

NMR Study of the Stabilities of Urea-Formaldehyde Resin Components Toward Hydrolytic Treatments

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SYNOPSIS

The solid residues of nine urea-formaldehyde (UF) resins after hydrolytic treatment at pH 4 and 86°C for 20 h and the solid residues of one UF resin after eight different hydrolytic treatments were examined by ^{13}C -CP-MAS NMR. The relative stability toward hydrolysis of each structural component in each UF resin was established for various hydrolytic conditions. In general, UF resins prepared from starting mixtures with a formal F/U molar ratio of 1.00 show a high degree of stability toward hydrolysis. Cross-linking methylene linkages in the UF resins show a higher susceptibility to hydrolytic treatments at pH 4 and 86°C than do linear methylene linkages. UF resins prepared with an F/U molar ratio of 2.00 are susceptible to hydrolysis at pH 4 and 86°C. Dimethylene ether linkages, methylols attached to tertiary amides, and poly (oxymethylene glycol) moieties are probably the main formaldehyde emitters in UF resin products. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Urea-formaldehyde (UF) resins¹ have been used widely as binders in various wood products. However, both poor durability and the emission of formaldehyde¹⁻¹⁶ are important drawbacks to the use of cured UF resin products. It has been widely believed that these deficiencies are due, to a considerable degree, to hydrolytic degradation of UF resins, especially under warm conditions of high humidity and high acidity. A detailed chemical knowledge of these degradative processes would be beneficial for the most effective utilization, and perhaps the improvement, of UF resin products.

The high-resolution solid-state ^{13}C -NMR technique that consists of the combination of cross-polarization (CP)¹⁷ with high-power ^1H decoupling and magic-angle spinning (MAS),¹⁸ referred to as ^{13}C -CP-MAS,¹⁹ has been shown to be a powerful tool in elucidating the structural details of UF resins,²⁰⁻²³ especially for insoluble resins. In this article, we present results of a continuing NMR-based study of UF resins. The aim of the work presented here was elucidation of the hydrolytic degradative char-

acteristics in 10 representative UF resins investigated.

EXPERIMENTAL

Samples

The preparation of solid UF resins from 37% formalin and urea or from a "*N,N'*-dimethylolurea reagent" have been described elsewhere.^{21,22} The *N,N'*-dimethylolurea reagent contains 92% (by wt) *N,N'*-dimethylolurea [$\text{HOCH}_2\text{NHC}(\text{O})\text{NHCH}_2\text{OH}$] and 8% (by wt) monomethylolurea [$\text{NH}_2\text{C}(\text{O})\text{NHCH}_2\text{OH}$]. The formaldehyde/urea/water ratios or "equivalent" formaldehyde/urea/water molar ratios (F/U/W) are based on the $\text{—CH}_2\text{O—}$ and $\text{NC}(\text{O})\text{N}$ moieties and H_2O present in the starting materials of the UF resin preparations. In this article, the solid UF resins are denoted in terms of the F/U/W molar ratios in the starting materials and the pH value of the preparative reaction mixture, e.g., 2.00/1.00/4.96(3) designates the solid UF resin prepared from a mixture with an F/U/W molar ratio of 2.00/1.00/4.96 at pH 3. The following

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seven previously described solid UF resins²¹ were subjected to hydrolytic treatment at pH 4 and 86°C for 20 h, all with a resin-to-water ratio of 1-to-50 by weight: 1.00/1.00/2.48(1), 1.00/1.00/2.48(3), 1.00/1.00/105(1), 1.00/1.00/105(5), 2.00/1.00/4.96(1), 2.00/1.00/25.0(3), and 2.00/1.00/107(3). One solid 2.00/1.00/4.96(3) UF resin was subjected to hydrolytic treatments at pH 1, 4, and 5 at 25°C and to hydrolytic treatments at pH 1, 4, 7, 9, and 12 at 86°C. The solid residues of these UF resins after hydrolytic treatments were collected by filtration or decanting for ¹³C-CP-MAS NMR investigation. Another solid investigated by ¹³C-CP-MAS NMR was prepared from a solution obtained by mixing 37% formalin and urea with an F/U/W molar ratio of 1.00/1.00/2.48 at pH 9 and 23°C for 12 h, followed by acidification by 85% phosphoric acid to pH 4 and maintaining the mixture at 86°C and pH 4 for 20 h. One previously described 1.90/1.00/4.96(1)²² UF resin prepared from the “*N,N'*-dimethylolurea reagent” was subjected to hydrolytic treatment at pH 4 and 86°C for 20 h, and the resulting residue was investigated by ¹³C-CP-MAS NMR.

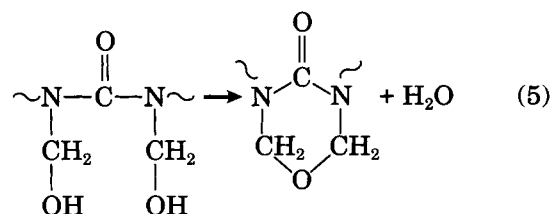
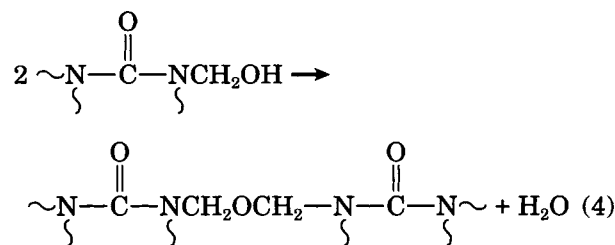
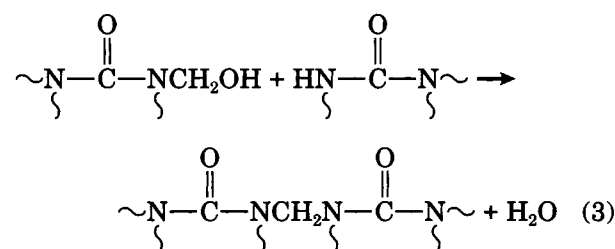
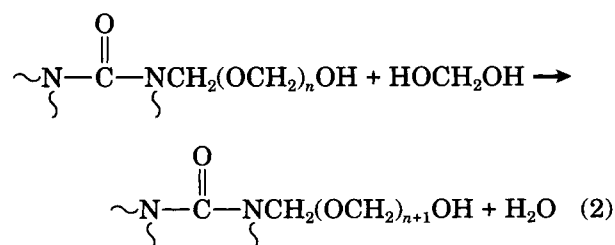
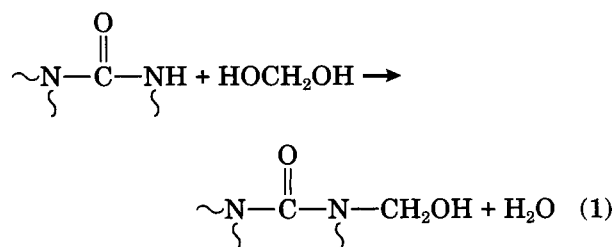
NMR Measurements

¹³C-CP-MAS NMR spectra were obtained at 50.3 MHz on a home-modified Nicolet NT-200 spectrometer. For UF resins at this field of 4.7 T, the residual line width due to the nuclear electric quadrupole effect²⁴⁻²⁹ of ¹⁴N on MAS averaging of the ¹³C—¹⁴N dipolar interaction is sufficiently small so that MAS averaging provides ¹³C peaks with enough resolution to permit reasonably accurate measurements of peak positions and intensities. Most spectra were obtained with a 1 ms CP contact time and 1 s repetition time, except for some variable contact-time experiments (*vide infra*) carried out to elucidate CP spin dynamics. ¹³C spectra of UF resin samples were also taken with the interrupted-decoupling (dipolar-dephasing) CP-MAS technique,³⁰⁻³² with a 50 μs interrupt period.

For all the UF resin samples of this study, MAS speeds of about 6.6 kHz provide spectra with small spinning sidebands placed outside the centerband region of the spectrum. A MAS speed of about 3.4 kHz was also used for some UF samples; it has been found that the relative intensities in CP-MAS spectra do not change with MAS speeds between 3.4 and 6.6 kHz for the rigid, hydrogen-bearing carbons²¹ of UF resin systems. Spectral deconvolutions were carried out using the Nicolet NTC software on the 1180 data system.

