^{13}C cross-polarization/magic-angle spinning nuclear magnetic resonance investigation of urea–formaldehyde resins made from *N,N'*-dimethylolurea or from paraformaldehyde

I-Ssuer Chuang and Gary E. Maciel*
Department of Chemistry, Colorado State University, Fort Collins, CO 80523-0002, USA
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^{13}C cross-polarization/magic-angle spinning nuclear magnetic resonance spectroscopy has been used to investigate urea–formaldehyde (UF) resins prepared at room temperature from reaction mixtures containing *N,N'*-dimethylolurea or various pretreated paraformaldehyde agents as a source of CH_2 groups. Resins prepared from reaction mixtures with various 'equivalent' formaldehyde-to-urea molar ratios and various pH values and reactant concentrations were examined. Structural changes in the UF resins that accompany variations in these parameters, and the dependence of the UF resin structures on the solubilities of *N,N'*-dimethylolurea or various pretreated paraformaldehyde agents in water are discussed along with the relative rates of various reactions at different pH values. Comparisons are made among the UF resins prepared from formalin, *N,N'*-dimethylolurea or various pretreated paraformaldehyde agents as a source of CH_2 groups in the resins. Valuable information on the mechanisms and reactivities of various reactions in the complicated UF resin system was drawn from these comparisons.

(Keywords: urea–formaldehyde resins; ^{13}C c.p.-m.a.s. n.m.r.; reaction mechanisms)

INTRODUCTION

From the 1940s to the 1970s, a large volume of information has been published on the kinetics and synthetic pathways of the initial reactions involved in the preparation of urea–formaldehyde (UF) resin systems[1,2]. However, little is known concerning how these reactions proceed during the condensation of higher-molecular-weight intermediates. There are four potentially reactive atomic sites in urea and two in formaldehyde, and several different kinds of linkages or functional groups can be formed in the various stages of the overall reaction between urea and formaldehyde. Hence, a large variety of structural moieties are likely in UF resins. Apart from the complexity of these reactions and their products, the insolubility of many UF resin products (especially, the cured resins) in a variety of solvents provided a formidable barrier to characterization by earlier methods. Therefore, various reaction conditions were deliberately avoided in many past studies in order to provide a soluble product that could be examined by liquid-sample techniques. Although such studies have contributed significantly towards the understanding of the properties and performance of UF resins, the details of the structure of the cured resins and the curing process have remained obscure because of the lack of proper tools to explore them.

The high-resolution solid-state ^{13}C nuclear magnetic resonance (n.m.r.) technique that consists of the combination of cross-polarization (c.p.)[3] with high-power ^{1}H decoupling and magic-angle spinning (m.a.s.)[4], namely ^{13}C c.p.-m.a.s. n.m.r.[5], has proven to be a powerful tool in elucidating the structural details of UF resins[6,7], especially for resins prepared under conditions in which an insoluble product is formed. In this paper, we present results of a continuing n.m.r.-based study aimed at elucidating structural details of UF resins and possible mechanisms for their formation.

As pointed out in a previous article[7], a systematic understanding of the synthesis of UF resins at room temperature is an important step towards the understanding of UF resins at their usual service temperature, namely, room temperature. In the present paper, we present the results of utilizing *N,N'*-dimethylolurea ($HOCH_2NHCONHCH_2OH$) or various pretreated paraformaldehyde agents as a source of methylol groups, and related linkages, in the syntheses of UF resins at room temperature under conditions of different pH values and reactant concentrations. Comparisons among UF resins prepared from *N,N'*-dimethylolurea, from various pretreated paraformaldehyde agents and urea, and from 37% formalin and urea are presented in order to shed light on the mechanism of various reactions in the complicated UF resin system.

