84							100	12	0.93	90	12	0.93	110	12	0.93	100	14	0.94
2.00/1.00/25.0 (3)	6.6	500	15	0.83							100	15	0.94	80	14	0.94	115	12	0.93	120	15	0.94
2.00/1.00/107 (3)	6.5	430	14	0.86							80	11	0.92	100	10	0.91	110	12	0.93	115	13	0.93
3.00/1.00/23.6 (3)	3.5	355	10	0.88	overlap with spinning sideband			140	7	0.89	120	9	0.91	100	10	0.91	120	9	0.91	115	11	0.92
	6.5	510	13	0.82	145	14	0.94	125	10	0.92	115	11	0.92	110	11	0.92	115	11	0.92	120	13	0.94
3.00/1.00/105 (5)	6.5	430	14	0.86							135	10	0.92	125	13	0.94	135	11	0.92	135	12	0.93

[a] The ratio is the F/U/W molar ratio of the starting materials: formaldehyde, urea, and water. The numbers inside parentheses indicate the pH value employed in the synthesis of each UF sample.

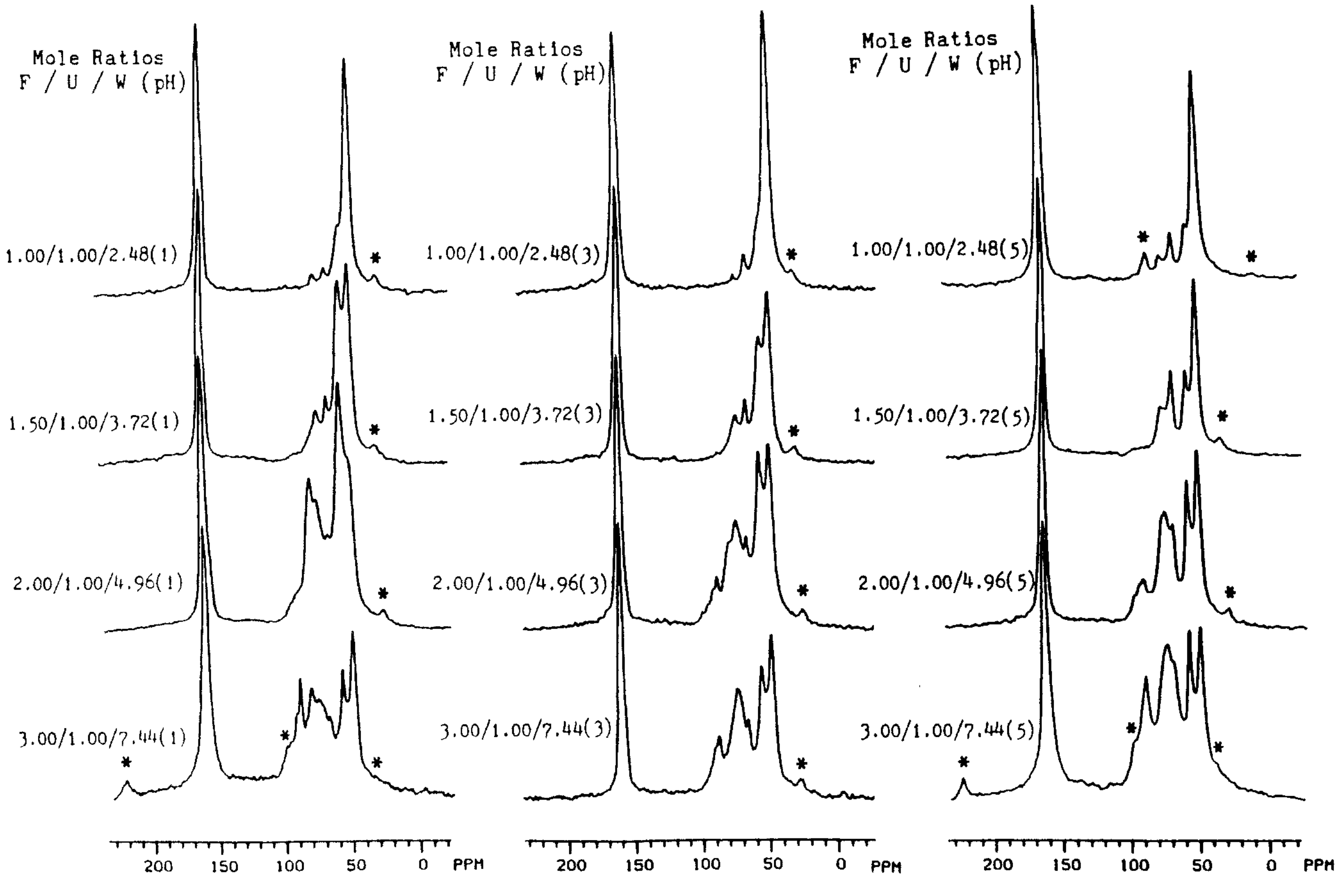


Figure 4. 50.3-MHz ^{13}C CP/MAS NMR spectra of UF resin samples prepared under concentrated conditions with four different F/U/W molar ratios, 1.00/1.00/2.48, 1.50/1.00/3.72, 2.00/1.00/4.96, and 3.00/1.00/7.44: (left column) pH 1; (middle column) pH 3; (right column) pH 5. Contact time = 1 ms; repetition time = 1 s. The number inside parentheses after each F/U/W molar ratio labeled in the figure indicates the pH value employed in each reaction mixture. Spinning sidebands are indicated by asterisks.

ppm), and methylene glycol (XIV, 83 ppm), for which detailed variable-contact-time experiments were not carried out. Such experiments are very time consuming and were performed on only a few specific samples in the present study, as shown partly in Table I. However, on the basis of the results shown in Table I, we assume that, for most other structural groups present in UF resins, experiments carried out with a 1-ms contact time and a spinning rate between about 3.2 and 6.5 kHz yield useful quantitative comparisons *within* a given sample. This assumption should be on firm ground for those relatively rigid ^{13}C nuclei attached to protons directly, such as in long-chain poly(oxymethylene glycols) (87–92 ppm), dimethylene ether linkages (X, 69 ppm; XI, 76 ppm), methylol groups (IV, 65 ppm; V, 72 ppm), and methylene linkages (I, 47 ppm; II, 54 ppm; III, 60 ppm). Therefore, direct interpretation for these moieties can be made, at least at a semiquantitative level.

5. Systematic Variations in the Parameters of Resin Preparation. (a) Overview. The results of ^{13}C CP/MAS NMR studies of those UF resins described in the Experimental Section are discussed here in three parts. The first part deals with the effect of F/U molar ratios on the structures of UF resins. The second part explores the effects of urea concentration on the UF resins at fixed F/U molar ratios. The third part concentrates on the effects of the pH values of reaction mixtures on the UF resins. These three parts are heavily interconnected with each other.

(b) Effect of F/U Molar Ratio. The initial (feed) molar ratio of formaldehyde to urea has a tremendous effect on the structure of the resulting UF resin. At all four F/U molar ratios, 1.00/1.00, 1.50/1.00, 2.00/1.00, and 3.00/1.00, three different urea concentrations have been employed to prepare the resin samples. These concentrations are specified by the following F/U/W molar ratios: 1.00/1.00/2.48, 1.00/1.00/12.5, 1.00/1.00/105, 1.50/1.00/3.72, 1.50/1.00/20.3, 1.50/1.00/105, 2.00/1.00/4.96, 2.00/1.00/25.0, 2.00/1.00/107, 3.00/1.00/7.44, 3.00/1.00/23.6, and 3.00/1.00/105. In the following discussion, we distinguish three urea concentration ranges at all four fixed F/U molar ratios in terms of the relative amounts of water and urea by corresponding ranges of W/U molar ratios, as follows: *concentrated*, 2.48–7.44; *intermediate*, 12.5–25.0; and *dilute*, 105–107. For each F/U molar ratio, the concentrated solution was prepared from 37% formalin and urea, with no added water.

(1) Concentrated Reaction Mixtures. At the highest possible urea concentrations (prepared with 37% formalin and urea without added water), the effects of the F/U molar ratio on the structure of the resulting UF resins are larger than among those prepared from the less concentrated mixtures, as will be seen in the ^{13}C spectra discussed below. The ^{13}C CP/MAS NMR spectra of UF resins prepared from concentrated mixtures at four F/U molar ratios and at pH 1, 3, and 5 are shown in the left, middle, and right columns of Figure 4, respectively. Two intense peaks at 47 and 160 ppm appearing in all these 12 spectra are assigned to linear-chain methylene linkages (I) and carbonyl groups in these UF resins, respectively.

At pH 1 (left column of Figure 4), one can see that with an increase of the F/U molar ratio from 1.00 to 1.50, the increased formaldehyde available goes mainly into forming more cross-linking and/or precursors of cross-linking, i.e., the methylene linkages (II, 54 ppm; III, 60 ppm) that connect tertiary amide moieties. When the tertiary amide attached to this methylene linkage (II or III) is attached to another methylene linkage (II or III) or a dimethylene ether linkage (XI, 76 ppm), it is already involved in cross-linking, if the tertiary amide is attached to a methylol group (Va, 72 ppm), then it constitutes a "precursor" of cross-linking, because the methylol group is capable of forming a methylene linkage or dimethylene ether linkage that constitutes cross-linking. Judging from the large increases of methylene linkages (II, 54 ppm; III, 60 ppm) that accompany the much smaller increase of internal methylols (Va, part of the 72 ppm peak) seen in the ^{13}C spectra with increasing F/U molar ratio, we conclude that the main portion of the additional methylene linkages formed with increased formaldehyde content are the cross-linking types. A much smaller portion of increased formaldehyde goes to form more methylols (IV, 65 ppm; V, 72 ppm) and dimethylene ether linkages (X, 69 ppm; XI, 76 ppm). A very small amount of poly(oxymethylene glycols) and/or hemiformals (XVIa and XVIb, 87–92 ppm, and/or VI, 87 ppm; XVIc, 88–92 ppm; XVId, 69 ppm; XVIe, 76 ppm) and urons (XIII, 79 ppm; XX, 156 ppm) also appear in the resin prepared from a mixture with the F/U/W molar ratio, 1.50/1.00/3.72 at pH 1, as revealed by the spectrum shown in Figure 4.

With a further increase of the F/U molar ratio from 1.50 to 2.00 at pH 1, the increased formaldehyde goes mainly to form more cross-linking and/or the precursors of cross-linking, as evidenced by the increase in intensity around 54 and 60 ppm attributed to methylene linkages (II, III), and to form more internal methylols (Va, 72 ppm) and/or *N,N*-dimethylols (Vb, 72 ppm). If the main contributor to the 72 ppm peak in the spectrum of the resin prepared from a mixture with a F/U molar ratio of 2.00 is internal methylols, then the main contributor to the increased 54 ppm peak in the spectrum is a precursor of cross-linking. At present, it is not possible to distinguish internal methylols from *N,N*-dimethylols in these 50.3-MHz ^{13}C CP/MAS NMR sectra; therefore, with abundant intensity around 72 ppm present in spectrum, it is difficult to distinguish cross-linking moieties from precursors of cross-linking.

The rest of the increased formaldehyde content that accompanies an increase of F/U molar ratio from 1.50 to 2.00 at pH 1 forms more dimethylene ether linkages (X, 69 ppm; XI, 76 ppm), poly(oxymethylene glycols) and/or hemiformals (XVIa and XVIb, 87–92 ppm, and/or VI, 87 ppm; XVIc, 88–92 ppm; XVId, 69 ppm; XVIe, 76 ppm), and urons (XIII, 79 ppm; XX, 156 ppm). The ^{13}C NMR results indicate that there are more methylene methyl ether groups formed from the increased methanol (in 37% formalin) accompanying higher F/U molar ratios; the existence of methylene methyl ether groups is indicated by the surviving 55 ppm peak in the corresponding 50-μs interrupted-decouping ^{13}C CP/MAS spectra (not shown here). With an increased amount of formaldehyde introduced at pH 1 by going from a F/U molar ratio of 2.00 to a F/U molar ratio of 3.00, the etherization of methylols (IV, 65 ppm; V, 72 ppm) by poly(oxymethylene glycols) to form hemiformals (VI, XVIc–e) and the insertion of formaldehyde between amide and methylene linkages (I, 47 ppm; II, 55 ppm; III, 60 ppm) to form dimethylene ether linkages (X, 69 ppm; XI, 76 ppm) become feasible. Besides the products of etherization and insertion, more methylols (IV, 65 ppm; V, 72 ppm) and more poly(oxymethylene glycols) and urons are seen in Figure 4 to be present in the resin prepared at pH 1 from a mixture with the F/U/W molar ratio of 3.00/1.00/7.44 than in the other resins represented in the left column of Figure 4.

In comparing the first two spectra of the middle column of Figure 4, corresponding to pH 3, one sees that the increased formaldehyde content associated with increasing the F/U molar ratio from 1.00 to 1.50 is accompanied by more cross-linking or an increase in the occurrence of cross-linking precursors, as indicated by the increased intensities around 54 and 60 ppm (attributed to methylene linkages (II, III)) and more methylols (IV, 65 ppm; V, 72 ppm). Some of the increased formaldehyde also goes to form dimethylene ether linkages (X, 69 ppm; XI, 76 ppm) and poly(oxymethylene glycols) and/or hemiformals (XVIa and XVIb, 87–92 ppm, and/or VI, 87 ppm; XVIc, 88–92 ppm; XVId, 69 ppm; XVIe, 76 ppm). In going from a F/U molar ratio of 1.50 to 2.00 at pH 3, the increased formaldehyde forms more methylols, dimethylene ether linkages of both kinds (X, 69 ppm; XI, 76 ppm), more short-chain poly(oxymethylene glycols) (and/or hemiformals), some urons (XIII, 79 ppm; XX, 156 ppm), and more cross-linking methylene linkages and/or precursors of cross-linking.

The methyl ethers of methylols attached to secondary or tertiary amide moieties (VII, 55 ppm), which are absent in resins prepared at pH 3 from a mixture with F/U molar ratios of either 1.00 or 1.50, begin to appear at a F/U molar ratio of 2.00, as indicated by the corresponding 50-μs interrupted-decoupling ^{13}C CP/MAS spectra (not shown here). With a further increase in formaldehyde content associated with going from a F/U molar ratio of 2.00 to 3.00, at pH 3, the formaldehyde produces a few more dimethylene ether linkages (XI, 76 ppm); however, the major portion of the increased formaldehyde goes to form methylols (V, 72 ppm), poly(oxymethylene glycols) (and/or hemiformals), and their methyl ethers, as shown in the bottom spectrum in the middle column of Figure 4.