RESULTS AND DISCUSSION

The formation of a UF polymer is believed to occur via some combination of the following reactions:



The numbering system used here for the structural fragments that one might expect to appear in UF resins is based primarily on what was used in previous articles.^{21,22} Some of the structures are listed in Table I, together with their ¹³C chemical shifts (given in ppm with respect to tetramethylsilane). The reactions represented in eq. (1) are reversible. The reaction products between urea and formalde-

Table I ^{13}C -NMR Chemical Shifts of Some of the Most Important Structural Fragments that May Exist in the UF Resins Discussed in This Article

Structural Fragment	Name of Group	Position Label	^{13}C Chemical Shift (ppm)
$\begin{array}{c} \text{O} \qquad \qquad \text{O} \\ \parallel \qquad \qquad \parallel \\ -\text{C}-\text{NH}-\text{CH}_2-\text{NH}-\text{C}- \\ \qquad \qquad \qquad \text{a} \end{array}$	Methylene linkage	Ia	47
$\begin{array}{c} \text{O} \qquad \qquad \text{O} \\ \parallel \qquad \qquad \parallel \\ -\text{C}-\text{N}-\text{CH}_2-\text{NH}-\text{C}- \\ \qquad \qquad \qquad \text{a} \\ \qquad \qquad \qquad \text{b} \\ \qquad \qquad \qquad \text{c} \\ \qquad \qquad \qquad \\ \qquad \qquad \qquad \text{CH}_2-\text{R} \end{array}$	Methylene linkage		
a: $\text{R} \equiv \text{OH}$	Cross-linking precursor	IIa	54
b: $\text{R} \equiv \text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-$	Cross-linking methylene	IIb	54
c: $\text{R} \equiv \text{OCH}_2-\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-$	Cross-linking methylene	IIc	54
$\begin{array}{c} \text{O} \qquad \qquad \text{O} \\ \parallel \qquad \qquad \parallel \\ -\text{C}-\text{N}-\text{CH}_2-\text{N}-\text{C}- \\ \qquad \qquad \qquad \text{a} \\ \qquad \qquad \qquad \qquad \qquad \\ \qquad \qquad \qquad \text{CH}_2- \qquad \qquad \text{CH}_2- \end{array}$	Methylene linkage (cross-linking)	IIIa	60
$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{NH}-\text{CH}_2-\text{OH} \\ \qquad \qquad \qquad \text{a} \end{array}$	Methylol	IVa	65
$\begin{array}{c} \text{O} \qquad \qquad \text{O} \\ \parallel \qquad \qquad \parallel \\ -\text{C}-\text{N}-\text{CH}_2\text{OH} \\ \qquad \qquad \qquad \text{a} \\ \qquad \qquad \qquad \text{b} \\ \qquad \qquad \qquad \\ \qquad \qquad \qquad \text{CH}_2-\text{R} \end{array}$	Pendant methylol	Va	72
a: ($\text{R} \equiv \text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-$ or $\text{OCH}_2-\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-$)			
b: $\text{R} \equiv \text{OH}$	Geminate methylol	Vb	72
$\begin{array}{c} \text{O} \\ \parallel \\ -\text{NH}-\text{C}-\text{NH}-\text{CH}_2-\text{O}-\text{CH}_3 \\ \qquad \qquad \qquad \text{a} \qquad \qquad \qquad \text{b} \end{array}$	Methylene methyl ether	VIIa VIIb	73 55
$\begin{array}{c} \text{O} \qquad \qquad \text{O} \\ \parallel \qquad \qquad \parallel \\ -\text{C}-\text{NH}-\text{CH}_2-\text{O}-\text{CH}_2-\text{N}-\text{C}- \\ \qquad \qquad \qquad \text{a} \qquad \qquad \qquad \\ \qquad \qquad \qquad \qquad \qquad \qquad \text{R} \end{array}$	Dimethylene ether linkage	Xa	69
(R \equiv H or $-\text{CH}_2-$)			

hyde can range from the simple one, monomethylolurea, $\text{H}_2\text{NC}(\text{O})\text{NHCH}_2\text{OH}$, to very complicated, widely cross-linked three-dimensional products,^{1,21} some involving uronic units (**XIII**). Even though

the C—N bonds connecting a uron unit with the remainder of the UF macromolecules are susceptible to hydrolysis,¹⁰ the uronic ring as a unit might *a priori* be stable toward hydrolysis.

Table I (Continued)

Structural Fragment	Name of Group	Position Label	¹³ C Chemical Shift (ppm)
$\begin{array}{c} \text{O} & & \text{O} \\ \parallel & & \parallel \\ -\text{C}-\text{N}-\text{CH}_2-\text{O}-\text{CH}_2-\text{N}-\text{C}- \\ & & \\ \text{CH}_2- & & \text{R} \end{array}$	Dimethylene ether linkage	XIa	76
(R ≡ H or -CH ₂ -)			
$\begin{array}{c} \text{O} \\ \parallel \\ \text{N}-\text{C}-\text{N} \\ \quad \\ \text{CH}_2 \quad \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O} \end{array}$	Disubstituted uron	XIIIa $\begin{array}{l} -\text{CH}_2- \\ > \text{C}=\text{O} \end{array}$ XIIIb	79 156
$\begin{array}{c} \text{O} \\ \parallel \\ > \text{N}-\text{C}-\text{N} < \end{array}$	Carbonyl		155–169
$\text{HOCH}_2\text{O}(\text{-CH}_2\text{-O})_n\text{-CH}_2\text{OH}$	Poly(oxymethylene glycols)	XIVab	87–92

Poor UF resin durability and formaldehyde emission¹⁻¹⁶ are due, to a considerable degree, to hydrolytic degradation of UF resins according to the back reactions represented in eq. (1) to eq. (4). Before one can effectively improve the performance of UF adhesives, it is important to understand what role each reaction plays in these disadvantages. A logical extension of previous ¹³C-CP-MAS studies of UF resins is the investigation of the hydrolytic degradation.

In ¹³C-CP-MAS spectra, the peak intensity of each peak depends not only on the relative concentration of the corresponding type of carbon environment, but also on the ¹H—¹³C cross-polarization efficiency. From a variable contact-time experiment, one can extract, for each individual peak in the ¹³C-CP-MAS spectrum³³ at a given MAS spinning speed under the Hartmann-Hahn rf match³⁴ condition, values of the ideal (full) cross-polarized ¹³C magnetization, T_{CH}^{-1} (the ¹H—¹³C cross-polarization rate constant), and $T_{1\rho}^{\text{H}}$ (the rotating-frame spin-lattice relaxation time of the proton set from which polarization is transferred to each ¹³C spin isochromat). With these three parameters obtained from a variable contact-time experiment, one can calculate the CP efficiencies and the "ideal" CP intensity for any CP contact time (e.g., 1 ms) for each individual peak at the given MAS speed. For a 1 ms CP contact time, the maximum difference among the cross-polarization efficiencies for the peaks of the rather rigid hydrogen-bearing carbons *within* a given UF spectrum was found to be 3%, even with a sample

spinning rate up to 6.7 kHz.²¹ Within a given UF spectrum, differences between the cross-polarization efficiencies in a CP-MAS experiment with a 1 ms contact time for carbonyl carbons (nonhydrogen-bearing) and "rigid" hydrogen-bearing carbons were found to range from 0 to 14%, depending on the sample and MAS speed.²¹ Hence, substantially quantitative comparisons *within a given UF sample* can be made directly from the raw ¹³C-CP-MAS-NMR intensities for carbon atoms that are directly attached to protons, such as methylene linkages (**Ia**, 47 ppm; **Ib**, 54 ppm; **IIIa**, 60 ppm), methylol groups (**IVa**, 65 ppm; **Va**, 72 ppm), dimethylene ether linkages (**Xa**, 69 ppm; **XIa**, 76 ppm), and long-chain poly(oxymethylene glycols) (**XIVab**, 87–92 ppm).

¹³C-NMR chemical shifts of some possible or likely structural fragments of UF resins have been discussed in detail in a previous article²¹ and are listed in Table I. These chemical shift values are based on liquid-state ¹³C-NMR studies of model compounds and UF resins^{22,35-44} and ¹³C-CP-MAS studies on *N,N'*-dimethylolurea, methylenediurea,²¹ and various solid UF resin products.²⁰⁻²² Due to the extensive inhomogeneous broadening (chemical shift dispersion) associated with amorphous solids, the chemical shifts are expressed only to the nearest ppm in Table I.

In liquid-sample ¹³C-NMR spectra of UF resins,^{22,35-44} the spectral region around 160 ppm can provide a good diagnostic tool for the determination of the chemical environments of the various carbonyl groups. However, in the ¹³C-CP-MAS spectra of

most *solid* UF resins,²⁰⁻²³ all the signals corresponding to carbonyl carbons appear at about 160 ppm without any fine structure. Therefore, this spectral region does not provide a good diagnostic tool for the determination of the various carbonyl environments of UF resins in a *solid* sample. Some of the exceptions to this general statement have been discussed in a previous article.²¹ One of the exceptions pertinent to this article is the carbonyl groups of disubstituted urons (**XIIIb**), which have a ¹³C chemical shift of 156 ppm^{21,36-38,43}; this peak is usually accompanied by a peak with twice its intensity at about 79 ppm,^{21,36-38,43} which is attributed to the dimethylene ether linkage (**XIIIa**) in disubstituted uronic rings. Later in this article, a 156 ppm shoulder of the 160 ppm peak and the 79 ppm peak are used to establish the existence of urons in some of the UF resins of this study.