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* To whom correspondence should be addressed

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EXPERIMENTAL

Samples

Reactions between a reagent that is nominally referred to as the '*N*,*N*′-dimethylolurea reagent' (Sigma Chemicals, containing 92 wt% *N*,*N*′-dimethylolurea and 8 wt% monomethylolurea) and urea (Mallinckrodt, analytical grade) have been carried out at six pH values (1, 3, 5, 7, 9 and 12) with two different equivalent formaldehyde-to-urea (F/U) molar ratios, 1.00/1.00 and 1.90/1.00. We employed 85% phosphoric acid or 5.0 M aqueous sodium hydroxide solutions to obtain the desired reaction-mixture pH values, which were monitored by a pH meter during the course of each reaction. By adding definite amounts of water to mixtures of the *N*,*N*′-dimethylolurea reagent and urea, the following concentrations, expressed by equivalent formaldehyde/urea/water (F/U/W) molar ratios, were obtained: 1.00/1.00/2.48, 1.00/1.00/12.5, 1.00/1.00/105, 1.90/1.00/4.96, 1.90/1.00/25.0 and 1.90/1.00/107. For this paper, the pH value of the reaction mixture is represented in parentheses, e.g. 1.00/1.00/105(1) represents the solid UF resin prepared from a mixture with an equivalent F/U/W molar ratio of 1.00/1.00/105 at pH 1. All the reactions were started at room temperature (23 ± 2°C) and allowed to proceed without any adjustment of reaction temperature thereafter; pertinent details of temperature changes during the reactions are discussed in the 'Results and discussion' section.

Reactions between paraformaldehyde (Fisher Scientific, purified) and urea were carried out at five different pH values (1, 3, 5, 9 and 12) in mixtures with an equivalent F/U/W ratio of 2.00/1.00/25.0, and at three different pH values (1, 3, 5) in mixtures with an equivalent F/U/W molar ratio of 2.00/1.00/107. The reactions between paraformaldehyde and urea at pH 1, 3 and 5 were carried out by procedures that were different from what is described above; details are presented in the 'Results and discussion' section.

The reaction conditions were maintained for 12 h, with the two exceptions specified below in the 'Results and discussion' section; after these 12 h periods, the resulting reaction mixtures were subjected to the specific treatments described here and in the 'Results and discussion' section. If there was any separable liquid in the reaction mixture, it was removed by decanting and the remaining precipitate portion was spread out on a watch glass for drying without any adjustment in pH value. In some cases, the reaction product remained a clear solution even after 12 h of reaction; such a solution was vacuum dried (10^{-2} Torr) at −5°C to produce solid samples for ^{13}C c.p.-m.a.s. studies. The results of other treatments of the reaction mixtures after the 12 h reaction period and their effects on the structures of the resulting UF resins will be discussed separately[8].

N.m.r. measurements

^{13}C c.p.-m.a.s. n.m.r. spectra were obtained at 50.3 MHz on a home-modified Nicolet NT-200 spectrometer, as described in a previous article[6]. At this field of 4.7 T, the residual nuclear electric quadrupole effects[9–15] of ^{14}N on ^{13}C through nuclear magnetic dipolar interactions are sufficiently averaged by magic-angle spinning that the resulting spectra provide enough resolution for reasonably accurate peak assignments and intensities in the ^{13}C c.p.-m.a.s. n.m.r. spectra of UF resin samples. Most spectra were obtained with a 1 ms c.p. contact time and a 1 s repetition time, except for some variable-contact-time experiments (*vide infra*), in which several different contact times (including 1 ms) were used for cross-polarization. Spectra of UF resins were also taken with the interrupted-decoupling (dipolar-dephrasing) c.p.-m.a.s technique[16] with a 50 μs interrupted-decoupling period.