At pH 5, in going from a F/U molar ratio of 1.00 to 1.50, one sees from the right column of Figure 4 that added formaldehyde methylolates primary amides to form methylols (IV, 65 ppm) and/or *N,N*-dimethylols (Vb, 72 ppm) and/or methylolates secondary amides to form internal methylols (Va, 72 ppm). The amount of dimethylene ether linkages (X, 69 ppm; XI, 76 ppm) is increased by going from a F/U molar ratio of 1.00 to 1.50, and poly(oxymethylene glycols) (and/or hemiformals) appear in the sample prepared with a F/U molar ratio of 1.50. The increase in the ^{13}C NMR intensity at 54 ppm seen in the right column of Figure 4 in progressing from the 1.00/1.00/2.48 case to the 1.50/1.00/3.72 case at pH 5 is mainly attributed to increased formation of cross-linking methylene linkages (II, 54 ppm) and/or precursors of cross-linking and, to a lesser extent, to methylene methyl ether formation, as indicated by the low intensity of the 55 ppm peak surviving in the corresponding 50-μs interrupted-decoupling ^{13}C CP/MAS spectra (Figure 5). In going from a F/U molar ratio of 1.50 to 2.00 at pH 5, the proportions of methylene methyl ethers, methylene linkages involved in cross-linking and/or precursors of cross-linking (II, 54 ppm), and methylols (IV, 65 ppm) increase. However, the major portion of the increased formaldehyde content goes to form more dimethylene ether linkages (X, 69 ppm; XI, 76 ppm), internal methylols (Va, 72 ppm) and/or *N,N*-dimethylols (Vb, 72 ppm), and poly(oxymethylene glycols) (and/or hemiformals) and their methyl ethers. These methyl ethers of poly(oxymethylene glycols) (and/or hemiformals) account for about 43% of the total methyl ethers present, according to the relative intensity of the 94 ppm peak in the ^{13}C CP/MAS spectrum shown in Figure 4 (2.00/1.00/4.96 (5)) and the fraction of the 55 ppm peak that survives in the corresponding 50-μs interrupted-decoupling spectrum (Figure 5c).

With the even larger F/U molar ratio of 3.00/1.00 at pH 5, the ^{13}C spectrum shows evidence of increased dimeth-

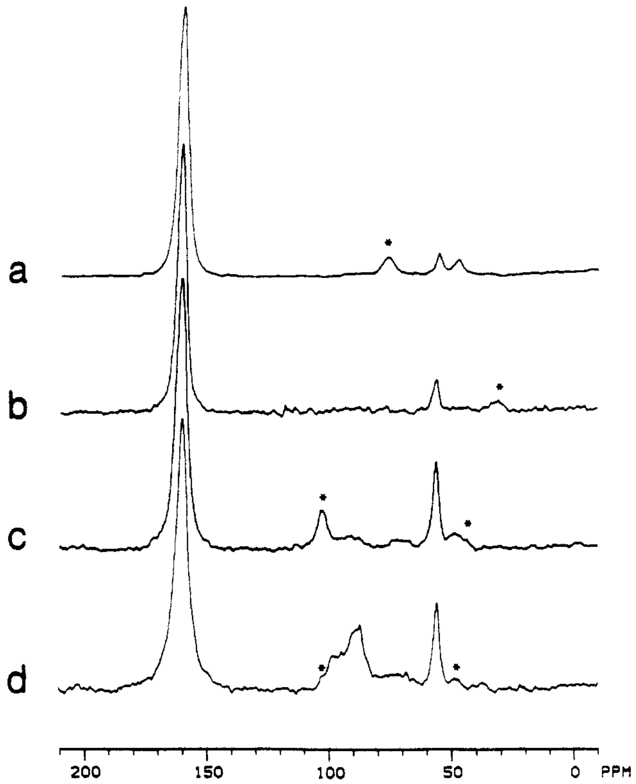


Figure 5. 50.3-MHz interrupted-decoupling ^{13}C CP/MAS NMR spectra of four UF resin samples prepared under concentrated conditions at pH 5 from mixtures with four different F/U molar ratios. Contact time = 1 ms; repetition time = 1 s; interrupted-decoupling period = 50 μs. F/U/W molar ratio: (a) 1.00/1.00/2.48; (b) 1.50/1.00/3.72; (c) 2.00/1.00/4.96; (d) 3.00/1.00/7.44. Spinning sidebands are indicated by asterisks.

ylene ether linkages (X, 69 ppm; XI, 76 ppm) and/or hemiformal moieties (–C(O)–N(R)–CH_2–$(OCH_2)_n$–OH; the methylene group has a ^{13}C chemical shift of 69 ppm (XVId) when attached to a secondary amide, 76 ppm (XVIe) when attached to a tertiary amide and 87–92 ppm (VI, XVIc) when not attached to any amide), and methylols (IV, 65 ppm; V, 72 ppm); and more short-chain poly(oxymethylene glycols) (XVIa and XVIb, 87–92 ppm) and their methyl ethers are formed (see Figure 5d). Some quantity of methylol groups probably exist in the form of *N,N'*-dimethylolurea and/or trimethylolurea, as indicated by the rather high intensities at 65 ppm and 72 ppm in the spectrum of the sample prepared with a F/U molar ratio of 3.00. The line width of the peak around 160 ppm is somewhat broadened inhomogeneously because of the great variety of environments surrounding the carbonyl carbon in the resin prepared at pH 5 from a mixture with a F/U molar ratio of 3.00.

The main constituents of UF resins prepared at pH 7 from reaction mixtures with four different F/U molar ratios under concentrated conditions are *N,N'*-dimethylolurea and/or monomethylolurea. This is indicated by spectral features similar to the characteristic *N,N'*-dimethylolurea patterns at about 160 and 65 ppm, which predominate in the spectra shown in the left column of Figure 6. One can see that the effects of changing the F/U molar ratio on the structures of UF resins formed from concentrated mixtures are small at pH 7. When the F/U molar ratio is changed from 1.00 to 1.50 and to 2.00 at pH 7, there are almost no changes in the corresponding ^{13}C CP/MAS NMR spectra. As mentioned above, the mixture prepared at pH 7 with a F/U/W molar ratio of 3.00/1.00/7.44 remained a clear solution even after 12 h of reaction. A soft solid was obtained after vacuum drying the reaction mixture at −5 °C for 35 h; the ^{13}C CP/MAS spectrum of the resulting solid is shown at the bottom of the left column in Figure 6. With excess formaldehyde, at a F/U molar ratio of 3.00, one sees that a small portion of the methylol groups form hemiformals with methylene glycol, as indicated by the 3.00/1.00/7.44 (7) spectrum of Figure 6 (the non-carbonyl groups of hemiformals (–C(O)–NH–CH_2–O–CH_2OH) appear at 69 ppm for the methylene ether carbons and at 87 ppm for methylol end group carbons (VIa)). About 60% of the 87 ppm peak intensity in the 3.00/1.00/7.44 (7) spectrum survives in the 50-μs interrupted-decoupling experiment (spectrum not shown). This interrupted-decoupling behavior indicates that methylol end groups of these hemiformals (VIb) are considerably mobile. Some of the excess formaldehyde in the F/U = 3.00 case is seen to form trimethylolurea or to have methylolated the monomethylolurea asymmetrically to form *N,N*-dimethylolurea (Vb), as evidenced by the appearance of the 72 ppm peak in the spectrum at the bottom of the left column in Figure 6. Some of the additional formaldehyde has been converted to poly(oxymethylene glycols) (87–92 ppm) in this 3.00/1.00/7.44 sample at pH 7.

The spectra displayed in the middle column of Figure 6 show that at pH 9 the resins prepared from four different F/U molar ratios under concentrated conditions consist mainly of *N,N'*-dimethylolureas and/or monomethylolurea; and the formation of hemiformals or *N,N*-dimethylols (Vb, 72 ppm) in the resulting UF resins is even less important than in the corresponding UF samples prepared at pH 7. In going from a F/U molar ratio of 1.00 to 1.50 at pH 9, there are small decreases in the intensities of the higher-frequency (lower-shielding) side of the doublet around 65 ppm, an indication that the resin prepared from a mixture with a F/U molar ratio of 1.00/1.00 contains a small quantity of dimethylene ether (X, 69 ppm) connecting two urea units.[27] There is only a very small amount of trimethylolurea and/or *N,N*-dimethylolurea in the sample prepared with a F/U molar ratio of 3.00 at pH 9, as indicated by the small 72 ppm peak in the bottom spectrum of the middle column of Figure 6.

The right column of Figure 6 shows that at pH 12 the effects of the F/U molar ratio on the structures of the UF resins formed are slightly greater than for the corresponding resins prepared at pH 7 and pH 9. In comparison to the left and middle columns of Figure 6, the spectra shown in the right column do not show the dramatic splittings around 65 ppm and around 160 ppm; furthermore, the spectra in the right column show shifts to lower shielding in both of those regions for resins prepared at pH 12 from mixtures with F/U molar ratios of 1.00 and 1.50. The causes of these differences between the ^{13}C CP/MAS spectra of samples prepared at pH 12 and those prepared at pH 7 and pH 9 are attributed to the formation of dimethylene ether (X, 69 ppm) linkages connecting two urea units as the major component at pH 12,[27] as indicated by the low-shielding shifts in both the 65 and 160 ppm regions of the spectrum of dimethylene ether diurea in comparison to that of *N,N'*-dimethylolurea in liquid-state ^{13}C NMR studies.[10,11,14,27] In comparison to the spectra of resins prepared with F/U molar ratios of 1.00 and 1.50 at pH 12, the high-shielding shifts in the 160 ppm region and the appearance of a high-shielding shoulder in the spectrum of a resin prepared with a F/U molar ratio of 2.00 at pH 12 indicate that the formation of *N,N'*-dimethylolureas and/or monomethylolureas becomes important under these conditions. The spectrum of the UF resin prepared from a mixture with a F/U molar ratio of 3.00 at pH 12 indicates that the main constituents of this resin are dimethylene ether linkages (X, 69 ppm). There

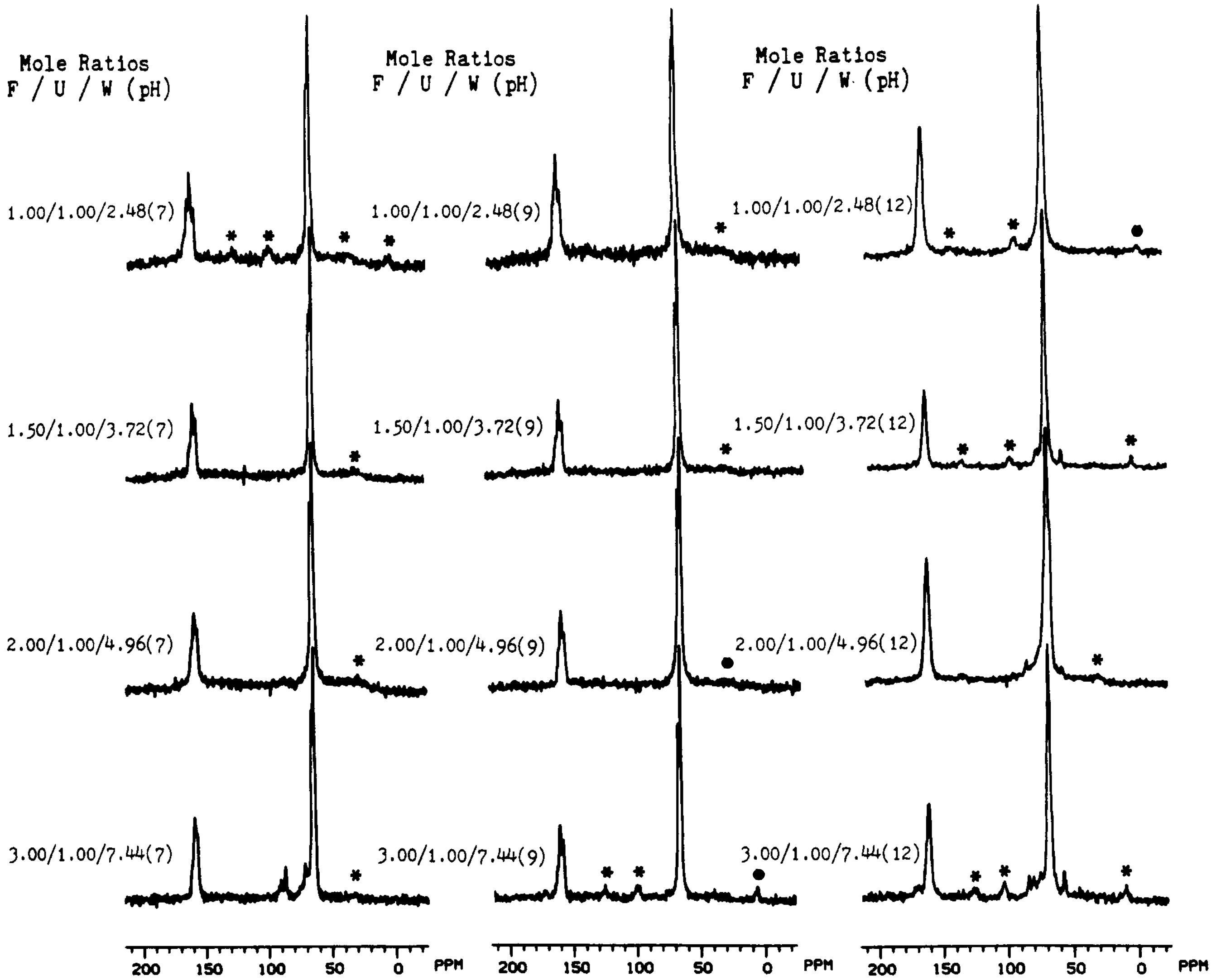


Figure 6. 50.3-MHz ^{13}C CP/MAS NMR spectra of UF resin samples prepared under concentrated conditions from mixtures with four different F/U/W molar ratios, 1.00/1.00/2.48, 1.50/1.00/3.72, 2.00/1.00/4.96, and 3.00/1.00/7.44. (left column) pH 7; (middle column) pH 9; (right column) pH 12. Contact time = 1 ms; repetition time = 1 s. The number inside parentheses after each F/U/W molar ratio labeled in the spectra indicates the pH value employed in each reaction mixture. Spinning sidebands are indicated by asterisks.

is no methylene methyl ether formed in the resin prepared at pH 12 from a concentrated mixture with a F/U molar ratio of 1.00, as indicated by the absence of a surviving 55 ppm peak in the 50-μs interrupted-decoupling spectrum (not shown here) of this resin; at the other three F/U molar ratios, the existence of small amounts of methylene methyl ethers in these three samples is confirmed by the interrupted-decoupling ^{13}C CP/MAS spectra (not shown here).

As shown in the spectra in the right column of Figure 6, there are no trimethylolureas and/or *N*,*N*-dimethylolureas formed in the sample prepared at pH 12 from a mixture with a F/U molar ratio of 1.00; however, for the three other F/U molar ratios, all the ^{13}C CP/MAS spectra show a small peak at about 72 ppm, which is attributed to methylene ether groups of methylene methyl ethers (VIII) and *N*,*N*-dimethylol groups of trimethylolureas and/or *N*,*N*-dimethylolureas. For these pH 12 cases, the relative intensity of the peak around 72 ppm is highest in the spectrum of the sample prepared from a mixture with a F/U molar ratio of 3.00. Besides containing dimethylene ether linkages (X), methylolurea, and methylene methyl ether structural units, the sample prepared at pH 12 from a mixture with a F/U molar ratio of 3.00 contains small amounts of uron (XII, 75 ppm; XIX, 157 ppm) and methylene glycol (XIV, 83 ppm); both components are absent in the samples prepared with the other three F/U molar ratios at pH 12.