Interrupted-decoupling ¹³C-CP-MAS spectra provide information on the strength of ¹H—¹³C magnetic dipolar interactions.³⁰⁻³² During the interrupted-decoupling period, ¹H—¹³C dipolar interactions cause dephasing of the ¹³C magnetization vectors; the weaker the dipolar interactions, the less extensive the dephasing. Therefore, the magnetization of a ¹³C nucleus without one or more directly attached protons, or a ¹³C nucleus in a rapidly rotating moiety, such as —CH₃, can substantially survive an interrupted-decoupling period of 50 μs. This kind of structural dependence of the interrupted-decoupling behavior is used in this article, as well as in a previous article,²¹ to distinguish methoxy groups (**VIIb**) of methylene ethers from methylene linkages (**II**) that connect secondary amide and tertiary amide groups. Both **VIIb** and **IIa** have roughly the same ¹³C chemical shift of about 55 ppm, but the ¹³C-NMR signal of a rapidly rotating methyl group in —OCH₃ can survive a 50 μs interrupted-decoupling period, whereas the signal originating from methylene linkages (**II**) cannot.

In general, the pH values of various woods range from 3.0 to 5.5.⁴⁵ Johns and Niazi observed a range of pH values from 4.00 to 5.86 for 10 hardwoods and 4.02 to 5.82 for nine softwoods.⁴⁶ Acid curing of UF resins provides a shorter press time and/or lower press temperature and has been the common practice for UF/wood products.¹¹ In some industrial applications, ammonium chloride is used as a latent catalyst; it can bring the pH value of a UF resin reaction mixture down to about 4.^{3,47} Our previous ¹³C-CP-MAS NMR studies of UF resins^{21,22} confirm the formation of linear methylene linkages (**Ia**) and cross-linking methylene linkages (**IIbc**, **IIIa**) under acidic conditions, at least at room temperature. Based on the pH values of various woods and on the

pH values often used in UF reaction mixtures for curing, we emphasize in this article the hydrolytic stabilities of UF resins at pH 4 and then extend the investigation to other pH values for one UF resin sample.

In a UF resin prepared from a reaction mixture with a formaldehyde-to-urea (F/U) molar ratio of 1.00/1.00, the predominant constituents formed under acidic conditions are straight-chain methylene linkages (**Ia**, 47 ppm) connecting two urea units (carbonyl, 160 ppm), with a substantial amount of cross-linking methylene linkages (**IIb**, 54 ppm) and small amounts of methylols (**IVa**, 65 ppm) and other minor products.^{21,22} Under basic conditions, UF reaction mixtures with an F/U molar ratio of 1.00/1.00 consist mainly of *N,N'*-dimethylolurea, monomethylolurea, and dimethylene ether linkages (**Xa**, 69 ppm). It is interesting to study the hydrolytic stabilities of these 1.00/1.00 UF resins first.

Figure 1 shows the ¹³C-CP-MAS spectra of the 1.00/1.00/2.48(3) UF resin before and after hydrolytic treatment at pH 4 and 86°C for 20 h. Peak positions at 47, 54, 65, 72, and 160 ppm of the ¹³C-CP-MAS spectrum of the 1.00/1.00/2.48(3) sample [Fig. 1(a)] have been assigned to linear methylene linkages (**I**), cross-linking methylene linkages (**IIb**), terminal methylols (**IVa**), pendant methylols (**Va**) and/or geminate methylols (**Vb**), and carbonyl groups, respectively. Careful comparison of parts (a) and (b) of Figure 1 indicates that, after hydrolytic treatment, a small amount of cross-linking methylene linkages (**IIb**, shoulder at 54 ppm) disappear and probably most of the pendant methylols (**Va**) and/or geminate methylols (**Vb**, 72 ppm) are degraded, whereas linear methylene linkages (**Ia**, 47 ppm) and terminal methylols (**IV**, 65 ppm) are relatively stable toward this hydrolytic treatment.

In a previous article,²¹ we indicated that a reaction mixture with a F/U/W molar ratio of 1.00/1.00/2.48 remained in a clear solution state at pH 9 and 23°C even after reacting for 12 h. The liquid-sample ¹³C-NMR spectrum showed that this clear solution consists mainly of *N,N'*-dimethylolurea, monomethylolurea, and urea.⁴⁸ A solid 1.00/1.00/2.48(9) sample was obtained by vacuum drying of that solution at -5°C.²¹ In a new experiment, we brought a clear 1.00/1.00/2.48(9) solution to pH 4 by addition of 85% phosphoric acid and kept the mixture at 86°C for 20 h. The resulting precipitate was collected and is designated as 1.00/1.00/2.48(9;4). The spectrum of the 1.00/1.00/2.48(9) solid, shown in Figure 2(a), indicates that the main constituents of this sample are *N,N'*-dimethylolurea and monomethylolurea; the splittings of the 160 ppm peak and the 65 ppm peak are the results of residual

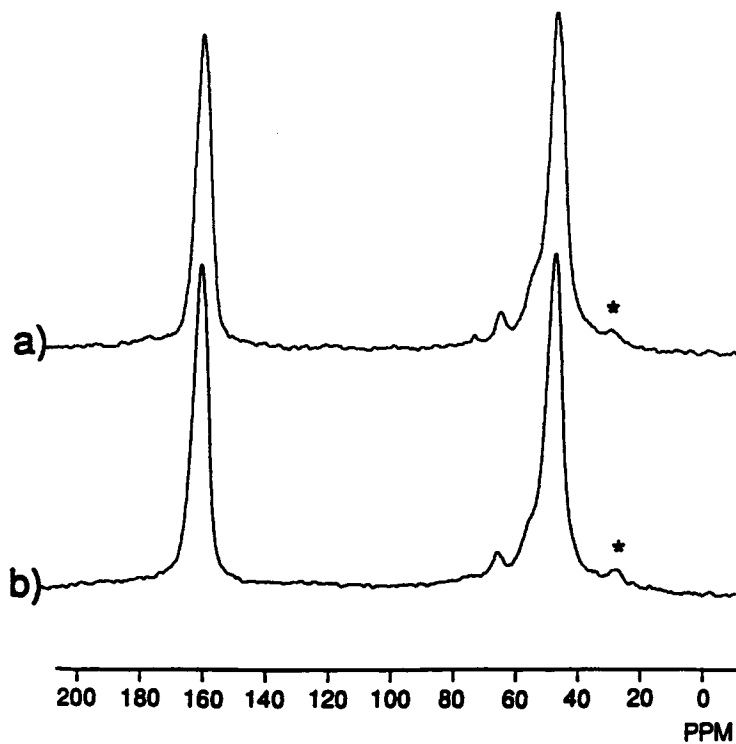


Figure 1 (a) 50.3 MHz ^{13}C -CP-MAS NMR spectra of a UF resin sample prepared from formalin and urea with an equivalent F/U/W molar ratio of 1.00/1.00/2.48 at pH 3 and (b) its solid residue after hydrolytic treatment at pH 4 and 86°C for 20 h. CP contact time = 1 ms; repetition time = 1 s. Spinning sidebands are indicated by asterisks.

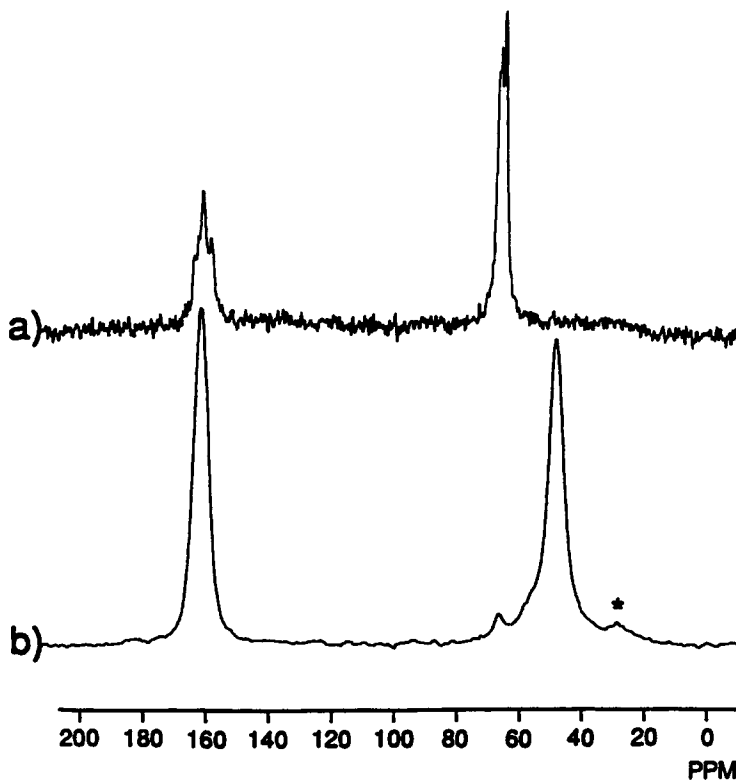


Figure 2 50.3 MHz ^{13}C -CP-MAS NMR spectra of solid UF resin 1.00/1.00/2.48 samples prepared at pH 9 (a clear solution): (a) solid obtained after vacuum drying of the clear solution at -5°C ; (b) solid residue resulting from bringing the solution to pH 4 and 86°C and kept in that condition for 20 h. CP contact time = 1 ms; repetition time = 1 s. Spinning sidebands are indicated by asterisks.

quadrupolar effects of ^{14}N on ^{13}C in the solid-state MAS NMR spectrum,^{20-22,24-29} as previously reported for polycrystalline powders of these substances.²¹ From the ^{13}C -CP-MAS spectrum of the 1.00/1.00/2.48(9; 4) sample [Fig. 2(b)], one can see that during the 20 h period at pH 4 and 86°C *N,N'*-dimethylolurea, monomethylolurea, and urea started to form linear methylene linkages (**Ia**, 47 ppm) and a small amount of cross-linking methylene linkages (**I**b****, 54 ppm) and methylol groups (**IVa**, 65 ppm). Previous ^{13}C -CP-MAS NMR studies indicated that acidity is required for the formation of methylene linkages^{21,22}; therefore, it is not surprising to find such linkages in the 1.00/1.00/2.48(9;4) resin.

The main constituents of the 1.00/1.00/2.48(1) UF resin represented in Figure 3(a) are linear methylene linkages (**Ia**, 47 ppm) and carbonyl groups (160 ppm), a substantial amount of cross-linking methylene linkages (**I**b****, 54 ppm) and some terminal methylols (**IVa**, 65 ppm) and methylene methyl ethers connected to secondary amides (**VIIb**, 55 ppm; **VIIa**, 73 ppm). From the ^{13}C -CP-MAS spectrum of the 1.00/1.00/2.48(1) UF resin after hydrolytic treatment at pH 4 and 86°C for 20 h [Fig.

3(b)], one sees that a substantial amount of cross-linking methylene linkages have undergone hydrolytic degradation. Even though UF resin 1.00/1.00/2.48(1) manifests more cross-linking methylene linkages (**I**b****, 54 ppm) than does the UF resin 1.00/1.00/2.48(3) [cf. Figs. 1(a) and 3(a)], the cross-linking methylene linkages in UF resin 1.00/1.00/2.48(3) survive the hydrolytic treatment much better than do those in the UF resin 1.00/1.00/2.48(1) [cf. Figs. 1(b) and 3(b)]. The formation of methylene linkages (**I**, **II**, **III**) in a UF resin is catalyzed by acid^{1,11,21,22}; therefore, the cross-linking methylene linkages (**II**) in UF resin 1.00/1.00/2.48(1) may have been formed so rapidly that there was insufficient time for them to adopt the thermodynamically most stable configurations. Hence, they may have been formed with considerable strain and were thus more susceptible to hydrolytic degradation.

The UF resins 1.00/1.00/105(1) and 1.00/1.00/105(5) were also subjected to hydrolytic treatments at pH 4 and 86°C for 20 h. The ^{13}C -CP-MAS spectra (not shown here) of the UF resin 1.00/1.00/105(1) and of its residue after hydrolytic treatment indicate that cross-linking methylene linkages (**I**b****, 54 ppm) only partially survive the hydrolytic treatment,

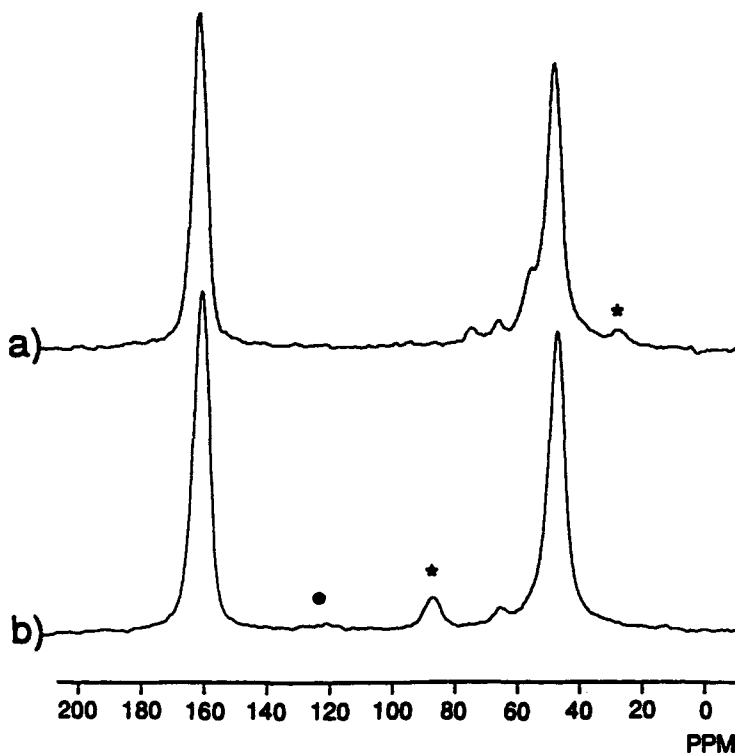


Figure 3 (a) 50.3 MHz ^{13}C -CP-MAS NMR spectra of a UF resin sample prepared from formalin and urea with an equivalent F/U/W molar ratio of 1.00/1.00/2.48 at pH 1 and (b) its solid residue after hydrolytic treatment at pH 4 and 86°C for 20 h. CP contact time = 1 ms; repetition time = 1 s. Spinning sidebands are indicated by asterisks.

similar to the case of UF resin 1.00/1.00/2.48(1) (*vide supra*). The ^{13}C -CP-MAS spectra (not shown here) of UF resin 1.00/1.00/105(5) before and after hydrolytic treatment at pH 4 and 86°C for 20 h are very similar to each other. This resin does not contain a large amount of cross-linking methylene linkages,²¹ and these methylene linkages, which were generated under the milder condition of pH 5, may be formed in thermodynamically more stable configurations than those formed under the harsher condition of pH 1.

As indicated in a previous article,²¹ the UF resins prepared from formalin and urea with an F/U molar ratio of 2.00/1.00 under acidic conditions show a wide variety of structures. In comparing those results with analogous data obtained on a 1.00/1.00 UF resin prepared under acidic conditions,²¹ we reported that 2.00/1.00 UF resins prepared under acidic conditions contain more cross-linking methylene linkages (IIbc, IIIa) and methylols (IVa, V) than does the 1.00/1.00 case prepared under similar conditions. The previously studied 2.00/1.00 UF resins were shown to generate some dimethylene ether

linkages (Xa, XIa), urons (XIIIa, XIIIb), short-chain and long-chain hemiformals, and methylene glycol and its oligomers. UF resins prepared earlier from the "*N,N'*-dimethylolurea reagent" with an "equivalent F/U molar ratio" of 1.90/1.00 at pH 1 provide a wide variety of structures, similar to that found in the previous study of 2.00/1.00 resins.²² Since our present study of hydrolytic behavior in 1.00/1.00 resins shows that the primary constituents in those resins are relatively stable to hydrolytic treatment, it is of interest to investigate the hydrolytic degradation of resins that are more highly cross-linked and contain a wide variety of structures.

In the ^{13}C -CP-MAS spectrum of UF resin 2.00/1.00/107(3), shown in Figure 4(a), most of the methylene-linkage peak intensity at 54 ppm can be assigned to cross-linking methylene linkages (IIbc, see Table I), because these methylene linkages are involved in cross-linking; part of the 54 ppm peak intensity arises from methylene linkages of cross-linking precursors. The non-methylol methylenes in the following structure belong to cross-linking precursors and have a ^{13}C chemical shift of 54 ppm:

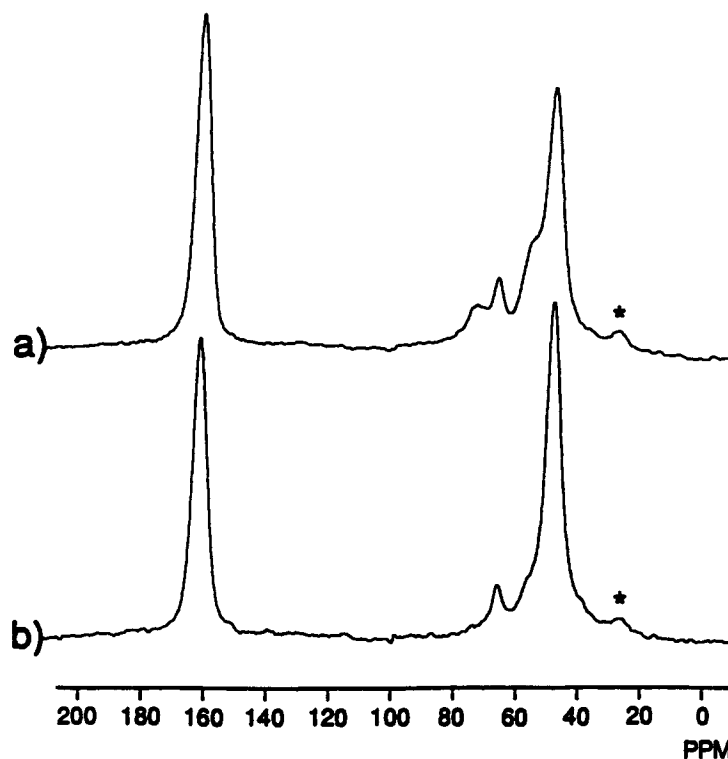
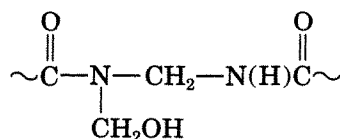


Figure 4 (a) 50.3 MHz ^{13}C -CP-MAS NMR spectra of a UF resin sample prepared from formalin and urea with an equivalent F/U/W molar ratio of 2.00/1.00/107 at pH 3 and (b) its solid residue after hydrolytic treatment at pH 4 and 86°C for 20 h. CP contact time = 1 ms; repetition time = 1 s. Spinning sidebands are indicated by asterisks.