(2) Reaction Mixtures at Intermediate Concentrations. As a result of decreasing the concentrations of urea and formaldehyde to the intermediate range by dilution with water, the effects of F/U molar ratio on the structures of UF resins formed are found to be smaller, relative to the corresponding effects in the concentrated reaction mixtures discussed above. The ^{13}C CP/MAS NMR spectra of samples prepared at intermediate concentrations from mixtures with the four different F/U molar ratios, 1.00, 1.50, 2.00, and 3.00, under acidic conditions are shown in the left (pH 1), middle (pH 3), and right (pH 5) columns of Figure 7, respectively. Figure 7 indicates that linear-chain methylene linkages (I, 47 ppm) connecting two urea units (160 ppm for carbonyls) are the major components in all 12 UF samples.

At pH 1, all four UF resins prepared at intermediate concentrations are seen to contain no significant concentrations of methyl ethers, as indicated by the absence of a surviving 55 ppm peak in the 50-μs interrupted-decoupling spectra (not shown) of these resins. In the top two spectra of the left column of Figure 7, corresponding to F/U molar ratios of 1.00 and 1.50, we note a large change in intensity associated with methylene linkages (II, 54 ppm; III, 60 ppm) accompanying a much smaller change in

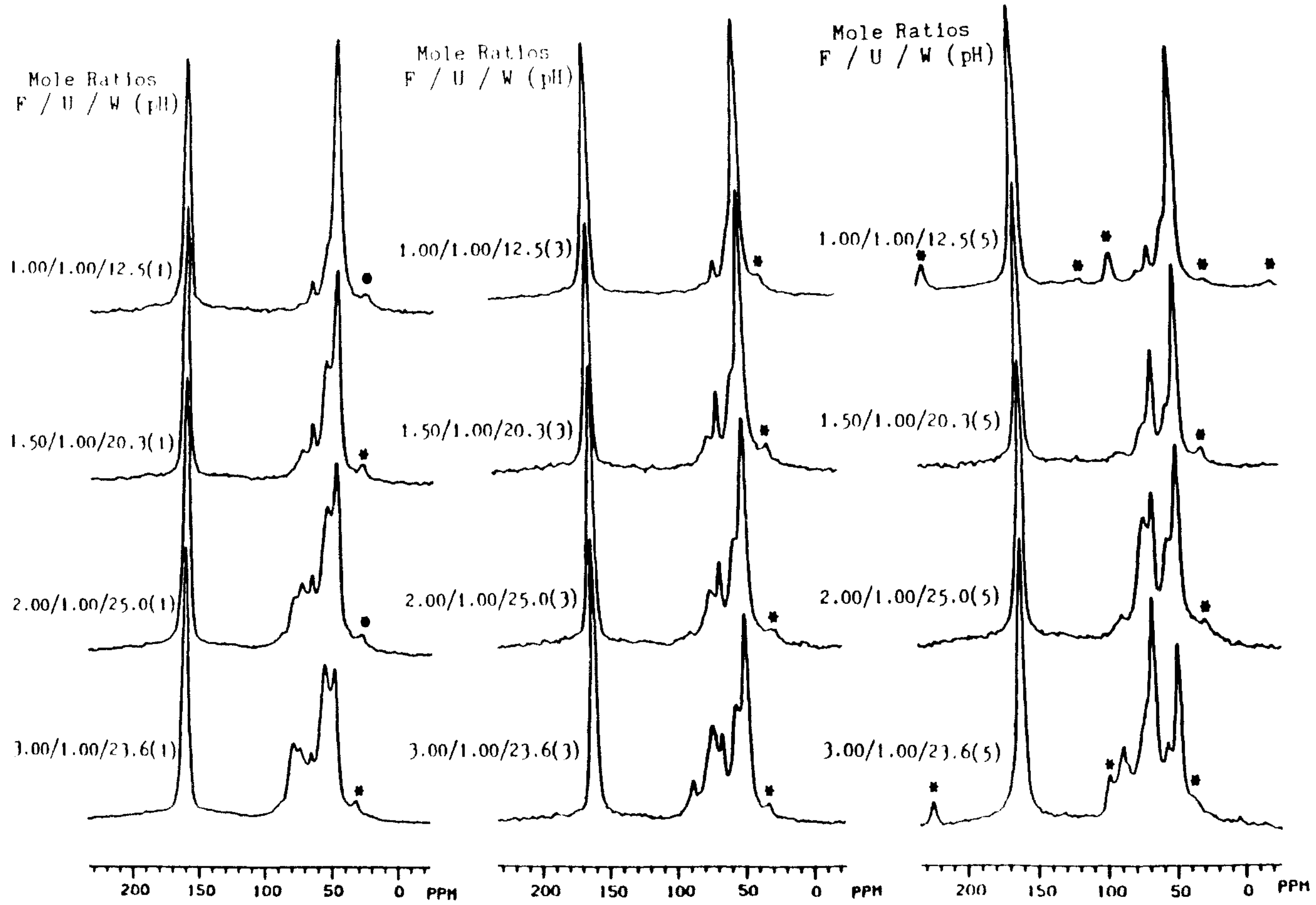


Figure 7. 50.3-MHz ^{13}C CP/MAS NMR spectra of UF resin samples prepared at intermediate concentrations from mixtures with four different F/U/W molar ratios, 1.00/1.00/12.5, 1.50/1.00/20.3, 2.00/1.00/25.0, and 3.00/1.00/23.6. (left column) pH 1; (middle column) pH 3; (right column) pH 5. Contact time = 1 ms; repetition time = 1 s. The number inside parentheses after each F/U/W molar ratio labeled in the spectra indicates the pH value employed in each reaction mixture. Spinning sidebands are indicated by asterisks.

intensity associated with internal methylols (Va, part of 72 ppm peak). These results imply that more cross-linking with methylene linkages and probably an increase in cross-linking precursors are formed in the solid portion of the resin prepared at pH 1 from a mixture with a F/U ratio of 1.50, compared to the case in which this ratio is 1.00. This situation is similar to the case of concentrated reaction mixtures described above. In addition to more cross-linking and cross-linking precursors, there are more methylols (IV, 65 ppm; V, 72 ppm) and dimethylene ether linkages (X, 69 ppm; XI, 72 ppm) formed in the resin resulting from the higher F/U mole ratio of 1.50; a small quantity of urons (XIII, 79 ppm; XX, 156 ppm) is also indicated in the spectrum of this resin, while there is still no sign of the existence of poly(oxymethylene glycol) structures (87–92 ppm) in this resin.

With a further increase in formaldehyde content at pH 1, associated with increasing the F/U molar ratio from 1.50 to 2.00, the spectra shown in the left column of Figure 7 show that more methylene linkages (II, 54 ppm; III, 60 ppm) involved in cross-linking and/or cross-linking precursors, more methylols (IV, 65 ppm), and substantially more dimethylene ether linkages (X, 69 ppm; XI, 76 ppm), internal methylols (Va, 72 ppm) and/or *N*,*N*-dimethylols (Vb, 72 ppm), and urons are formed in the resin. A small amount of poly(oxymethylene glycols) and/or hemiformals (XVIa and XVIb, 87–92 ppm, and/or VI, 87 ppm; XVIc, 88–92 ppm; XVId, 69 ppm; XVIe, 76 ppm) are indicated in the spectrum of the sample prepared at pH 1 from a mixture with a F/U molar ratio of 2.00. When even more formaldehyde is available at pH 1, with a F/U molar ratio of 3.00, the proportions of methylene linkages involved in cross-linking and/or cross-linking precursors (II, 54 ppm; III, 60 ppm), methylols (IV, 65 ppm; V, 72 ppm), and urons (XIII, 79 ppm; XX, 156 ppm) are increased further. The intensity of ^{13}C signals associated with dimethylene ether linkages (X, 69 ppm; XI, 76 ppm) in the resin increases slightly with an increase in the F/U molar ratio from 2.00 to 3.00 at pH 1. Among these intermediate concentration samples prepared at pH 1, only a small amount of poly(oxymethylene glycols) and/or hemiformals are seen to be present in the solid portion of the sample, even with the highest F/U molar ratio of 3.00. In comparison to the concentrated reaction mixtures, at pH 1 the effects of changing the F/U molar ratio on the structure of UF resins is seen to be simpler and less extensive for the intermediate concentration cases.

At pH 3 (see middle column, Figure 7), the largest changes observed in the ^{13}C CP/MAS spectra accompanying an increase in the F/U molar ratio from 1.00 to 1.50 are an increase in cross-linking through methylene linkages (II, 54 ppm; III, 60 ppm) and increases in methylols (IV, 65 ppm; V, 72 ppm) and dimethylene ether linkages attached to secondary amides (X, 69 ppm). There are probably also increases in the amounts of methylene linkages in cross-linking precursors and dimethylene ether linkages attached to tertiary amide(s) (XI, 76 ppm). The increased formaldehyde content accompanying the increase in the F/U molar ratio from 1.5 to 2.00 at pH 3 produces more dimethylene ether linkages (X, 69 ppm; XI, 76 ppm), internal methylols (Va, 72 ppm) and/or *N*,*N*-dimethylols (Vb, 72 ppm), and slightly more single terminal methylols (IV, 65 ppm) and methylene linkages (II, 54 ppm) involved in cross-linking and/or in precursors of cross-linking. Very small amounts of poly(oxymethylene glycols) and/or hemiformals (XVIa and XVIb, 87-92 ppm, and/or VI, 87 ppm; XVIc, 88-92 ppm; XVId, 69 ppm; XVIe, 76 ppm) appear in the spectrum of the precipitate portion of the resin prepared at pH 3 from a mixture with a F/U molar ratio of 2.00. When the F/U molar ratio is changed from 2.00 to 3.00 at pH 3, the spectrum shows evidence of the formation of more dimethylene ether linkages (X, 69 ppm; XI, 76 ppm) and/or hemiformals (VI, 87 ppm; XVIc, 88-92 ppm; XVId, 67 ppm; XVIe, 76 ppm) formed from condensation reactions between methylols attached to secondary or tertiary amides and poly(oxymethylene glycols) and the formation of more internal methylols (Va, 72 ppm) and/or *N,N*-dimethylols (Vb, 72 ppm), poly(oxymethylene glycols) (XVIa and XVIb, 87-92 ppm), and methylene glycol (XIV, 83 ppm). There is more intensity in the 54 ppm (methylene, II) peak in the spectrum of the resin prepared at pH 3 from the mixture with a F/U molar ratio of 3.00 than in the spectrum of the corresponding sample prepared from a F/U molar ratio of 2.00; this enhancement of the 54 ppm peak is presumably due to the cross-linking precursors, $-C(O)NHCH_2N(CH_2OH)C(O)-$, as indicated by the accompanying increase in intensity at about 72 ppm (presumably partly due to internal methylols, Va).

At pH 5 (right column, Figure 7), the major change seen in the spectra of the solid portions of the resins in going from a F/U molar ratio of 1.00 to 1.50 is an increase in the methylolation of amides, primarily the marked formation of more methylol groups attached to secondary amide units (IV, 65 ppm), and slightly more internal methylols (Va, 72 ppm) and/or *N,N*-dimethylols (Vb, 72 ppm). Accompanying the increase in these methylolation products is the formation of more dimethylene ether linkages (X, 69 ppm) and the occurrence of small amounts of poly(oxymethylene glycols) and/or hemiformals (XVIa and XVIb, 87-92 ppm, and/or VI, 87 ppm; XVIc, 88-92 ppm; XVId, 69 ppm; XVIe, 76 ppm). With the further increase in formaldehyde content associated with progressing from a F/U molar ratio of 1.50 to 2.00 at pH 5, similar tends prevail. However, the increase in the amounts of methylolation products of secondary amides with higher formaldehyde content exceeds the increase in methylolation products of primary amides, as indicated by the larger increase in intensity at 72 ppm in comparison to that at 65 ppm in the spectrum; and the formation of new dimethylene ether linkages attached to tertiary amide structures (XI, 76 ppm) exceeds the formation of new dimethylene ether linkages attached to secondary amide moieties (X, 69 ppm). Similar to the case mentioned above for pH 3 with a F/U molar ratio of 3.00, the increase in cross-linking precursors (methylenes, II) in going from a F/U molar ratio of 1.50 to 2.00 probably is responsible for the enhancement of the 54 ppm peak. The amount of poly(oxymethylene glycols) (and/or hemiformals) in the solid resin portion continues to grow as the F/U molar ratio is increased further at pH 5. At a F/U molar ratio of 3.00 at pH 5, the main noncarbonyl constituents in the solid resin portion are linear-chain methylene linkages (I, 47 ppm) and methylol groups (IV, 65 ppm), presumably mainly in the form of *N,N'*-dimethylolureas and/or trimethylolureas.

Substantial amounts of methylene glycol (XIV, 83 ppm), poly(oxymethylene glycols) and/or hemiformals (XVIa and XVIb, 87-92 ppm, and/or VI, 87 ppm; XVIc, 88-92 ppm; XVId, 69 ppm; XVIe, 76 ppm) are present in the resin isolated from a pH 5 reaction mixture with an initial F/U molar ratio of 3.00 (bottom spectrum, right column of Figure 7). Some methylene glycols and/or poly(oxymethylene glycols) etherize the methylols attached to amide moieties to form hemiformals (VI, XVc-e). Large amounts of methylene linkages (I, 47 ppm; II, 54 ppm) are present in this resin. The environments of the carbonyl carbons are highly heterogeneous, so the line width of the 160 ppm peak in the spectrum is large in the sample prepared from a mixture with a F/U molar ratio of 3.00; associated with these changes is the possible production of urons (XII, 75 ppm; XIII, 79 ppm; XIX, 157 ppm; XX 156 ppm) in this resin.

For the intermediate concentration cases at pH 7, 9, and 12, the spectral and structural trends and changes observed for the UF resins accompanying changes in the F/U molar ratio are similar to the corresponding trends and changes discussed above for the concentrated resin mixtures. However for the intermediate cases, these trends and changes in the spectra (not shown here) are less pronounced. No further discussion of the F/U molar ratio effect on those systems will be given here.

Two sets of experiments were performed on reaction mixtures with a F/U/W molar ratio of 2.00/1.00/25.0 at pH 7. The first experiment employed the "standard" 12-h reaction time of this investigation; at the end of this period, a clear solution was obtained. A solid sample suitable for ^{13}C CP/MAS NMR study was obtained from this clear solution by vacuum drying at -5 °C for 2 days. In the second experiment the entire reaction mixture was vacuum dried at -5 °C for 4 days immediately after mixing the 37% formalin, urea, and water with the same F/U/W molar ratio of 2.00/1.00/25.0 at pH 7; a soft, sticky solid was obtained by this procedure. Both ^{13}C CP/MAS NMR spectra (not shown here) of these two 2.00/1.00/25.0 (7) samples show the splitting characteristic of *N,N'*-dimethylolurea, together with a suggestive shoulder at about 72 ppm. From the result obtained after 12 h of reaction at room temperature, we can be certain that the methylolation of urea by 37% formalin is not quenched at room temperature at pH 7. From the results of the experiment in which the reaction mixture was vacuum dried at -5 °C immediately, with no room-temperature reaction period, we learn that the methylolation of urea by 37% formalin is not quenched at -5 °C and pH 7. Therefore, the procedure of bringing the temperature of the reaction mixture down to 0 °C and neutralizing to a pH value of 7 does *not* guarantee quenching of the methylolation of urea by 37% formalin.