The methylol groups in these cross-linking precursors are capable of forming methylene linkages (**IIb**, **IIIa**) or dimethylene ether linkages (**XIa**) and thereby transforming into a cross-linking methylene linkage (**IIb** or **c**) under the appropriate conditions. The methylene linkages (**IIa**) of cross-linking precursors are always accompanied by pendant methylol (**Va**). If a UF reaction mixture contains a large concentration of methylol groups before curing by acid, there will be a large amount of cross-linking precursors remaining in the UF resin cured under mild acidic conditions.^{21,22} On the other hand, if formaldehyde methylolates a secondary amide in a cured UF resin at a later stage of polymerization, it may be difficult for these newly formed methylols (**Va**) to form cross-links, so only a cross-linking precursor is formed.

It is interesting and important to investigate the role that these cross-linking precursors play in formaldehyde emission from UF resin products. There is a substantial amount of cross-linking precursor in UF resin 2.00/1.00/107(3), as indicated by the intensity at about 72 ppm (**Va**) and strong intensity at 54 ppm (**II**) in the spectrum of Figure 4(a). After hydrolytic treatment at pH 4 and 86°C for 24 h, UF resin 2.00/1.00/107(3) has probably lost most of its cross-linking precursors, as indicated by the ¹³C-CP-MAS spectrum [Fig. 4(b)] of the hydrolytic residue of 2.00/1.00/107(3) resin. The linear methylene linkages (**I**, 47 ppm) and terminal methylols (**IVa**, 65 ppm) largely survive the hydrolytic treatment. From Figure 4, we can conclude that a UF resin that is rich in cross-linking precursors is probably a major formaldehyde emitter, because the most probable hydrolytic reaction of cross-linking precursors is the back reaction of eq. (1). The products of this reaction are formaldehyde (detected as methylene glycol in a trap) and linear methylene linkages (**Ia**).

The ¹³C-CP-MAS spectrum of UF resin 2.00/1.00/25.0(3) shows²¹ slightly stronger peaks at 72 and 54 ppm than those of Figure 4(a). However, the ¹³C-CP-MAS spectrum (not shown here) of UF resin 2.00/1.00/25.0(3) after hydrolytic treatment at pH 4 and 86°C for 20 h is very similar to that of Figure 4(b), showing a very weak 72 ppm peak; therefore, most of the cross-linking precursors probably undergo hydrolytic degradation to emit

formaldehyde (detected as methylene glycol) and produce linear methylene linkages (**I**) under those conditions. Linear methylene linkages (**Ia**, 47 ppm), cross-linking methylene linkages (**IIbc**, and terminal methylols (**IVa**, 65 ppm) are apparently relatively stable toward hydrolytic treatment for 20 h at pH 4 and 86°C, behavior that is similar to that of UF resin 2.00/1.00/107(3).

Computer deconvolution of the ¹³C-CP-MAS spectrum of UF resin 1.90/1.00/4.96(1) prepared from the "*N,N'*-dimethylolurea reagent" [Fig. 5(a)] shows that this resin contains mainly linear methylene linkages, cross-linking methylene linkages (**IIbc**, 54 ppm; **IIIa**, 60 ppm), and cross-linking precursors (**IIa**, 54 ppm, and **Va**, 72 ppm; **IIIa**, 60 ppm and **Va**), terminal methylols (**IVa**, 65 ppm), urons (**XIIIa**, 79 ppm; **XIIIb**, 156 ppm), dimethylene ether linkages (**Xa**, 69 ppm; **XIa**, 76 ppm), and some polyoxymethylene glycols (**XIVab**, 88–92 ppm).²² After comparing Figure 5(a) with the ¹³C-CP-MAS spectrum [Fig. 5(b)] of the solid residue of resin 1.90/1.00/4.96(1) after hydrolytic treatment at pH 4 and 86°C for 20 h, we conclude that most of the poly(oxymethylene glycol) moieties, cross-linking precursors, and dimethylene ether linkages were eliminated from the UF resin by the hydrolytic treatment. A large portion of the terminal methylols (**IVa**, 65 ppm) disappear, although a substantial amount still remain in the residual resin. Without an accompanying 72 ppm peak, the 54 and 60 ppm peaks in the spectrum of Figure 5(b) can be assigned to cross-linking methylene linkages (**IIbc**) and double cross-linking methylene linkages (**IIIa**). With the strong intensities at 47, 54, and 60 ppm in the spectrum of Figure 5(b), one can conclude that all these three types of methylene linkages (**Ia**; **IIb**; **IIIa**) are relatively stable toward the hydrolytic treatment at pH 4 and 86°C for 20 h.

The ¹³C-CP-MAS spectrum of UF resin 2.00/1.00/4.96(1) prepared from formalin and urea is shown in Figure 6(a). Based on the deconvolution of this spectrum, we conclude that this resin contains²¹ all the major components found in UF resin 1.90/1.00/4.96(1), but with slightly different proportions of each component.²¹ UF resin 2.00/1.00/4.96(1) also contains a substantial amount of methylene methyl ether moieties (**VIIIb**, 55 ppm; **VIIa**, 73 ppm). The existence of the methoxy groups (**VIIIb**, 55 ppm) of methylene methyl ethers was established in the 2.00/1.00/4.96(1) UF resin by the interrupted-decoupling ¹³C-CP-MAS spectrum (not shown here). We conclude that most of the intensity of the 54 ppm (**II**) peak in the spectrum of Figure 6(a) is probably due to cross-linking precursors, be-

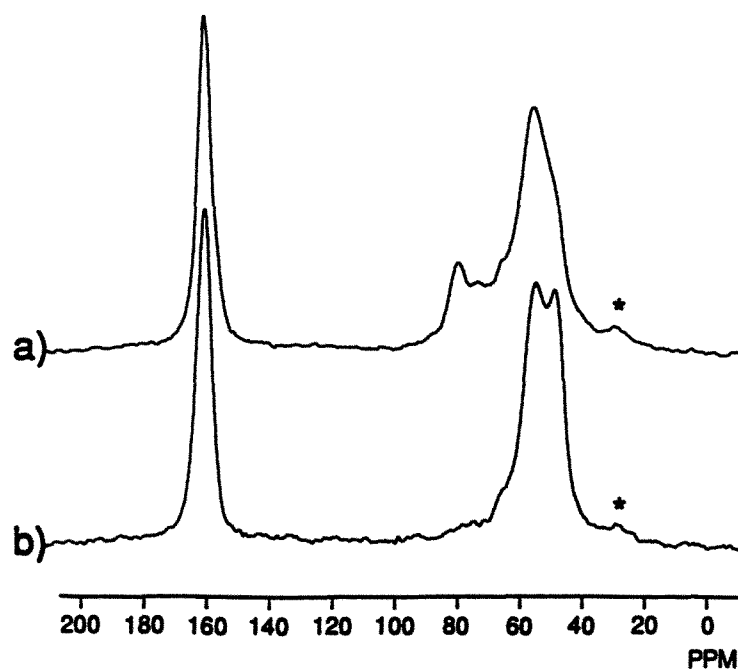


Figure 5 (a) 50.3 MHz ^{13}C -CP-MAS NMR spectra of a UF resin sample prepared from the "*N,N'*-dimethylolurea reagent" (see text) with an equivalent F/U/W molar ratio of 1.90/1.00/4.96 at pH 1 and (b) its solid residue after hydrolytic treatment at pH 4 and 86°C for 20 h. CP contact time = 1 ms; repetition time = 1 s. Spinning sidebands are indicated by asterisks.