According to De Jong and De Jonge,[39] the pH dependence of the rate of methylolation of urea by formaldehyde is relatively flat from pH 5 to pH 8; the rate constant is about 10^{-4} L/(mol s) at 35 °C, with an activation energy of 14 kcal/mol. One can estimate that at about -5 °C the methylolation of urea should occur to a significant extent within 1 day at pH 7 in the reaction mixture with a F/U/W molar ratio of 2.00/1.00/25.0, so the result described above for the 2.00/1.00/25.0 (7) sample without any prior reaction at room temperature appears to be understandable. However, for resins prepared at pH 7 from reaction mixtures with F/U molar ratios of 1.00, 1.50, 2.00, and 3.00, the absence of methylene-linkage peaks at 47 ppm (I), 54 ppm (II), and 60 ppm (III) in the ^{13}C CP/MAS NMR spectra (Figure 6, left column and some other spectra not shown here) indicate that either vacuum drying at -5 °C or room-temperature reaction conditions at pH 7 substantially quenches the formation of methylene linkages described in eq 3.

(3) Dilute Reaction Mixtures. Figure 8 shows the spectra of resins prepared at pH 1 (left column), pH 3 (middle column), and pH 5 (right column) from dilute

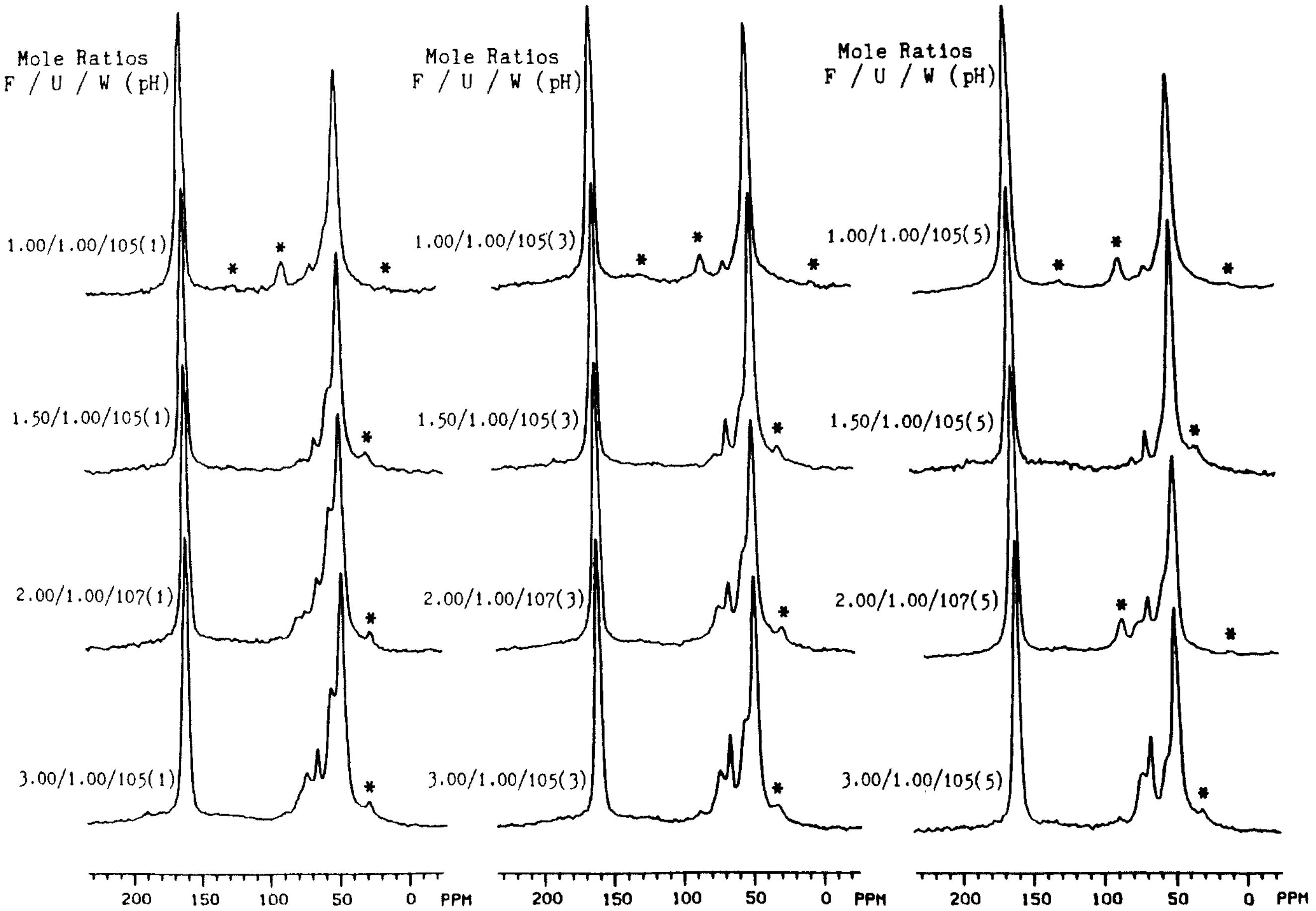


Figure 8. 50.3-MHz ^{13}C CP/MAS NMR spectra of UF resin samples prepared under dilute conditions from mixtures with four different F/U/W molar ratios, 1.00/1.00/105, 1.50/1.00/105, 2.00/1.00/107, and 3.00/1.00/105. (left column) pH 1; (middle column) pH 3; (right column) pH 5. Contact time = 1 ms; repetition time = 1 s. The number inside parentheses after each F/U/W molar ratio labeled in the spectra indicates the pH value employed in each reaction mixture. Spinning sidebands are indicated by asterisks.

mixtures with F/U molar ratios of 1.00, 1.50, 2.00, and 3.00. Solid UF resins were also prepared at pH 7, 9, and 12 from dilute mixtures by vacuum drying of the clear solutions after 12 h of reaction at 23 °C; the spectral differences (not shown here) observed among these vacuum-dried resins due to variation in the F/U molar ratios were found to be smaller than those observed for the more concentrated reaction mixtures discussed above.

In the solid portions of UF resins prepared at pH 1 (left column of Figure 8), slightly increased amounts of cross-linking through methylene linkages (V, 54 ppm; III, 60 ppm), of methylols (IV, 65 ppm; V, 72 ppm), and of dimethylene ether linkages (X, 69 ppm; XI, 76 ppm) are observed in the spectra in progressing from a F/U molar ratio of 1.00 to 1.50; however, the extent of these changes is small. The same kinds of trends occur to a greater extent when the F/U molar ratio is increased from 1.50 to 2.00 at pH 1. In addition, the formation of urons (XIII, 79 ppm; XX, 156 ppm) is noticeable in the sample with a F/U molar ratio of 2.00. With more formaldehyde made available by going from a F/U molar ratio of 2.00 to 3.00 at pH 1, the amount of cross-linking through methylene linkages (III, 60 ppm) seems to decrease, presumably because of the insertion of formaldehyde to form dimethylene ether linkages (XI, 76 ppm); however, the proportions of methylols and dimethylene ether linkages continue to grow. Because any excess formaldehyde, if it exists, in the reaction mixture with a F/U molar ratio of 3.00 is removed along with the supernatant liquid portion and because of the general dilution effect in this set of samples, only a small portion of the initial formaldehyde is ultimately found in the form of dimethylene ether linkages (X, 69 ppm; XI, 76 ppm), poly(oxymethylene glycols), and/or hemiformals (XVIa and XVIb, 87–92 ppm, and/or VI, 87 ppm; XVIc, 88–92 ppm; XVId, 69 ppm; XVIe, 76 ppm); this behavior stands in contrast to the cases described above for concentrated and intermediate reaction mixtures with the F/U molar ratio, 3.00.

One can see by examining the middle and right columns of Figure 8 that trends which are similar to what were discussed above for pH 1 are also observed to about the same extent for the effects of changing the F/U molar ratios at pH 3 and pH 5 in dilute reaction mixtures.

(c) Concentration Effects at Fixed F/U Molar Ratios. As discussed in section 5b, the reaction between 37% formalin and urea under neutral or basic conditions at room temperature (23 ± 2 °C) produces mainly monomethylolurea, *N,N′*-dimethylolurea (IV, 65 ppm; carbonyl, 160 ppm), and/or dimethylene ether linkages connecting two urea units (X, 69 ppm; carbonyl, 160 ppm). Some of the reaction mixtures investigated here remain in a clear liquid state even after 12 h of reaction time; solids suitable for ^{13}C CP/MAS NMR study were obtained by vacuum drying these liquid reaction mixture at −5 °C. This procedure cannot prevent further methylolation of urea by formaldehyde (vide supra) and/or further formation of dimethylene ether linkages;[27] therefore, a ^{13}C CP/MAS NMR study alone cannot provide a complete picture of concentration effects on the structures of UF resin prepared under neutral or basic conditions. According to the ^{13}C CP/MAS NMR results, the effects of concentration (in the range of this investigation) on the structure of UF resins prepared under neutral or basic conditions are small variations in the amounts of some minor species, such as methylene methyl ethers (VII, 55 ppm; VIII, 73 ppm), urons (XII, 75 ppm; XIX, 157 ppm), and methylene glycol

(XIV, 83 ppm), and possibly small variations in the proportions of methylolureas relative to dimethylene ether linkages.[27] In the following discussion, we summarize the major concentration effects on the UF resins prepared under acidic conditions.

(1) F/U Molar Ratio 1.00/1.00. With this F/U molar ratio, UF resins were prepared at three different concentrations, corresponding to the following F/U/W molar ratios: 1.00/1.00/2.48, 1.00/1.00/12.5, and 1.00/1.00/105. The ^{13}C CP/MAS NMR spectra of UF resins prepared at pH 1 from reaction mixtures with these three F/U/W molar ratios are shown in the left columns of Figures 4, 7, and 8, respectively. The major difference between the spectrum of the 1.00/1.00/2.48 (1) sample in Figure 4 and those of the related samples, 1.00/1.00/12.5 (1) in Figure 7 and 1.00/1.00/105 (1) in Figure 8, are in the peaks at about 73 and 55 ppm in the 1.00/1.00/2.48 (1) spectrum; the differences in those peaks have been attributed to the presence of methylene methyl ethers (VIII, VIIa) in the UF 1.00/1.00/2.48 (1) sample. The spectra of samples 1.00/1.00/12.5 (1) and 1.00/1.00/105 (1) in Figures 7 and 8, respectively, both show a very small peak around 72 ppm, which is attributed to internal methylols (Va) and/or *N,N*-dimethylols (Vb). Comparison of these three spectra indicates that, except for this dramatic concentration effect on the formation of methylene methyl ethers, there are no major concentration effects on the UF resin structure for F/U = 1.00/1.00 at pH 1.

The ^{13}C CP/MAS NMR spectra of UF resins prepared at pH 3 from mixtures with F/U/W molar ratios of 1.00/1.00/2.48, 1.00/1.00/12.5, and 1.00/1.00/105 are shown in the middle columns of Figures 4, 7, and 8, respectively. Comparison of those spectra reveals that the concentration effects on the structures of UF resins prepared at pH 3 from mixtures with a F/U molar ratio of 1.00 are also very minor; all three samples consist of urea units (160 ppm) connected predominately by linear-chain methylene linkages (I, 47 ppm) and to a much less extent by cross-linking methylene linkages (V, 54 ppm). A negligible amount of methylene methyl ethers are formed from all three samples.

The right columns of Figures 4, 7, and 8 show the ^{13}C CP/MAS NMR spectra of UF resins prepared at pH 5 from mixtures with F/U/W molar ratios of 1.00/1.00/2.48, 1.00/1.00/12.5, and 1.00/1.00/105, respectively. The peaks around 55, 65, and 73 ppm are seen to be decreased in their intensities at the higher dilutions. As discussed above, the interrupted-decoupling spectrum shown in Figure 5a indicates that about 40% of the 55 ppm peak for sample 1.00/1.00/2.48 (5) in Figure 4 and almost all of the 73 ppm peak in that spectrum are attributed to methylene methyl ethers ($-NH-CH_2OCH_3$).

For all the UF samples prepared with an initial F/U molar ratio of 1.00 at the three different concentrations and three pH values (1, 3, and 5), the methylene linkages (II, 54 ppm) that connect one tertiary amide group and one secondary amide group are seen to have their lowest contribution in the most dilute reaction mixture. From the intensities of the 55 ppm peaks in the interrupted-decoupling spectra (1.00/1.00/2.48 (5) shown in Figure 5a and the other eight spectra not shown here), we can see that almost all of the 73 ppm peaks in the spectra of the top rows of Figures 4, 7, and 8 are well-accounted for by the methylene groups of methylene methyl ethers (VIII); therefore, there is a negligible amount of internal methylol groups (Va, 72 ppm) and/or *N,N*-dimethylol groups (Vb, 72 ppm). In light of the absence of internal methylol groups (Va), one can see that all the methylene linkages (II, 54 ppm) that connect one tertiary amide and one secondary amide and do not survive the 50-μs interrupted-decoupling period are involved in cross-linking or branching of linear chains. For an initial F/U molar ratio of 1.00/1.00, all of the UF samples prepared at the three different concentrations and three pH values (1, 3, and 5) show significant amounts of this kind of cross-linking in these resins.

(2) F/U Molar Ratio 1.50/1.00. Samples have been prepared from mixtures with a F/U molar ratio of 1.50/1.00 at three different overall concentrations, corresponding to F/U/W molar ratios of 1.50/1.00/3.72, 1.50/1.00/20.3, and 1.50/1.00/105. The liquid portion removed from the reaction mixture with a F/U/W molar ratio of 1.50/1.00/105 and pH 1 was vacuum dried at −5 °C; no signal was observed in the ^{13}C CP/MAS NMR spectrum of the resulting solid after 3000 accumulations. Therefore, it is certain that the liquid portion of the reaction mixture contains very little, if any, urea or paraformaldehyde. This vacuum-generated solid is mainly sodium phosphate formed by neutralization of the reaction mixture to pH 7 by sodium hydroxide solution.

The ^{13}C CP/MAS NMR spectra of the solid portions of the three F/U = 1.50/1.00 reaction mixtures specified above are shown for pH 1 in the left columns of Figures 4, 7, and 8. The corresponding 50-μs interrupted-decoupling experiments (spectra not shown here) indicate that only a very small amount of methylene methyl ethers (VIIa, 55 ppm; VIII, 73 ppm) exist in the concentrated 1.50/1.00/3.72 (1) reaction mixture and a negligible amount of methylene methyl ether exists in the two more dilute 1.50/1.00/20.3 (1) and 1.50/1.00/105 (1) reaction mixtures. The following trends can be noted in going from the 1.50/1.00/3.72 (1) spectrum in Figure 4 to the 1.50/1.00/20.3 (1) spectrum in Figure 7 to the 1.50/1.00/105 (1) spectrum in Figure 8: The relative intensity at about 47 ppm increases, whereas the relative intensities at about 54, 60, 65, 69, 73, and 76 ppm decrease markedly. Therefore, we determine that at pH 1, the overall dilution of a F/U = 1.50/1.00 reaction mixture disfavors the formation of cross-linking methylene linkages (II, 54 ppm; III, 60 ppm), dimethylene ether linkages (X, 69 ppm; XI, 76 ppm), and methylol groups (IV, 65 ppm; V, 72 ppm) but favors the formation of linear-chain methylene linkages (I, 47 ppm). The concentration effects at pH 1 are much more obvious among these samples prepared with a F/U molar ratio of 1.50/1.00 than with the samples prepared with a F/U molar ratio of 1.00/1.00.

The ^{13}C CP/MAS NMR spectra of three samples prepared at pH 3 from mixtures with F/U/W molar ratios of 1.50/1.00/3.72, 1.50/1.00/20.3, and 1.50/1.00/105 are presented in the middle columns of Figures 4, 7, and 8. The corresponding 50-μs interrupted-decoupling experiments performed on these three samples (spectra not given here) show that methylene methyl ether groups are not significant contributors to the 55 ppm peak. For these F/U = 1.50 systems, we observe trends in the concentration effects on resins structures for pH = 3 that are similar to those described above for pH = 1. A small difference between these similar trends is the smaller variation in relative intensities around 65 ppm (methylols, IV) in the spectra of the resins prepared at pH 3.

The right columns of Figures 4, 7, and 8 include the ^{13}C CP/MAS NMR spectra of UF resins prepared at pH 5 from mixtures with F/U/W molar ratios of 1.50/1.00/3.72, 1.50/1.00/20.3, and 1.50/1.00/105, respectively. In comparing the 1.50/1.00/3.72 (5) spectrum of Figure 4 and the 1.50/1.00/20.3 (5) spectrum of Figure 7, one sees that the main differences lie in the relative intensities at about 55, 65, and 73 ppm. As indicated in the above discussion of Figure 5b, about 40% of the 55 ppm peak in the 1.50/1.00/3.72 (5) spectrum of Figure 4 survives the interrupted-decoupling experiment because of the rapid motions attributed to methoxy groups of methylene methyl ethers ($-CH_2OCH_3$) and hence about 70% of the 73 ppm peak can be attributed to $-OCH_2-$ groups in methylene methyl ethers. In contrast to the high concentration of methylene methyl ethers found in the resin prepared at pH 5 from a mixture with a F/U/W molar ratio of 1.50/1.00/3.72, the 50-μs interrupted-decoupling ^{13}C CP/MAS NMR spectrum (not shown here) of the resin prepared at pH 5 from a mixture with a F/U/W molar ratio of 1.50/1.00/20.3 reveals that much smaller fractions of the 55 and 73 ppm peaks can be attributed to methylene methyl ethers. In the absence of methylene methyl ether formation from methylol groups (IV, 65 ppm) and methanol, methylol groups are expected to be more prominent, as confirmed by the 65 ppm peak in the 1.50/1.00/20.3 (5) spectrum of Figure 7. In the absence of a substantial $-CH_2-$ contribution from methylene methyl ethers to the 73 ppm peak, that peak in the 1.50/1.00/20.3 (5) spectrum of Figure 7 can be attributed to internal methylol groups (Va) and/or *N,N*-dimethylol moieties (Vb).

On the basis of the above arguments, we can say that the major variations among the F/U = 1.50/1.00 spectra for pH 5 in Figures 4 and 7 are due to the much higher concentration of methylene methyl ether groups in the resin prepared from a mixture with a F/U/W molar ratio of 1.50/1.00/3.72 than for the 1.50/1.00/20.3 case. The ^{13}C CP/MAS spectra show that both samples contain significant amounts of methylene linkages (II, 54 ppm) involved in cross-linking and/or in cross-linking precursors and of internal methylol groups (Va) and/or *N,N*-dimethylol groups, which account for 30% of the 72 ppm peak in the 1.50/1.00/3.72 (5) spectrum of Figure 4 and all of the 73 ppm peak in the 1.50/1.00/20.3 (5) spectrum of Figure 7.

The concentrations of single terminal methylol groups (IV, 65 ppm) are high in both of the F/U = 1.50/1.00 samples obtained at pH 5 from the more concentrated reaction mixtures. In comparison to the 1.50/1.00/20.3 (5) spectrum in Figure 7, the 1.50/1.00/105 (5) spectrum in Figure 8 indicates that much of the 72 ppm peak (Va, internal methylols; Vb, *N,N*-dimethylols) and 65 ppm peak (IV, terminal methylols), and some of the 54 ppm peak (II, methylene linkages involved in cross-linking and/or in the cross-linking precursors) are absent. This observation indicates that dilution from a F/U/W molar ratio of 1.50/1.00/20.3 to 1.50/1.00/105 is accompanied by reductions in the formation of methylol groups and methylene linkages (II, 54 ppm) involved in cross-linking and/or cross-linking precursors in the resin.

(3) F/U Molar Ratio 2.00/1.00. At pH 1, UF resins were prepared with the following three overall concentrations (F/U/W molar ratios): 2.00/1.00/4.96, 2.00/1.00/25.0, and 2.00/1.00/107. The left columns of Figures 4, 7, and 8 show the ^{13}C CP/MAS NMR spectra of samples prepared at these three concentrations. The spectrum of the sample prepared at pH 1 from a mixture with a F/U/W molar ratio of 2.00/1.00/4.96 shows the existence of methylene methyl ether ($-CH_2OCH_3$) moieties (methoxy peak at about 55 ppm which survives 50-μs interrupted decoupling), in contrast to the absence of this group in the other two F/U = 2.00/1.00 samples prepared under more dilute conditions. Other effects that accompany increased dilution are an increase in the relative intensity at 47 ppm (methylene linkages, I) and sharp decreases in intensity at 54 ppm (methylene linkages, II) 65 ppm (methylols, IV), 69 ppm (dimethylene ether linkages, X), 72 ppm (methylols, V), 76 ppm (dimethylene ether linkages, XI), 79 ppm (dimethylene ether of urons, XIII), and the region around 88 ppm (poly(oxymethylene glycols) and/or hemiformals). The ^{13}C CP/MAS NMR results of these resins prepared at pH 1 and F/U = 2.00/1.00 indicate that dilution favors the formation of linear-chain methylene linkages (I, 47 ppm) but disfavors the formation of methylene linkages (II, 54 ppm) involved in cross-linking and/or in cross-linking precursors, of dimethylene ether linkages (X, XI), and of various methylols (IV, V). All three UF resins prepared at pH 1 from mixtures with a F/U molar ratio of 2.00/1.00 contain a substantial amount of cross-linking and/or cross-linking precursors, as evidenced by high intensities at about 54 ppm (methylene linkages, II) and 60 ppm (methylene linkages, III) in the spectra. The sample prepared from the most concentrated mixture, 2.00/1.00/4.96 (1), contains a substantial amount of internal methylol groups (Va, 72 ppm) and/or *N,N*-dimethylol groups (Vb, 72 ppm), as evidenced in the corresponding 2.00/1.00/4.96 (1) spectrum of Figure 4.

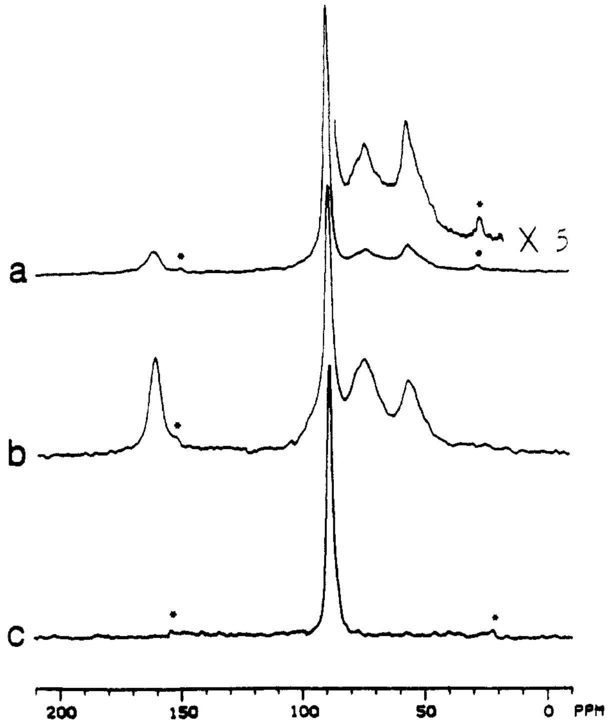


Figure 9. 50.3-MHz ^{13}C CP/MAS NMR spectra of two UF resin samples and paraformaldehyde: (a) solid sample obtained by vacuum drying the liquid portion of a reaction mixture with a F/U/W molar ratio of 2.00/1.00/44.6 after 12 h of reaction at pH 3; (b) solid sample obtained by vacuum drying the liquid portion of a reaction mixture with a F/U/W molar ratio of 3.00/1.00/105 after 12 h of reaction at pH 5; (c) paraformaldehyde. Contact time = 1 ms; repetition time = 1 s. Spinning sidebands are indicated by asterisks.

UF resins have been prepared at pH 3 from mixtures with a F/U molar ratio of 2.00/1.00 at four different concentrations that correspond to the following F/U/W molar ratios: 2.00/1.00/4.96, 2.00/1.00/25.0, 2.00/1.00/44.6, and 2.00/1.00/107. The liquid portion removed from the reaction mixture with an initial F/U/W molar ratio of 2.00/1.00/44.6 was neutralized to pH 7 and vacuum dried at −5 °C for 34 h; the solid obtained by this vacuum-drying procedure amounted to less than 10% of the total solids obtained from this initial reaction mixture. The ^{13}C CP/MAS NMR spectrum of this small portion of solid is presented in Figure 9a. The predominant peak at 88 ppm in this spectrum is very similar to the spectrum of paraformaldehyde (Figure 9c), including the 50-μs interrupted-decoupling behavior (cf., Figure 10b). This fact indicates that some unreacted formaldehyde is present in the liquid portion, which apparently polymerizes to paraformaldehyde during the vacuum drying at −5 °C and pH 7 for 34 h. The 88 ppm peak corresponding to polymerized formaldehyde constitutes about 65% of the total ^{13}C NMR intensity in the spectrum shown in Figure 9a. From Figure 9a and the fact that vacuum drying of the liquid portion yielded less than 10% of the total solids, one sees that the water solubility of UF resins that contain methylene linkages (I, 47 ppm; II, 54 ppm) is very small, even though one might expect the water solubility to be assisted by the presence of methylol groups (IV, 65 ppm; V, 72 ppm).

The middle columns of Figures 4, 7, and 8 include the ^{13}C CP/MAS NMR spectra of UF resins prepared at pH 3 from mixtures with F/U/W molar ratios of 2.00/1.00/4.96, 2.00/1.00/25.0, and 2.00/1.00/107, respectively. The structural trends associated with concentration effects are very similar to those discussed above for the pH 1 case. As in that case, all the UF resins prepared at pH 3 from mixtures with a F/U molar ratio of 2.00/1.00 contain substantial amounts of cross-linking and/or cross-linking precursors, as indicated by high intensities at about 54 ppm (methylene linkages, II) and 60 ppm (methylene linkages, III) in the spectra of these samples.

The right columns of Figures 4, 7, and 8 include the ^{13}C CP/MAS spectra of UF resins prepared at pH 5 from mixtures with F/U/W molar ratios of 2.00/1.00/4.96, 2.00/1.00/25.0, and 2.00/1.00/107, respectively. The difference in relative intensity at 55 ppm between the 2.00/1.00/4.96 (5) spectrum of Figure 4 and the 2.00/1.00/25.0 (5) spectrum of Figure 7 can be attributed to the increased formation of methoxy groups in methylene methyl ethers ($-N(R)-CH_2OCH_3$ and $R-OCH_2-(OCH_2)_n-OCH_3$) from methanol and various methylols in the reaction mixture prepared with lower dilution. There is no significant amount of methylene methyl ethers in the resin prepared at pH 5 from a mixture with a F/U/W molar ratio of 2.00/1.00/25.0, as indicated by the absence of a 55 ppm peak in the 50-μs interrupted-decoupling spectrum (not shown) corresponding to the 2.00/1.00/25.0 (5) spectrum in Figure 7. The intensity difference in the 65 ppm peak between the 2.00/1.00/4.96 (5) spectrum of Figure 4 and the 2.00/1.00/25.0 (5) spectrum of Figure 7 is attributed to the formation of methylene methyl ethers ($-NHCH_2-OCH_3$) from methanol and methylols attached to secondary amines (IV, 65 ppm) in the concentrated reaction mixture with F/U/W molar ratio 2.00/1.00/4.96. In this case a substantial portion of the methylol moieties are tied up by methanol in the form of methylene methyl ethers; in contrast, in the more dilute reaction mixture with a F/U/W molar ratio of 2.00/1.00/25.0, methylene methyl ethers are not formed, so the free methylols (IV, 65 ppm) are again observed with larger intensity.

The spectral trends observed in connection with going from the 2.00/1.00/25.0 (5) spectrum of Figure 7 to the 2.00/1.00/107 (5) spectrum of Figure 8 are decreases in the relative intensities around 54 ppm (methylene linkages, II), 65 ppm (IV, methylols), 72 ppm (V, internal methylols and/or *N,N*-dimethylols), 69 and 76 ppm (X, XI, dimethylene ether linkages), and the region extending from 87 to 92 ppm (poly(oxymethylene glycols) and/or their hemiformals). The ^{13}C CP/MAS NMR results of these two diluted F/U = 2.00/1.00 resins prepared at pH 5 indicate that dilution reduces the formation of methylene linkages (II) involved in cross-linking and/or in cross-linking precursors, of dimethylene ether linkages (X, XI), internal methylols (Va) and/or *N,N*-dimethylol (Vb), as well as methylols (IV) attached to secondary amide groups. However, in all of these three F/U = 2.00/1.00 cases at pH 5, the ^{13}C CP/MAS results show that there are substantial amounts of methylene linkages (II, 54 ppm; III, 60 ppm) involved in cross-linking and/or in the precursors of cross-linking and of internal methylols and/or *N,N*-dimethylols present in the resulting UF resins.

(4) F/U Molar Ratio 3.00/1.00. With the F/U/W molar ratio 3.00/1.00/7.44, even after 12 h at room temperature, the reaction mixture at pH 1 remained in a viscous liquid state, instead of solidifying within 2 min, as was found with the other three resin systems prepared from lower F/U molar ratios at pH 1 under concentrated conditions. After spreading the 3.00/1.00/7.44 (1) reaction mixture on a watch glass for 1 day, a soft flexible film was formed; this is the solid on which the 3.00/1.00/7.44 (1) spectrum of Figure 4 was obtained. The 3.00/1.00/23.6 (1) reaction mixture obtained after 12 h of reaction was highly viscous and a solid component could not readily be removed directly. After spreading this material on a watch glass at pH 1 for 40 h, two apparently different solids components formed: (1) a transparent film, which consists of only a small portion of the total solids, and (2) a white solid below the transparent film. The ^{13}C CP/MAS NMR spectrum of this white solid is shown in Figure 7 (3.00/1.00/23.6 (1)).