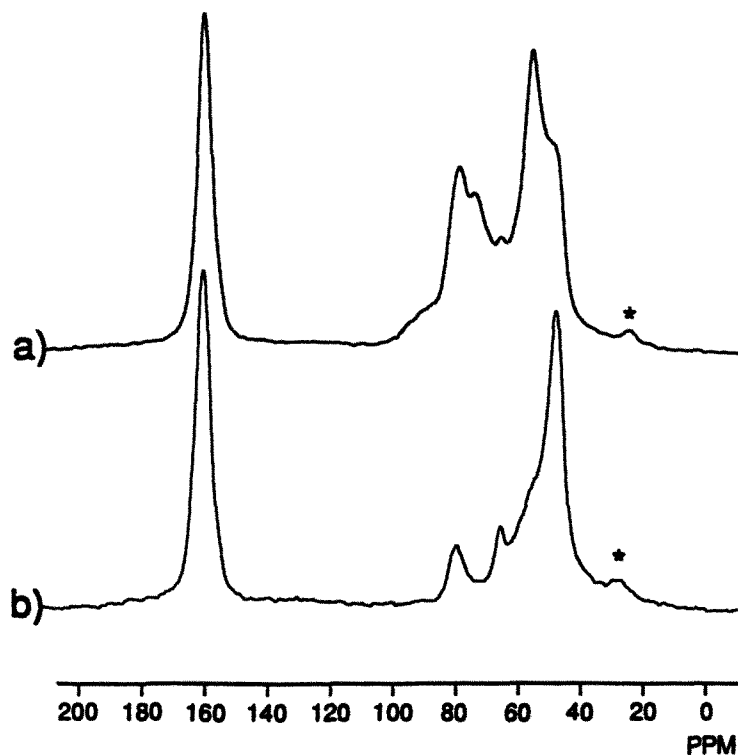


Figure 6 (a) 50.3 MHz ^{13}C -CP-MAS NMR spectra of a UF resin sample prepared from formalin and urea with an equivalent F/U/W molar ratio of 2.00/1.00/4.96 at pH 1 and (b) its solid residue after hydrolytic treatment at pH 4 and 86°C for 20 h. CP contact time = 1 ms; repetition time = 1 s. Spinning sidebands are indicated by asterisks.

cause of the accompanying strong peak intensity at 72 ppm (**Va**). From Figure 6(b), we see that these cross-linking precursors largely do not survive the hydrolytic treatment. All the methoxy groups (**VIIb**, 54 ppm) have been depleted from UF resin 2.00/1.00/4.96(1) after hydrolytic treatment, as indicated by the absence of a surviving peak at 55 ppm in the interrupted-decoupling ^{13}C -CP-MAS spectrum (not shown here) corresponding to Figure 6(b). A substantial amount of the urons in UF resin 2.00/1.00/4.96(1) survived the hydrolytic treatment, as indicated by the strong peak intensity at 79 ppm (**XIIIa**) and the shoulder at 156 ppm (**XIIIb**) in the spectrum of Figure 6(b). The strong peak intensities at 54 ppm (**II**) and 60 ppm (**IIIa**) in this spectrum, without an accompanying strong peak intensity at 72 ppm, informs us that a substantial amount of cross-linking methylene linkages of both kinds (**IIb** and **IIIa**) survived the hydrolytic treatment. There is also a substantial methylol content (**IVa**, 65 ppm) in the residue of UF resin 2.00/1.00/4.96(1) after hydrolytic treatment. Similar to the behavior seen in other UF resins that we have investigated, the linear methylene linkage (**Ia**, 47 ppm) is relatively stable toward hydrolytic degradation in comparison to other components in the 2.00/1.00/4.96(1) UF resin.

In addition to subjecting nine representative UF resins to hydrolytic treatment at pH 4 and 86°C for 20 h, we also studied a single UF resin under several different hydrolytic treatments. On the basis of the results presented earlier in this article, we chose for this purpose a 2.00/1.00/4.96(3) UF resin as the subject of eight different hydrolytic treatments. As described previously,²¹ the ^{13}C -CP-MAS spectrum of UF resin 2.00/1.00/4.96(3), shown in Figure 7(a), indicates that the resin contains all three types of methylene linkages (**Ia**, 47 ppm; **II**, 54 ppm; **IIIa**, 60 ppm), terminal methylol groups (**IVa**, 65 ppm), cross-linking precursors (**IIa**, 54 ppm, and **Va**, 72 ppm), both kinds of dimethylene ether linkages (**Xa**, 69 ppm; **XIa**, 76 ppm) and substantial amounts of urons (**XIIIa**, 79 ppm, and **XIIIb**, 156 ppm) and long-chain poly(oxymethylene glycols) (**XIVab**, 88–92 ppm, not surviving the interrupted-decoupling period). This 2.00/1.00/4.96(3) UF resin also contains a substantial amount of methoxy groups (**VIIb**, 54 ppm) and short-chain poly(oxymethylene glycols) (84–92 ppm), as indicated by the surviving peak intensities at 54 ppm and at 84–92 ppm in the interrupted-decoupling ^{13}C -CP-MAS spectrum (not shown here). After one portion of UF resin 2.00/1.00/4.96(3) was stirred at pH 5 and 25°C for 15

min, a solid residue was collected and the ^{13}C -CP-MAS spectrum of this residue is shown in Figure 7(b). The interrupted-decoupling ^{13}C -CP-MAS spectrum (not shown here) corresponding to Figure 7(b) indicates that all the short-chain poly(oxymethylene glycols) (84–92 ppm) and a portion of the methoxy groups (**VIIb**, 54 ppm) were eliminated from this UF resin in 15 min by hydrolytic treatment at pH 5 and 25°C. Figure 7(b) also indicates that a small amount of cross-linking precursors (**IIa**, 54 ppm; **Va**, 72 ppm) disappear from this UF resin when it is treated with water at pH 5 and 25°C. The rest of the fragments in UF resin 2.00/1.00/4.96(3) show good hydrolytic stabilities at pH 5 and 25°C, at least in this 15 min period.

Figure 7(c) and (d) show the ^{13}C -CP-MAS spectra of residues of UF resin 2.00/1.00/4.96(3) after hydrolytic treatments at 25°C for 20 h at pH 4 [Fig. 7(c)] and pH 1 [Fig. 7(d)]. The 25°C hydrolytic treatment at pH 4 eliminates about two-thirds of the uron units (**XIIIa**, 79 ppm; **XIIIb**, 156 ppm), most of the short-chain poly(oxymethylene glycols) (84–92 ppm, which survive in the corresponding interrupted-decoupling ^{13}C -CP-MAS spectrum, not shown here), a major portion of the methoxy groups (**VIIb**, 54 ppm), a substantial amount of cross-linking precursors (**IIa**, 54 ppm; **Va**, 72 ppm) and dimethylene ether linkages (**Xa**, 69 ppm; **XIa**, 76 ppm). Linear methylene linkages (**Ia**, 47 ppm) and cross-linking methylene linkages (**IIbc**, 54 ppm; **IIIa**, 60 ppm) and long-chain poly(oxymethylene glycols) (88–92 ppm, not surviving the interrupted-decoupling ^{13}C -CP-MAS experiment) show good stabilities toward hydrolytic treatment at pH 4 and 25°C for 20 h.

As indicated by Figure 7(d), hydrolytic treatment at pH 1 and 25°C for 20 h has a big effect on the structure of UF resin 2.00/1.00/4.96(3). Most of the short-chain and long-chain poly(oxymethylene glycols) (84–92 ppm) were eliminated from UF resin 2.00/1.00/4.96(1) under this treatment. Also, most of the cross-linking precursors (**IIa**, 54 ppm; **Va**, 72 ppm), dimethylene ether linkages (**Xa**, 69 ppm; **XIa**, 76 ppm), urons (**XIIIa**, 79 ppm; **XIIIb**, 156 ppm), half of the terminal methylols (**IVa**, 65 ppm) and all the methylene methyl ether moieties (**VIIb**, 54 ppm; **VIIa**, 73 ppm) are absent from the residue of UF resin 2.00/1.00/4.96(3) after hydrolytic treatment of pH 1 and 25°C for 20 h. The three types of methylene linkages (**Ia**, 47 ppm; **IIbc**, 54 ppm; **IIIa**, 60 ppm) in this resin are relatively stable toward this hydrolytic treatment.

Five samples of UF resin 2.00/1.00/4.96(3) were

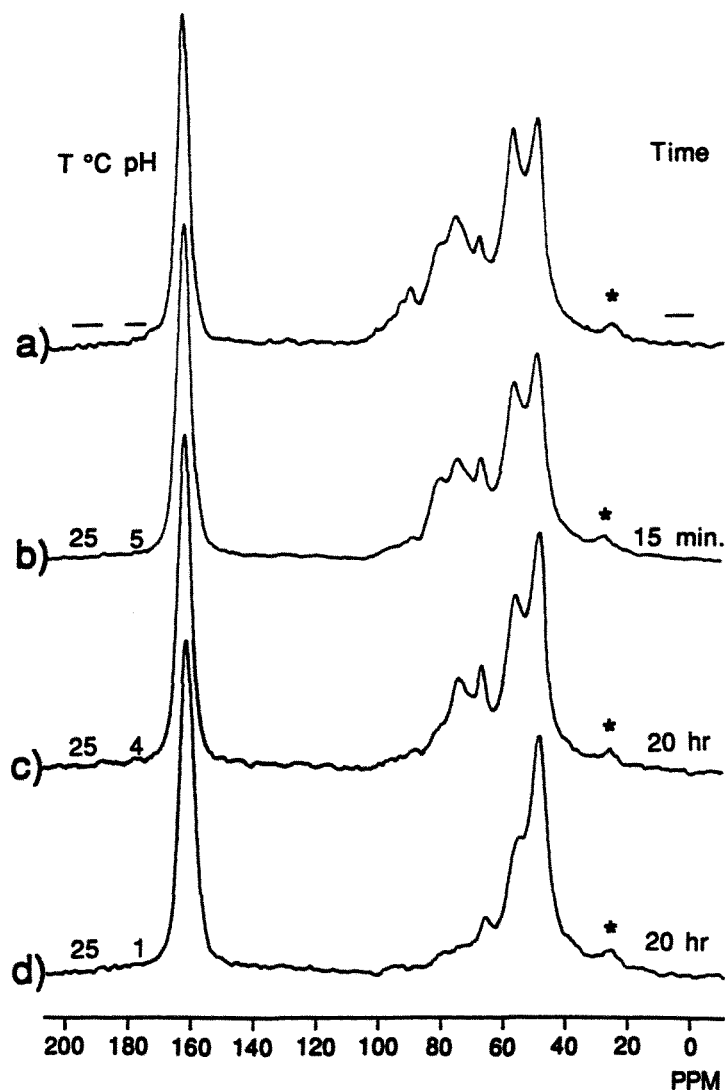


Figure 7 (a) 50.3 MHz ^{13}C -CP-MAS NMR spectra of a UF resin sample prepared from formalin and urea with an equivalent F/U/W molar ratio of 2.00/1.00/4.96 at pH 3 and its solid residues after three different hydrolytic treatments at 25°C: (b) at pH 5 for 15 min; (c) at pH 4 for 20 h; (d) at pH 1 for 20 h. CP contact time = 1 ms; repetition time = 1 s. Spinning sidebands are indicated by asterisks.

subjected to hydrolytic treatments for 20 h at 86°C and at five different pH values: 12, 9, 7, 4, and 1. ^{13}C -CP-MAS spectra of the five residues are shown in Figure 8. Figure 8(a) indicates that the residue of UF resin 2.00/1.00/4.96(3) after hydrolytic treatment at pH 12 and 86°C for 20 h has been depleted of most of the cross-linking precursors (**IIa**, 54 ppm; **Va**, 72 ppm), two-thirds of the methylols (**IVa**, 65 ppm) and urons (**XIIIa**, 79 ppm; **XIIIb**, 156 ppm), most of the short-chain poly(oxymethylene glycols) (84–92 ppm), dimethylene ether linkages (**Xa**, 69 ppm; **XIa**, 76 ppm), and some portion of the methylene methyl ether groups (**VIIb**, 55 ppm;

VIIa, 73 ppm). In comparison to the hydrolytic treatment at pH 12, the ^{13}C -CP-MAS spectrum in Figure 8(b) shows that the milder hydrolytic treatment at pH 9 yields a smaller effect on UF resin 2.00/1.00/4.96(3). The major differences between Figure 8(a) and (b) are the stronger peak intensities at 72 ppm (**Va**, 72 ppm) and 65 ppm in Figure 8(b) than in Figure 8(a). The ^{13}C -CP-MAS spectrum of Figure 8(c) represents the UF resin 2.00/1.00/4.96(3) residue after hydrolytic treatment at pH 7 and 86°C for 20 h. Figures 8(b) and (c) are very similar to each other and imply that the hydrolytic behavior of this UF resin is similar at pH 9 or at

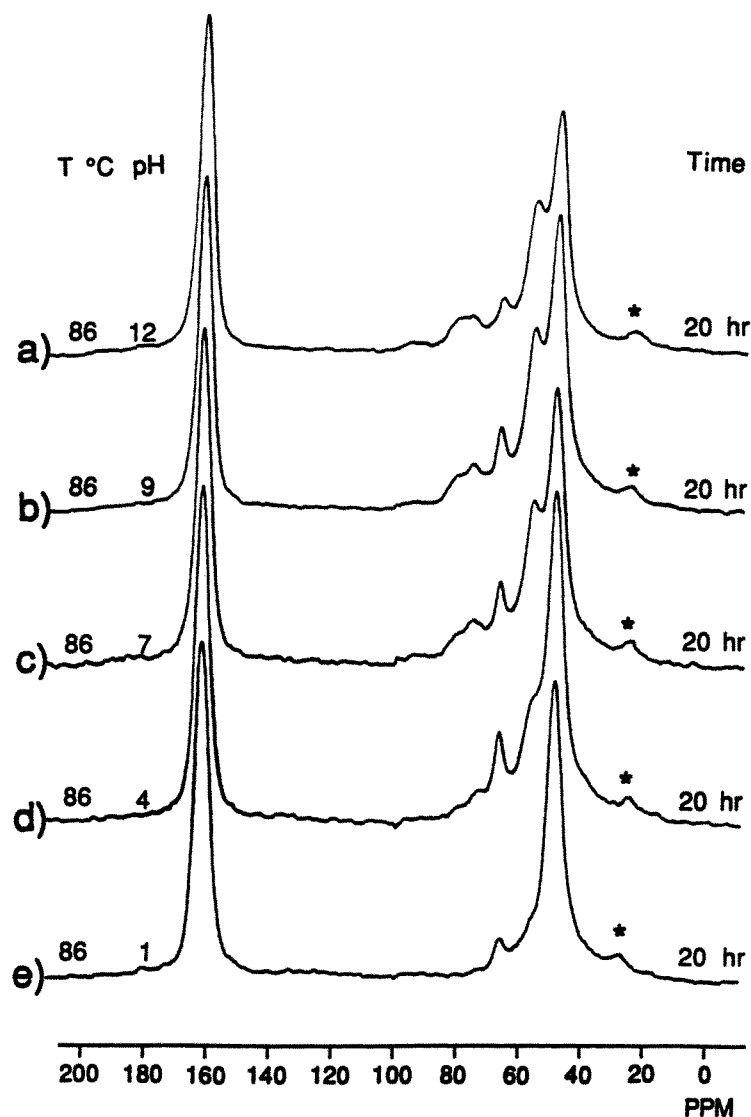


Figure 8 50.3 MHz ^{13}C -CP-MAS NMR spectra of solid residues of a UF resin sample (prepared from formalin and urea with an equivalent F/U/W molar ratio of 2.00/1.00/4.96 at pH 3) after hydrolytic treatments at 86°C and at five different pH values for 20 h: (a) pH 12; (b) pH 9; (c) pH 7; (d) pH 4; (e) pH 1. CP contact time = 1 ms; repetition time = 1 s. Spinning sidebands are indicated by asterisks.

pH 7. Figure 8(d) shows the ^{13}C -CP-MAS spectrum of the residue of UF resin 2.00/1.00/4.96(3) after a hydrolytic treatment at pH 4 and 86°C for 20 h. This spectrum shows that most of the cross-linking precursors (**IIa**, 54 ppm; **Va**, 72 ppm), dimethylene ether linkages (**Xa**, 69 ppm; **XIa**, 76 ppm), urons (**XIIIa**, 79 ppm; **XIIIb**, 156 ppm), poly-(oxymethylene glycols) (**XIVab**, 84–92 ppm), and methylene methyl ether groups (**VIIb**, 55 ppm; **VIIa**, 72 ppm) are eliminated from UF resin 2.00/1.00/4.96(3) by this hydrolytic treatment. However, linear methylene linkages (**Ia**, 47 ppm) and cross-

linking methylene linkages (**IIbc**, 54 ppm; **IIIa**, 60 ppm) in UF resin 2.00/1.00/4.96(3) display good stabilities toward the 20 h hydrolytic treatment at pH 4 and 86°C.

Figure 8(e) shows the ^{13}C -CP-MAS spectrum of the residue of UF resin 2.00/1.00/4.96(3) after a harsh hydrolytic treatment at pH 1 and 86°C for 20 h. This spectrum shows that all the dimethylene ether linkages (**Xa**, 69 ppm; **XIa**, 76 ppm), urons (**XIIIa**, 79 ppm; **XIIIb**, 156 ppm), methylene methyl ether groups (**VIIb**, 55 ppm; **VIIa**, 73 ppm), almost all the cross-linking precursors (**IIa**, 54 ppm;

Va, 72 ppm), and about two-thirds of the terminal methylols (**IVa**, 65 ppm) were eliminated by this harsh treatment. Some of the cross-linking methylene groups (**IIIbc**, 54 ppm) have undergone hydrolytic degradation, although the linear methylene linkages (**Ia**, 47 ppm) show a high stability toward this harsh treatment.