The reaction mixture obtained from a mixture with an initial F/U/W molar ratio of 3.00/1.00/105 after 12 h of reaction at pH 1 was semisolid; it was divided into two portions. All of the first portion was vacuum dried at −5 °C for 30 h; the spectrum of the resulting powder is shown in Figure 1c. The second portion was separated into liquid and solid components, and the solid component was spread on a watch glass and allowed to dry in air for 1 day; the spectrum of this solid sample is shown in Figure 8 (3.00/1.00/105 (1)). The liquid component of this second portion was vacuum dried at −5 °C after neutralization to pH 7; the ^{13}C CP/MAS NMR spectrum of the resulting solid (not given here) shows a strong peak at about 88 ppm, with no other substantial signals. This spectrum is almost identical to the spectrum of paraformaldehyde shown in Figure 9c; the interrupted-decoupling behaviors of these two samples are also essentially the same (cf., Figure 10b). Without any UF component present, the excess formaldehyde in the separated liquid component of the second portion was converted to paraformaldehyde by vacuum drying at −5 °C and pH 7; in contrast to this conversion, most of the excess formaldehyde that accompanies an abundance of UF components in the undivided reaction mixture (first portion) was converted to urons by vacuum drying at −5 °C and pH 1, as indicated in Figure 1c and discussed above.

The 3.00/1.00/7.44 (1) spectrum in Figure 4 has intense peaks at about 47, 55, 65, 69, 72, 76, 79, 88, 92, and 160 ppm. The spectrum (not shown) from a 50-μs interrupted-decoupling experiment shows that about 80% of the 88 and 92 ppm contributions in the 3.00/1.00/7.44 (1) spectrum of Figure 4 survive interrupted decoupling; therefore, they are attributed to mobile species, such as short-chain poly(oxymethylene glycols) ($HOCH_2-(OCH_2)_n-OH$, with a small value of n) or their ethers with the methylols (IV, V) ($-N(R)-CH_2O-(CH_2O)_nH$) and/or their ethers with methanol ($-OCH_2-(OCH_2)_n-OCH_3$). The same interrupted-decoupling spectrum shows that about 40% of the 55 ppm intensity, which is about the same as the total intensity of the 94 ppm shoulder of the 3.00/1.00/7.44 (1) spectrum in Figure 4, is attributed to the methoxy

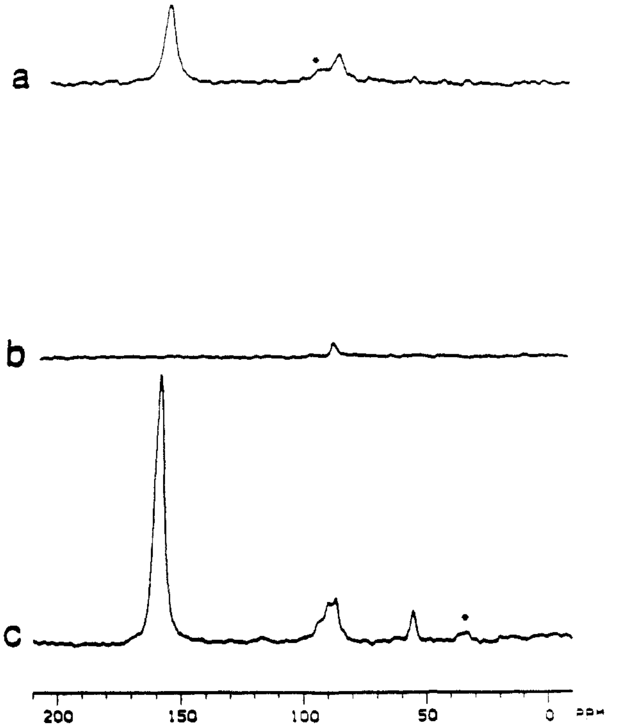


Figure 10. (a, b) 50.3-MHz interrupted-decoupling ^{13}C CP/MAS spectra corresponding to the samples in Figure 9b,c, respectively. (c) 50.3-MHz interrupted-decoupling ^{13}C CP/MAS spectrum of sample prepared with a F/U/W molar ratio of 3.00/1.00/7.44 at pH 3. Contact time = 1 ms; repetition time = 1 s; interrupted decoupling period = 50 μs. Spinning sidebands are indicated by asterisks.

groups (VIIc) of methyl ethers ($R-(OCH_2)_nOCH_3$); and only about 60% of the 55 ppm intensity is attributed to methylene linkages (II, 54 ppm) that connect one secondary amide and one tertiary amide. Therefore, the proportion of these type-II methylene linkages in the 3.00/1.00/7.44 (1) spectrum of Figure 4 is unusually low.

On the basis of the 3.00/1.00/7.44 (1) spectrum in Figure 4 and the fact that excess formaldehyde existed in the reaction mixture from which the corresponding sample was isolated, it appears that some of the excess formaldehyde was incorporated into methylene linkages in the UF resin to form dimethylene ether linkages (X, 69 ppm; XI, 76 ppm). Part of the excess formaldehyde of the 3.00/1.00/7.44 (1) reaction mixture has methylolated urea moieties to form internal methylol groups (Va) and/or *N,N*-dimethylol moieties (Vb), as revealed by the peak around 72 ppm in the spectrum; however, the existence of the peak at 79 ppm and the shoulder at 156 ppm indicate that a large fraction of the methylol groups that have been formed on the two ends of the same urea unit have condensed to form urons (XIII, XX). The remaining excess formaldehyde of the 3.00/1.00/7.44 (1) mixture apparently forms short-chain poly(oxymethylene glycols) (XVIa and XVIb, 87–92 ppm), which may exist as separate entities or attached to methylols in the form of hemiformals (VI, 87 ppm; XVIc, 88–92 ppm; XVId, 69 ppm; XVIe, 76 ppm), or can react with methanol to form methyl ethers (VIIc, 55 ppm; XVIII, 94 ppm). This last possibility may account for all the methoxy groups (VIIc, 55 ppm) observed in the ^{13}C CP/MAS spectrum of this UF resin sample. The peak around 94 ppm in the 3.00/1.00/7.44 (1) spectrum of Figure 4 is attributed to the methylene groups attached to methoxy in these methylene methyl ethers (XVIII). The high concentrations of various dimethylene ether linkages (X, 69 ppm; XI, 76 ppm), methylols (IV, 65 ppm; V, 72 ppm), and short-chain poly(oxymethylene glycols) (87–92 ppm) and their ethers in this UF resin are perhaps responsible for the fact that the 3.00/1.00/7.44 (1) reaction mixture did not solidify after the normal reaction procedure.

The 3.00/1.00/23.6 (1) spectrum of Figure 7 shows strong peaks at about 160, 54, and 47 ppm and weaker peaks at bout 79, 72, and 65 ppm. All of the 54 ppm peak intensity is attributed to methylene linkages connecting one secondary amide and one tertiary amide (II), as revealed by the essentially complete elimination of that peak from the corresponding 50-μs interrupted-decoupling spectrum (not shown). The shoulder at about 60 ppm is assigned to methylene linkages connecting two tertiary amide moieties (III). All other peaks in the 3.00/1.00/23.6 (1) spectrum of Figure 7 were also assigned as described above. The spectrum (not shown here) of the film sample obtained from the reaction mixture with an initial F/U/W molar ratio of 3.00/1.00/23.6 and pH 1 has a stronger shoulder at about 156 ppm and a stronger peak around 79 ppm than in the 3.00/1.00/23.6 (1) spectrum of Figure 7 (obtained on the powder sample isolated from the same reaction mixture). The increased intensities at about 156 and 79 ppm in the spectrum of the film sample result from the additional formation of urons (XIII, XX) in that sample.

As shown in the 3.00/1.00/105 (1) spectrum of Figure 8, the indicated resin sample contains a significant quantity of dimethylene ether linkages (X, 69 ppm; XI, 76 ppm), internal methylols (Va, 72 ppm), and/or *N,N*-dimethylols (Vb, 72 ppm); this spectrum also shows the existence of very small amounts of urons and poly(oxymethylene glycols), which contribute to the intensities of the 79 ppm peak, the 156 shoulder, and the 88 ppm peak. The main carbon-based structural constituents of this UF resin, except carbonyl groups, are methylene linkages of all three types (I, 47 ppm; II, 54 ppm; III, 60 ppm) and methylol groups (IV, 65 ppm). In moving from the 3.00/1.00/7.44 (1) spectrum of Figure 4 to the 3.00/1.00/23.6 (1) spectrum of Figure 7, the major spectral changes can be interpreted as due to the removal of the elements of formaldehyde from various dimethylene ether linkages (X, 69 ppm; XI, 76 ppm) to form the corresponding methylene linkages (I, 47 ppm; II, 54 ppm; III, 60 ppm) in response to the dilution of the reaction mixture by water. Part of the change in moving from the 3.00/1.00/23.6 (1) spectrum of Figure 7 to the 3.00/1.00/105 (1) spectrum of Figure 8 can be attributed to dilution; part of it can be blamed on the removal of excess formaldehyde in the liquid phase, which is rich in formaldehyde and was eliminated from this sample (vide supra).

The same three concentrations were employed at pH 3 to synthesize UF resins from reaction mixtures with an initial F/U molar ratio of 3.00/1.00 as discussed above for pH 1. A film and a powder portion were obtained from the reaction mixture with a F/U/W molar ratio of 3.00/1.00/7.44; the ^{13}C CP/MAS NMR spectrum of the powder portion is shown in the middle column of Figure 4. The corresponding 50-μs interrupted-decoupling spectrum shown in Figure 10c indicates that the region from 84 to 95 ppm substantially survives interrupted decoupling (63%), in contrast to the case of paraformaldehyde (see Figure 10b); therefore, the chains of poly(oxymethylene glycols) (and/or hemiformals) responsible for this part of the spectrum are short and relatively mobile. The same interrupted-decoupling spectrum (Figure 10c) shows that about 12% of the intensity around 55 ppm in the 3.00/1.00/7.44 (3) spectrum of Figure 4 survives the 50-μs interrupted-decoupling period. The surviving 55 ppm peak has about the same intensity as the shoulder at about

94 ppm (XVIII) in Figure 4 (3.00/1.00/7.44 (3)); therefore, the entire intensity of the surviving 55 ppm peak is attributed to methoxy groups (VIIc) in methyl ethers ($R(OCH_2)_nOCH_3$) of poly(oxymethylene glycols) and/or of hemiformals.

Comparing the ^{13}C CP/MAS NMR spectrum (not shown here) of the film portion obtained from the reaction mixture with a F/U/W molar ratio of 3.00/1.00/7.44 and pH 3 with that of the powder portion (Figure 4, (3.00/1.00/7.44 (3)) reveals that the intensity at 55 ppm is increased in the film-portion spectrum relative to the 47-ppm peak intensity in the powder case; this pattern can be accounted for by formation of more methoxy groups (VIIc) in the film sample. The region from 88 ppm to 92 ppm is also more intense in the film portion, because of the formation of more short, mobile poly(oxymethylene glycols) and/or hemiformals. Therefore, the major difference between the powder and film samples obtained from the 3.00/1.00/7.44 (3) reaction mixture can be attributed to the formation of more short, mobile poly(oxymethylene glycols) (and/or hemiformals) and of roughly double the amount of methyl ethers ($R-(OCH_2)_n-OCH_3$) in the film sample, as revealed by the corresponding 50-μs interrupted-decoupling ^{13}C CP/MAS NMR spectra (solid portion shown in Figure 10c; film portion not shown here).

The ^{13}C CP/MAS NMR spectra of powder portions obtained similarly (to the pH 1 case discussed above) from reaction mixtures with F/U/W molar ratios of 3.00/1.0/23.6 and 3.00/1.00/105 at pH 3 are shown in Figures 7 (middle column) and 8 (middle column), respectively. The dilution trends observed for F/U = 3.00/1.00 at pH 3 in progressing from Figure 4 (3.00/1.00/7.44 (3)) to Figure 7 (3.00/1.00/23.6 (3)) and Figure 8 (3.00/1.00/105 (3)) are obvious: relative to the intensity of the 47 ppm peak (I, linear methylene linkages), the intensity at 55 ppm decreases by about half in this progression and intensities in the regions extending from 69 to 76 ppm and from 88 and 95 ppm decrease dramatically. However, changes in relative intensities around 65 ppm are very minor. All three spectra show that there are substantial amounts of cross-linking or cross-linking precursors in these resins, as revealed by the intensities at about 54, 60, and 76 ppm, which are attributed to methylene linkages attached to one tertiary amide moiety (II), methylene linkages attached to two tertiary amide moieties (III), and dimethylene ether linkages attached to tertiary amides (XI), respectively. The extent of cross-linking is decreased by the H_2O dilution effect in the reaction mixture.

There are substantial amounts of dimethylene ether linkages (X, 69 ppm; XI, 76 ppm) present in the two samples prepared from the more concentrated reaction mixtures (Figure 4, 3.00/1.00/7.44 (3) and Figure 7, 3.00/1.00/23.6 (3)). The dilution effect and the removal of excess unreacted formaldehyde along with the liquid portion from the most dilute reaction mixture (Figure 8, 3.00/1.00/105 (3)) causes a dramatic decrease in the amount of dimethylene ether linkages (X, 69 ppm; XI, 76 ppm) in the resin formed, in comparison to the two corresponding resins obtained from the more concentrated reaction mixtures. The spectra of the two samples obtained from the more concentrated reaction mixtures (with F/U/W molar ratios 3.00/1.00/7.44 and 3.00/1.00/23.6) at pH 3 show that they contain substantial amounts of methylol groups attached to tertiary amide moieties (V, 72 ppm); the sample obtained from the most dilute reaction mixture (3.00/1.00/105 (3)) contains less, but still a substantial amount, of these methylol groups.

UF resins were synthesized at pH 5 from reaction mixtures with F/U/W molar ratios of 3.00/1.00/7.44, 3.00/1.00/23.6, and 3.00/1.00/105; ^{13}C CP/MAS spectra of these samples are shown in the right columns of Figures 4, 7, and 8, respectively. The liquid portion of the pH 5 reaction mixture with a F/U/W molar ratio of 3.00/1.00/105 was neutralized and vacuum dried at −5 °C for 1 day; the ^{13}C CP/MAS NMR spectrum of the resulting solid is shown in Figure 9b. The liquid portion of the reaction mixture at pH 5 with a starting F/U/W molar ratio of 3.00/1.00/105 is seen to contain predominantly unreacted formaldehyde, which appears in polymerized form as paraformaldehyde (88 ppm) under vacuum drying.

The spectrum in Figure 4 (3.00/1.00/7.44 (5)) shows that the UF resin prepared at pH 5 from a 3.00/1.00/7.44 reaction mixture is rich in methylene linkages (I, 47 ppm; II, 54 ppm), methoxy groups (VII, 55 ppm, surviving in the interrupted-decoupling spectrum shown in Figure 5d), dimethylene ether linkages (X, 69 ppm; XI, 76 ppm), methylene ethers (VIII, 73 ppm, IX, 80 ppm), short-chain poly(oxymethylene glycols) and their ethers (83–94 ppm, surviving intensely in the interrupted-decoupling spectrum shown in Figure 5d), and methylol groups (IV, 65 ppm; Va and/or Vb, 72 ppm).

With dilution at pH 5 to a F/U/W molar ratio of 3.00/1.00/23.6, the concentrations of all components except H_2O are decreased; under these conditions, a large portion of the methylols (IV, 65 ppm) remain unreacted instead of forming methylene methyl ethers, dimethylene ether linkages, or hemiformals ($-NR-CH_2O-(CH_2O)_nH$). A large portion of these methylol groups probably exists in the form of *N,N'*-dimethylolurea and/or trimethylolurea. For a resin produced from an identical reaction mixture with the longer reaction time of 52 h (instead of the standard 12-h of this study), the ^{13}C CP/MAS spectrum (not shown here) displays increases in the amounts of methylene methyl ethers and dimethylene ether linkages; this result implies that at pH 5 ether formation is much slower at a F/U/W molar ratio of 3.00/1.00/23.6 than at 3.00/1.00/7.44 (cf. Figure 7 (3.00/1.00/23.6 (5) and Figure 4 (3.00/1.00/7.44 (5)).

With further dilution at pH 5 to 3.00/1.00/105 and removal of excess formaldehyde along with the liquid portion, the resulting precipitate yields a ^{13}C CP/MAS NMR spectrum (Figure 8, right column) that is similar to those of UF resins prepared at pH 5 with lower F/U molar ratios. Comparing Figures 7 (3.00/1.00/23.6 (5)) and 8 (3.00/1.00/105 (5)), the peak intensities around 65 and 72 ppm are seen to be much lower for the product of the more dilute reaction mixture, even though the amounts of these methylol groups are still high even in that case. Comparing Figures 4 (3.00/1.00/7.44 (5)), 7 (3.00/1.00/23.6 (5)), and 8 (3.00/1.00/105 (5)), one sees that the concentration of ethers is highest for the resin prepared from the most concentrated reaction mixture and lowest for the resin prepared from the most dilute reaction mixture. For the pH 5 mixture with a F/U/W molar ratio of 3.00/1.00/23.6, a 52-h reaction time produces more ether groups than does a 12-h reaction time, as mentioned above. This result indicates that at pH 5, the reaction mixture with an initial F/U/W molar ratio of 3.00/1.00/23.6 is still not in an equilibrium state after 12 h of reaction, presumably because of the smaller rate of ether formation (relative to methylol formation).

(d) pH Effects. As mentioned at the beginning of this section, methylolation reactions of urea units (eq 1) are catalyzed by both acids and bases, whereas the formation of methylene linkages (I, II, III, eq 3) are catalyzed by acids but not bases. The interplay of methylolation reactions and formation of methylene linkages, together with the formation of dimethylene ether linkages, accounts largely for the complexity and variety in UF resins. Therefore, one expects to observe large pH effects on the structures of UF resins. Following the discussion in the preceding two sections, we here summarize explicitly the effects of pH on the structures of the resulting UF resins.

Under neutral or alkaline conditions and at room temperature (23 ± 2 °C), the major constituents of resins (see Figure 6) prepared from mixtures obtained from 37% formalin and urea with F/U molar ratios ranging from 1.00 to 3.00, with or without added water, are *N,N'*-dimethylolurea, monomethylolurea (IV, 65 ppm), and/or dimethylene ether linkages (X, 69 ppm). Very small amounts of trimethylolurea (IV, 65 ppm; Vb, 72 ppm) and/or *N,N*-dimethylolurea (Vb, 72 ppm) exist in the resins prepared from mixtures with a F/U molar ratio of 3.00 at pH 7 and 12. At pH 12, methylene methyl ethers exist in very small proportions in the resin products from all three concentrated reaction mixtures with F/U molar ratios of 1.50, 2.00, and 3.00; these ethers are absent in all samples prepared at pH 7 and 9. One can also see that dimethylene ether linkages (X, XI), trimethylolurea and/or *N,N*-dimethylolurea (Vb), poly(oxymethylene glycols) (XVIa, XVIb), and/or hemiformals (VI, XVIc–e) formed from methylols and poly(oxymethylene glycols) have their minimum contributions (or complete absence) at pH 9. No methylene linkages (I, II, III) were observed in any of those reaction mixtures prepared under neutral or alkaline conditions from 37% formalin and urea, with or without added water, which agrees with the view that the formation of methylene linkages are catalyzed only by acids.

When the pH value becomes lower than 7, the formation of methylene linkages (I, II, III), dimethylene ether linkages (X, XI) and urons (XII, XIII), together with the methylolation of amide groups, all become important; and the resulting UF resins are structurally more complex and more pH dependent. Therefore, in the following discussion, we concentrate on pH effects on the structures of UF resins prepared from mixtures at pH values lower than 7.

(1) F/U Molar Ratio 1.00. Because the rate and equilibrium constants for the formation of asymmetrical *N,N*-dimethylolurea are both far smaller than the corresponding quantities for monomethylolurea and/or symmetrical *N,N'*-dimethylolurea,[5] for reaction mixtures with a F/U molar ratio of 1.00 we expect the final products prepared under acidic conditions to be simple and most of the resins to be formed as linear chains; this is because of the limited amount of formaldehyde available in building the framework of the resins. The ^{13}C CP/MAS spectra of resins prepared at pH 1, 3, and 5 from mixtures with a F/U/W molar ratio of 1.00/1.00/2.48 display major features that are mutually very similar (top row of Figure 4). These three samples consist mainly of carbonyl groups (160 ppm), linear-chain methylene linkages (I, 47 ppm), and some cross-linking methylene linkages (II, 54 ppm). In addition to these main constituents, there are small amounts of methylols (IV, 65 ppm; V, 72 ppm), methylene methyl ethers (VII, 55 ppm; VIII, 73 ppm), dimethylene ether linkages (X, 69 ppm), and cross-linking methylene linkages (III, 60 ppm). Methylene methyl ethers (as revealed by the surviving 55 ppm peak in the 50-μs interrupted-decoupling spectrum shown in Figure 5a) have their highest proportions in the sample prepared at pH 5 and are negligible in the sample prepared at pH 3. Most of the intensity at about 73 ppm in the ^{13}C CP/MAS NMR spectra of those two samples prepared at pH 1 and pH 5 is attributed to the methylene groups of methylene methyl ethers ($-C(O)-N(H)-CH_2-O-CH_3$, VIII); the rest of the 73 ppm intensity is attributed to internal methylols (Va, 72 ppm) and/or *N,N*-dimethylols (Vb, 72 ppm).

With a modest degree of dilution by water, corresponding to changing the F/U/W molar ratio from 1.00/1.00/2.48 to 1.00/1.00/12.3, the pH effects on the structures of UF resins become smaller, as indicated by a comparison of the ^{13}C CP/MAS NMR spectra in the top row of Figure 7 and those in the top row of Figure 4. Variations in the contents of methylene methyl ether and methylol moieties among these three samples are smaller than the corresponding differences for samples prepared from more concentrated reaction mixtures. With further dilution to a F/U/W molar ratio of 1.00/1.00/105, the pH effects on the structures of UF resins prepared at pH 1, 3, and 5 become even smaller (cf., top row of Figure 8): the main spectral/structural features of UF resin samples prepared at pH 3 and 5 are mutually very similar; the proportions of cross-linking methylene linkages (II, 54 ppm; III, 60 ppm) and of methylols (IV, 65 ppm) are slightly higher in the sample prepared at pH 1 than in the samples prepared at pH 3 and 5.

(2) F/U Molar Ratio 1.50. With increasing amounts of formaldehyde available relative to the case of a F/U molar ratio of 1.00, pH effects on methylolation rates[1] and on the formation rates of methylene linkages[1,27] and of dimethylene ether linkages play larger roles in determining the structures of UF products. The ^{13}C CP/MAS NMR spectra of samples prepared with a F/U molar ratio of 1.50 at pH 1, 3, and 5 are shown in the second rows of Figures 4, 7, and 8 for three different concentrations.

For resins prepared from concentrated reaction mixtures at the three pH values under discussion (1, 3, 5), methylene linkages (II, 54 ppm; III, 60 ppm) involved in cross-linking and/or in cross-linking precursors decrease dramatically with increasing pH value, as indicated by the large decrease in the intensities of the peaks at 54 and 60 ppm in the spectra in the second row of Figure 4 (from left to right); in addition much smaller changes in the intensities of 72 ppm (partly due to internal methylols, Va) are observed. The amount of dimethylene ether linkages attached to tertiary amide moieties (XI, 76 ppm) decreases steadily with increasing pH, whereas the amount of dimethylene ether linkages attached to secondary amide groups (X, 69 ppm) increases slightly with increasing pH. About 70% of the intensity at 73 ppm and 40% of the intensity at about 55 ppm in the spectrum of the sample prepared at pH 5 are attributed to the methylene part and methoxy part of methylene methyl ethers ($-C(O)-NH-CH_2-OCH_3$), respectively. The amount of methylene methyl ethers was determined from the intensity of the surviving 55 ppm peak in the 50-μs interrupted-decoupling spectrum, such as that shown in Figure 5b, as discussed above. The total amount of methylene methyl ethers is highest in the sample prepared at pH 5 and is negligible in the sample prepared at pH 3. The total amount of methylol groups (IV, 65 ppm; V, 72 ppm) in these samples remains almost constant in going from pH 1 to 3, whereas that of single terminal methylol groups (IV, 65 ppm) is highest in the sample prepared at pH 5 among these three samples (pH 1, 3, 5), and that of internal methylols (Va, 72 ppm) and/or *N,N*-dimethylols (Vb, 72 ppm) is lowest in the sample prepared at pH 5. As mentioned above, in the 1.50/1.00/3.72 (5) resin, only about 30% of the intensity at 73 ppm is attributed to methylol groups and the other 70% is attributed to the methylene groups (VIII, 73 ppm) of methylene methyl ether moieties.

The spectra of samples prepared at pH 1 and 3 are more similar to each other than is either to the spectrum of the corresponding sample prepared at pH 5.

With some water dilution to a F/U/W molar ratio of 1.50/1.00/20.3 (cf., second row of Figure 7), differences in the extent of methylene linkages involved in cross-linking and/or in the precursors of cross-linking (II, 54 ppm; III, 60 ppm) among the samples prepared at the three pH values under discussion (1, 3, 5) are seen to be smaller than for the concentrated (1.50/1.00/3.72) samples. Only a very small quantity of methylene methyl ethers is seen to exist in the sample prepared at pH 5 and a negligible amount of these ethers exist in the samples prepared at pH 1 and 3, as indicated by the intensities of the surviving 55 ppm peak in the 50-μs interrupted-decoupling spectra of these three samples (not shown here). The quantities of single terminal methylols (IV, 65 ppm) in samples prepared at pH 1 and 3 are seen to be about the same, whereas this quantity is unusually high in the sample prepared at pH 5. This latter observation is due partly to the smaller rate of formation of methylene linkages from methylolureas (see eq 3) at lower acidity[1,27] and partly to the fact that the liquid portion of the reaction mixture at pH 5 was not removed from the solid portion because of separation difficulties. The appearance of a very small quantity of poly(oxymethylene glycols) and/or hemiformals (XVIa and XVIb, 87–92 ppm, and/or VI, 87 ppm; XVIc, 88–92 ppm; XVId, 69 ppm; XVIe, 76 ppm) in the sample prepared at pH 5 is also attributed to the nonremoval of the liquid portion, which is rich, relative to the solid portion, in formaldehyde and methylolureas. As is the case for samples prepared from concentrated reaction mixtures, the spectra of these three acidic 1.50/1.00/20.3 samples display the highest proportion of dimethylene ether linkages attached to secondary amides (X, 69 ppm) in the sample prepared at pH 5, whereas dimethylene ether linkages attached to tertiary amides (XI, 76 ppm) appear in the lowest proportion in the sample prepared at pH 5. Except for the unusually high proportion of single terminal methylols in the samples prepared at pH 5, pH effects on the structures of UF resins are decreased by dilution to a F/U/W molar ratio of 1.50/1.00/20.3 from 1.50/1.00/3.72, as seen by comparing the spectra in the second rows of Figures 4 and 7.

With further dilution to a F/U/W molar ratio of 1.50/1.00/105 (cf., the second row of Figure 8), the pH effect is seen to decrease even further. The cross-linking methylene linkages (II, 54 ppm; III, 60 ppm) experience decreased proportions with increasing pH values, although to a lesser extent than in the case of resins prepared from the two more concentrated reaction mixtures mentioned above. The total proportion of single terminal methylol groups (IV, 65 ppm) is about the same in these three 1.50/1.00/105 samples, as indicated in the second row of Figure 8. None of these three samples contains a significant quantity of methylene methyl ethers, as indicated by the absence of a 55 ppm peak in the 50-μs interrupted-decoupling ^{13}C CP/MAS spectra of these three samples (not shown here). There are very small amounts of dimethylene ether linkages (X, 69 ppm; XI, 76 ppm) in all three samples. In comparison to the cases of F/U molar ratio 1.00, the pH effects play a much greater role in determining the proportion of cross-linking through methylene linkages and/or cross-linking precursors in samples prepared with a F/U molar ratio of 1.50; however, these pH effects decrease with increasing dilution.

(3) F/U Molar Ratio 2.00. With higher F/U molar ratios, the formations of dimethylene ether linkages and urons become more important under acidic conditions, as discussed earlier in this paper. The ^{13}C CP/MAS NMR spectra of samples prepared from mixtures with a F/U molar ratio of 2.00 at three different concentrations and at pH 1, 3, and 5 are shown in the third rows of Figures 4, 7, and 8, respectively. Examination of the spectra shown in the third row of Figure 4 reveals that under the most concentrated conditions (2.00/1.00/4.96), the amounts of methylene linkages (II, 54 ppm; III, 60 ppm) involved in cross-linking and/or in the precursors of cross-linking decrease dramatically with increasing pH value.

The proportion of urons (XX, 156 ppm; XIII, 79 ppm) in the samples prepared with a F/U/W molar ratio of 2.00/1.00/4.96 decreases dramatically by going from pH 1 to 3 and from pH 3 to 5. The total amounts of methylols (IV, 65 ppm; V, 72 ppm) in these three 2.00/1.00/4.96 samples prepared under the most concentrated condition at pH 1, 3, and 5 are not dramatically different from each other. Samples prepared with a F/U molar ratio of 2.00 under the most concentrated condition at pH 1 and pH 3 contain approximately the same small amounts of methylene methyl ethers ($-C(O)N(R)-CH_2OCH_3$ and $R(OCH_2)_nOCH_3$), as indicated by the surviving 55 ppm peak in the 50-μs interrupted-decoupling spectra (not shown here), whereas the sample prepared at pH 5 contains a larger amount of methylene methyl ethers (see Figure 5c). There are only slight differences in the contents of poly(oxymethylene glycols) and/or hemiformals (XVIa and XVIb, 87–92 ppm, and/or VI, 87 ppm; XVIc, 88–92 ppm; XVId, 69 ppm; XVIe, 76 ppm) in these three samples prepared under concentrated conditions at pH 1, 3, and 5. Due to severe overlaps in the signals at about 69 and 76 ppm in these spectra, variation in the quantity of dimethylene ether linkages (X, 69 ppm; XI, 76 ppm) with pH variation is very difficult to ascertain; nevertheless, the spectra seem to indicate that for samples prepared from the most concentrated mixtures, the one prepared at pH 5 contains the largest amount of dimethylene ether linkages attached to secondary amides (X, 69 ppm), whereas the sample prepared at pH 1 contains the largest amount of dimethylene linkages attached to tertiary amide moieties (XI, 76 ppm).