CONCLUSIONS

^{13}C -CP-MAS-NMR is a powerful tool in the investigation of the stabilities of UF resin components toward hydrolytic treatments. For UF resins prepared with an F/U molar ratio of 1.00/1.00, the major components are linear methylene linkages (**Ia**), cross-linking methylene linkages (**IIIbc**), and terminal methylols (**IVa**). Linear methylene linkages (**Ia**) show a higher stability toward hydrolytic treatment at pH 4 and 86°C than do cross-linking methylene linkages (**IIIbc**) in the 1.00/1.00 UF resins investigated.

UF resins prepared with an F/U molar ratio of 2.00/1.00 from formalin and urea, or with an F/U molar ratio of 1.90/1.00 from the "*N,N'*-dimethylolurea reagent," contain a wide variety of components, and some of these components are susceptible to hydrolytic degradation at pH 4 and 86°C; these include dimethylene ether linkages (**Xa**; **XIa**), poly(oxymethylene glycols) (**XIVab**), and methylol groups (**Va**) attached to tertiary amides. These hydrolytically susceptible components are probably the main formaldehyde emitters in UF resin products. Linear methylene linkages (**Ia**) and cross-linking methylene linkages (**IIIb**) are relatively stable toward hydrolytic treatments in these 2.00/2.00 UF resins.

Studies of the hydrolytic treatment of a UF resin with an F/U/W molar ratio of 2.00/1.00/4.96 at 25°C indicate that most of the dimethylene ether linkages (**Xa**; **XIa**) and short-chain poly(oxymethylene glycols) are susceptible to hydrolysis at pH 4. Even though methylol groups (**Va**) are relatively stable to 25°C hydrolytic treatment at pH 4, they display a high susceptibility to hydrolytic treatment at the same temperature and pH 1.

The results of subjecting the same 2.00/1.00/4.96 UF resin to hydrolytic treatments at five different pH values at 86°C indicate that both methylol groups (**Va**) and dimethylene ether linkages (**Xa**; **XIa**) are susceptible to hydrolytic treatment, especially at high pH or low pH values; the latter moieties are especially susceptible to 86°C hydrolytic treatments under acidic conditions. Cross-linking

methylene linkages (**IIIb**) show some degree of susceptibility to 86°C hydrolytic treatment at pH 1, but less susceptibility at higher pH values investigated.

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REFERENCES

1. B. Meyer, *Urea-Formaldehyde Resin*, Addison-Wesley, Reading, MA, 1979.
2. H. G. Freeman and R. E. Kreibich, *Forest Prod. J.*, **18**(7), 39 (1968).
3. R. H. Gillespie, *Forest Prod. J.*, **18**(8), 35 (1968).
4. R. L. Christensen, *Forest Prod. J.*, **22**(4), 17 (1972).
5. P. R. Steiner, *Forest Prod. J.*, **23**(12), 32 (1973).
6. P. Robitschek and R. L. Christensen, *Forest Prod. J.*, **26**(12), 43 (1976).
7. E. Roffael, in *Proceedings of the 12th International Particleboards Symposium W.S.U.*, 1978, pp. 233-249.
8. T. G. Mathews, A. R. Hawthorne, C. R. Daffron, T. J. Reed, and M. D. Corey, in *Proceedings of the 17th International Particleboards Symposium W.S.U.*, 1983, pp. 179-202.
9. G. E. Myers and M. Nagaoka, *Wood Sci.*, **13**, 140 (1981).
10. G. E. Myers, *Wood Sci.*, **15**, 127 (1982).
11. G. E. Myers, *Forest Prod. J.*, **33**(4), 49 (1983).
12. G. E. Myers, *Forest Prod. J.*, **34**(5), 35 (1984).
13. G. E. Myers, *Forest Prod. J.*, **35**(6), 57; **35**(9), 20 (1985).
14. G. E. Myers and J. A. Koutsky, *Forest Prod. J.*, **37**(9), 56 (1987).
15. G. Meyer, K. Hermans, and D. C. Smith, *J. Appl. Polym. Sci. Appl. Polym. Symp.*, **40**, 27 (1984).
16. B. Meyer, B. A. K. Andrews, and R. M. Reinhardt, Eds., *Formaldehyde Release from Wood Products*, ACS Symposium Series 316, American Chemical Society, Washington, DC, 1986.
17. A. Pines, M. G. Gibby, and J. S. Waugh, *J. Chem. Phys.*, **59**, 569 (1973).
18. E. R. Andrew, *Prog. Nucl. Magn. Reson. Spectrosc.*, **8**, 1 (1972).
19. J. Schaefer and E. O. Stejskal, *J. Am. Chem. Soc.*, **98**, 1031 (1976).
20. G. E. Maciel, N. M. Szeverenyi, T. A. Early, and G. E. Myers, *Macromolecules*, **16**, 598 (1983).
21. I. Chuang and G. E. Maciel, *Macromolecules*, **25**, 3204 (1992).
22. I. Chuang and G. E. Maciel, *Polymer*, to appear.
23. S. S. Jada, *J. Macromol. Sci.-Chem.*, **A27**, 361 (1990).
24. N. Zumbulyadis, P. M. Henrichs, and R. H. Young, *J. Chem. Phys.*, **75**, 1603 (1981).
25. A. Naito, S. Ganapathy, and C. A. McDowell, *J. Chem. Phys.*, **74**, 5393 (1981).

26. J. G. Hexem, M. H. Frey, and S. J. Opella, *J. Am. Chem. Soc.*, **103**, 224 (1981).
27. R. K. Harris, P. Jonsen, K. J. Packer, and C. Campbell, *Magn. Reson. Chem.*, **24**, 977 (1986).
28. A. C. Olivieri, L. Frydman, and L. E. Diaz, *J. Magn. Reson.*, **75**, 50 (1987).
29. R. K. Harris and A. C. Olivieri, *Prog. Nucl. Magn. Reson. Spectrosc.*, **24**, 435 (1992).
30. S. J. Opella and M. H. Frey, *J. Am. Chem. Soc.*, **101**, 5854 (1979).
31. S. J. Opella, M. H. Frey, and T. A. Cross, *J. Am. Chem. Soc.*, **101**, 5856 (1979).
32. L. B. Alemany, D. M. Grant, T. D. Alger, and R. J. Pugmire, *J. Am. Chem. Soc.*, **105**, 6697 (1983).
33. M. Mehring, *Principles of High Resolution NMR in Solids*, Springer-Verlag, New York, 1983, p. 153.
34. S. R. Hartmann and E. L. Hahn, *Phys. Rev.*, **128**, 2042 (1962).
35. A. J. J. de Breet, W. Dankelman, W. G. B. Huysmans, and J. de Wit, *Angew. Makromol. Chem.*, **62**, 7 (1977).
36. I. Y. Slonim, S. G. Alekseyeva, Y. G. Urman, B. M. Arshava, B. Y. Aksel'rod, and I. M. Gurman, *Polym. Sci. U.S.S.R.*, **19**, 899 (1977).
37. I. Y. Slonim, S. G. Alekseyeva, Y. G. Urman, B. M. Arshava, B. Y. Aksel'rod, and L. N. Smirnova, *Polym. Sci. U.S.S.R.*, **19**, 920 (1977).
38. J. R. Ebdon and P. E. Heaton, *Polymer*, **18**, 971 (1977).
39. B. Tomita and S. Hatono, *J. Polym. Sci. Polym. Chem. Ed.*, **16**, 2509 (1978).
40. I. Y. Slonim, S. G. Alekseyeva, Y. G. Urman, B. M. Arshava, and B. Y. Aksel'rod, *Polym. Sci. U.S.S.R.*, **20**, 1661 (1979).
41. I. Y. Slonim, S. G. Alekseyeva, Y. G. Urman, B. M. Arshava, B. Y. Aksel'rod, I. M. Gurman, and L. N. Smirnova, *Polym. Sci. U.S.S.R.*, **20**, 2659 (1979).
42. A. Sebenik, U. Osredkar, M. Zigon, and I. Vizovisek, *Angew. Makromol. Chem.*, **102**, 81 (1982).
43. H. Pasch, I. S. Dairanieh, and B. Al-Tahou, *J. Polym. Sci. Polym. Chem.*, **28**, 2049 (1990).
44. H. Pasch, G. Hovakeemian, and S. Lahalih, *J. Polym. Sci. Polym. Chem.*, **29**, 525 (1991).
45. A. J. Stamm, *Wood and Cellulose Science*, Ronald Press, New York, 1964, Chap. 10.
46. W. E. Johns and K. A. Niazi, *Wood Fiber*, **12**(4), 255 (1980).
47. G. E. Maciel and I. Chuang, unpublished results.
48. G. E. Maciel and I. Chuang, unpublished results.

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