With some dilution to a F/U/W molar ratio of 2.00/1.00/25.0 (third row of Figure 7), none of the three samples prepared at pH 1, 3, and 5 contains methyl ethers of any kind, as indicated by the absence of the 55 ppm peak in the 50-μs interrupted-decoupling spectra of these three samples (not shown here). As discussed above, pH effects on the structures of UF resins decrease with increasing dilution. The amounts of methylene linkages involved in cross-linking and/or in the cross-linking precursors (II, 54 ppm; III, 60 ppm) decrease about one-third in going from pH 1 to 3 and remain almost unchanged in going from pH 3 to 5. Other changes that accompany an increase of pH value from 1 to 3 are slight decreases in the amounts of dimethylene ether linkages attached to secondary amides (X, 69 ppm) and of internal methylols (Va, 72 ppm) and/or *N,N*-dimethylols (Vb, 72 ppm) and large decreases in the amounts of dimethylene ether linkages attached to tertiary amides (XI, 76 ppm) and urons (XIII, 79 ppm and XX, 156 ppm). The unusually high abundance of methylols (IV, 65 ppm; V, 72 ppm) and dimethylene ether linkages attached to secondary amides (X, 69 ppm) in the sample prepared at pH 5 is partly due to the nonremoval of the liquid portion of the reaction mixture, as in the case of the reaction mixture with a F/U/W molar ratio of 1.50/1.00/20.3 (vide supra). All these three 2.00/1.00/25.0 samples contain only very small amounts of poly(oxymethylene glycols) and/or hemiformals (XVIa and XVIb, 87–92 ppm, and/or VI, 87 ppm; XVIc, 88–92 ppm; XVId, 69 ppm; XVIe, 76 ppm); the sample prepared at pH 5 has the highest proportion of these glycols (and/or hemiformals) among these three samples.

For the most dilute reaction mixture, with a F/U/W molar ratio of 2.00/1.00/107 (third row of Figure 8), pH effects on the structures of UF resins prepared under acidic conditions are even smaller than for the more concentrated reaction mixtures. The proportions of methylene linkages involved in cross-linking and/or in precursors of cross-linking (II, 54 ppm; III, 60 ppm) decrease steadily with increasing pH value; however, the extent of the pH effect on the proportion of these methylene linkages is smaller than in resins prepared from the two concentrated reaction mixtures mentioned above. The quantities of dimethylene ether linkages of either type (X, 69 ppm; XI, 76 ppm) are small in all three 2.00/1.00/107 samples prepared under acidic conditions. Some urons (XX, 156 ppm; XIII, 79 ppm) are observed in samples prepared at pH 1, and much smaller amounts of urons are seen in samples prepared at pH 3 and 5. All three of these samples prepared from the most dilute reaction mixtures at pH 1, 3, and 5 contain negligible amounts of poly(oxymethylene glycols) and/or hemiformals (XVIa and XVIb, 87–92 ppm, and/or VI, 87 ppm; XVIc, 88–92 ppm; XVId, 69 ppm; XVIe, 76 ppm), as expected from the fact that any excess formaldehyde had been removed from the precipitates along with the liquid portions of the reaction mixture.

(4) F/U Molar Ratio 3.00. The ^{13}C CP/MAS NMR spectra of samples prepared at three different concentrations at pH 1, 3, and 5 are presented in the bottom rows of Figures 4, 7, and 8, respectively. With the excess formaldehyde corresponding to this F/U ratio, the resins prepared under concentrated (F/U/W molar ratio 3.00/1.00/7.44) and acidic conditions are seen to contain a large amount of ethers and poly(oxymethylene glycols). The sample prepared at pH 5 (bottom right of Figure 4) contains the largest amount of methyl ethers, which contribute about 50% of the intensity in the 55 ppm peak of the spectrum; this interpretation is indicated by the intensity of the surviving 55 ppm peak in the 50-μs interrupted-decoupling spectrum (Figure 5d). The sample prepared at pH 3 contains a slightly smaller quantity of the same sort of methyl ethers than the sample prepared at pH 1. However, both samples contain much less methyl ethers than the sample prepared at pH 5. After taking into account the contribution from methyl ethers to the spectrum of sample 3.00/1.00/7.44 (5), the remainder of the intensity in the 54 ppm peak of the spectrum is attributed to methylene linkages involved in cross-linking and/or in the precursors of cross-linking (II, 54 ppm); therefore, the proportions of these methylene linkages are about the same in the samples prepared at pH 3 and 5, with a slightly smaller amount present in the sample prepared at pH 1 (cf., spectra of bottom row in Figure 4). The unusually low proportion of methylene groups involved in cross-linking and/or precursors of cross-linking in the sample prepared at pH 1 is attributed to the insertion of formaldehyde into the methylene linkages (II, 54 ppm) to form dimethylene ether linkages attached to a secondary amide at one end and a tertiary amide at the other end (X, 69 ppm; XI, 76 ppm). This kind of dimethylene ether formation is most prevalent at pH 1 and least prevalent at pH 5 among these three pH values.

Due to severe overlapping in the 60 ppm region of the spectra in the bottom row in Figure 4, the proportions of methylene linkages (III, 60 ppm) involved in cross-linking and/or in the precursors of cross-linking are not easy to ascertain. However, after deconvolution of their spectra it seems that all three 3.00/1.00/7.44 samples contain a significant amount of these types of structures. The proportions of dimethylene ether linkages (X, 69 ppm; XI, 76 ppm), hemiformals (VI, 87 ppm; XVIc, 88–92 ppm; XVId, 69 ppm, and/or XVIe, 76 ppm), methylols (IV, 65 ppm; V, 72 ppm), urons (XX, 156 ppm and XIII, 79 ppm), methylene glycol (XIV, 83 ppm), and short-chain poly(oxymethylene glycols) (XVIa and XVIb, 87–92 ppm) are quite high in the 3.00/1.00/7.44 sample prepared at pH 5.

The immediate structural environments of carbonyl groups of the 3.00/1.00/7.44 samples prepared at pH 1 and 5 are complicated. Therefore, line widths of the peaks at about 160 ppm in the spectra of these two samples are large. Methylene glycol (VIV, 83 ppm) and poly(oxymethylene glycols) and/or hemiformals (XVIa and XVIb, 87–92 ppm, and/or VI, 87 ppm; XVIc, 88–92 ppm; XVId, 69 ppm; XVIe, 76 ppm) in these three 3.00/1.00/7.44 samples are relatively mobile, as indicated by the surviving intensity in the region from 83 to 94 ppm in the interrupted-decoupling spectra (Figure 5d for pH 5; Figure 10c for pH 3; spectrum not shown here for pH 1). The high mobilities of these poly(oxymethylene glycols) and/or hemiformals are attributed to the short chains of these structures. Long-chain poly(oxymethylene glycols), the major constituents of paraformaldehyde, do not yield an intense interrupted-decoupling ^{13}C spectrum (Figure 10b). Parts of the methylols in the three 3.00/1.00/7.44 samples prepared at pH 1, 3, and 5 form hemiformals ($-C(O)-N(R)-CH_2O-(CH_2O)_nH$) with poly(oxymethylene glycols).

Besides forming hemiformals with poly(oxymethylene glycols), methylol groups on both sides of the same urea unit can combine to form urons (XII, 75 ppm; XIII, 79 ppm; XIX 157 ppm; XX, 156 ppm). As revealed in the bottom row of Figure 4, all three 3.00/1.00/7.44 samples (at pH 1, 3, 5) contain some portions of urons, with the highest proportion occurring in the sample prepared at pH 1. With the degree of dilution represented by the F/U/W molar ratio of 3.00/1.00/23.6 (bottom row of Figure 7), the formations of not only hemiformals but also dimethylene ether linkages become less favorable. Liberated from being tied up as dimethylene ether linkages, the methylene groups involved in cross-linking (II, 54 ppm; III, 60 ppm) assume the highest proportion in the sample prepared at pH 1 among the 3.00/1.00/23.6 samples prepared at pH values of 1, 3, and 5. The proportion of cross-linking and/or cross-linking precursors in the resins decreases with increasing pH value in these three 3.00/1.00/23.6 samples.

In accordance with the limited water solublity of *N,N'*-dimethylolurea (12 g/100 g) and other methylolureas, most molecules containing unreacted methylolurea groups have limited solubility at pH 5 and contribute to precipitates. The room-temperature formation rates of methylene linkages from methylolureas are small at pH 5.[27] Therefore, the major portion of the largely undissolved methylolureas do not undergo condensation reactions to form methylene linkages (eq 3). However, as discussed under the section on concentration effects above, with the longer reaction time of 52 h instead of 12 h, more methylene methyl ethers and dimethylene ethers (X, 69 ppm; XI, 76 ppm) are formed from these methylolureas. With higher formation rates of methylene linkages from methylolureas (eq 3) at pH 1 and 3,[27] the effect of low methylolurea solubilities is less constraining; therefore, the proportions of cross-linking and/or cross-linking precursors are higher and the average chain lengths larger in the 3.00/1.00/23.6

samples prepared at the two lower pH values than in the 3.00/1.00/23.6 sample prepared at pH 5. The amounts of internal methylols (Va, 72 ppm) and/or *N,N*-dimethylols (Vb, 72 ppm) are about the same in these three 3.00/1.00/23.0 samples. The amounts of relatively mobile poly(oxymethylene glycols) and/or hemiformals (XVIa and XVIb, 87–92 ppm, and/or VI, 87 ppm; XVIc, 88–92 ppm; XVId, 69 ppm; XVIe, 76 ppm) in the samples increase with increasing pH value, as indicated by the surviving intensities in the region extending from 88 to 92 ppm in the 50-μs interrupted-decoupling spectra of these three 3.00/1.00/23.6 samples (not shown here); those results also indicate that the unreacted formaldehyde (presumably in the form of poly(oxymethylene glycols) in aqueous solution) has its lowest concentration at pH 1. A large portion of the methylol moieties in the 3.00/1.00/23.6 sample prepared at pH 1 has been transformed into urons (XII, 76 ppm; XIII, 79 ppm; XIX, 157 ppm; XX 156 ppm); the amount of these urons in the sample prepared at pH 3 from a 3.00/1.00/23.6 mixture is much lower.

With further dilution to a F/U/W molar ratio of 3.00/1.00/105 (spectra in the bottom row of Figure 8), the proportion of methylene linkages (II, 54 ppm; III, 60 ppm) involved in cross-linking and/or in the precursors of cross-linking in these three acidic 3.00/1.00/105 samples decreases with increasing pH value, although the extent of this pH dependence is moderate and all three samples contain substantial amounts of cross-linking and/or cross-linking precursors. The proportion of methylols (IV, 65 ppm; V, 72 ppm) in the samples increases slightly with increasing pH value in this 3.00/1.00/105 system. Similar to the case of other F/U molar ratios, the proportion of dimethylene ether linkages attached to secondary amides (X, 69 ppm) is highest in the sample prepared at pH 5, whereas the proportion of dimethylene ether linkages attached to tertiary amides (XI, 76 ppm) decreases dramatically with increasing pH value. All three 3.00/1.00/105 samples contain very small amounts of poly(oxymethylene glycols) and/or hemiformals (XVIa and XVIb, 87–92 ppm, and/or VI, 87 ppm; XVIc, 88–92 ppm; XVId, 69 ppm; XVIe, 76 ppm).

Summary and Conclusions

The ^{13}C CP/MAS study of UF resins prepared at room temperature provides a wide range of systematic information concerning the effects of pH, concentration, and F/U molar ratio on the structures of the solid portions of resins formed under these conditions. At pH values of 7 or higher, the major or only constituents of the solid portions of resins prepared from reaction mixtures with F/U molar ratios of 1.00, 1.50, 2.00, and 3.00 are constructed of methylolureas and dimethylene ether linkages. Small portions of methylene methyl ethers are produced in the samples prepared at pH 12 from mixtures with F/U molar ratios of 1.50, 2.00, and 3.00. Reaction mixtures with a F/U molar ratio of 3.00 produce very small quantities of trimethylolurea and/or *N,N*-dimethylolurea in samples prepared at pH 7, 9, and 12. The methylolation rate of urea by 37% formalin is large enough to produce substantial quantities of methylolureas even at pH 7 and −5 °C within 24 h, although the formation of methylene linkages is negligible at pH values of 7 or higher at room temperature (23 ± 2 °C).

The structures of UF resins prepared under acidic conditions with different F/U molar ratios at different concentrations and pH values range from very simple to very complicated. The effects of F/U molar ratio and of pH value on the resin structure are larger for more concentrated reaction mixtures and become much smaller with dilute reaction mixtures. In addition to the predominant linear-chain methylene linkages, the resins prepared even with a F/U molar ratio of 1.00 at pH 1, 3, and 5 contain substantial amounts of cross-linking methylene linkages. The proportion of cross-linking increases by increasing the F/U molar ratio from 1.00 to 2.00 and increases by decreasing the pH from 5 to 1. With a F/U molar ratio of 3.00, methylene linkages, dimethylene ether linkages, methylols and their hemiformals become major constituents in concentrated reaction mixtures under acidic conditions. The tendency to form dimethylene ether linkages attached to secondary amides is highest at pH 5 among three acidic pH values investigated (pH 1, 3, 5), whereas the tendency to form dimethylene ether linkages attached to tertiary amides is highest at pH 1. Those samples prepared under acidic conditions from concentrated reaction mixtures with F/U molar ratios of 2.00 and 3.00 contain substantial amounts of disubstituted urons. The proportions of these urons decrease with increasing pH value. The presence of excess formaldehyde with UF resins in concentrated reaction mixtures causes formation of short-chain hemiformals with methylol groups under acidic conditions. In the absence of UF resins, such as when the excess formaldehyde was contained in a liquid phase and removed along with the liquid portion from the precipitate, the excess formaldehyde polymerizes to form long-chain paraformaldehyde. For the three acidic pH regimes investigated (pH 1, 3, 5), the tendency for methanol from 37% formalin to form methylene methyl ethers with methylols in resins is highest at pH 5 and lowest at pH 3 in concentrated mixtures with F/U molar ratios of 1.00, 1.50, and 2.00. With a F/U molar ratio of 3.00, methanol tends to form methylene methyl ethers with poly(oxymethylene glycols) (and/or with hemiformals) instead of methylols attached to resins under acidic conditions.

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