For some sticky resin samples, there was a tendency in long-term 6.5 kHz m.a.s. experiments for the sample to push out the cap of the spinner; these sticky samples were spun at about 3.2 kHz, or at two different spinning speeds near 3.2 kHz to distinguish spinning sidebands from the centrebands of resin signals. For all other resin samples, m.a.s. speeds of 6.5 kHz were used, providing spectra with spinning sidebands outside the centreband region of resin signals. For some samples c.p.-m.a.s. experiments were carried out at both 6.5 kHz and about 3.2 kHz in order to study the possible effects of sample spinning speeds on the spectra[17]. In quantitative ^{13}C c.p.-m.a.s. n.m.r. comparisons, it was found that for a m.a.s. speed up to 6.5 kHz and 1 ms c.p. contact time, *within* the spectrum of a given UF sample intensities were reproducible within 3% for ^{13}C nuclei attached directly to hydrogen and in relatively rigid frameworks (e.g. not CH_3 groups).

RESULTS AND DISCUSSION

Background remarks

Overview of thermal, pH and solubility behaviours. As mentioned in the 'Experimental' section, all the reactions reported in this paper started at room temperature (23 ± 2°C) without any adjustment of reaction temperature thereafter. *Table 1* summarizes the highest temperatures attained in those 11 reactions which evolved heat quickly and thereby generated a substantial increase of the reaction temperature during the first few minutes of reaction. In these 11 exothermic reactions, the reaction temperatures quickly and spontaneously returned to room temperature without any external action. Except for the 11 reactions listed in *Table 1*, there was no appreciable change in reaction temperature for the other reactions described in this paper.

For all of the pH values investigated, during the 12 h period of the reaction between the *N*,*N*′-dimethylolurea

Table 1 The highest temperatures spontaneously reached in UF resin reaction mixtures that evolve heat quickly

Equivalent F/U/W molar ratio	Starting material^{a}	pH	Highest temperature attained (°C)
1.00/1.00/2.48	*N*,*N*′-Dimethylolurea^{b}	1	38
		3	33
1.00/1.00/12.5	*N*,*N*′-Dimethylolurea^{b}	1	38
		3	33
1.90/1.00/4.96	*N*,*N*′-Dimethylolurea^{b}	1	33
		3	30
1.90/1.00/25.0	*N*,*N*′-Dimethylolurea^{b}	1	33
		3	30
2.00/1.00/25.0	Paraformaldehyde pretreated with base^{c}	1	40
		3	31
	Paraformaldehyde pretreated at 66°C^{d}	1	40

^{a} The source of methylols or various CH_2-based linkages in UF resin
^{b} Contaminated with 10 mol% of monomethylolurea
^{c} Aqueous NaOH solution at pH 9 for 12 h
^{d} For 6.5 h

reagent and urea in water or of just the *N,N'*-dimethylolurea reagent itself in water, at most a slight decrease (−0.2) in pH was observed; in most cases no pH change was observed. Similar pH behaviour was observed during the 12 h or 83 h reaction period in reactions between urea and treated or untreated paraformaldehyde. A Cannizzaro reaction[18] of formaldehyde generated from *N,N'*-dimethylolurea or paraformaldehyde probably is not a significant reaction at pH values less than or equal to 12 at room temperature; therefore, one need not worry that the pH values of the reaction systems might change during the 12 h reaction period because of such a process.

Owing to the finite solubility of *N,N'*-dimethylolurea in water (12 g/100 g) at room temperature and the formation under acidic conditions of UF resin structures with even smaller solubility in water[7], the reaction mixtures with 'equivalent' F/U/W molar ratios (*vide infra*) of 1.00/1.00/2.48, 1.90/1.00/4.96 and 1.90/1.00/25.0 remained in a milky state during the entire 12 h reaction period for the reactions of the *N,N'*-dimethylolurea reagent, urea and water or of the *N,N'*-dimethylolurea reagent and water; this behaviour was observed at all six pH values investigated. For the reaction between the *N,N'*-dimethylolurea reagent and urea in water with an equivalent F/U/W molar ratio of 1.00/1.00/12.5, the five reaction mixtures prepared at pH 1, 3, 5, 7 and 9 remained in a milky state during the 12 h reaction period; however, the reaction mixture prepared at pH 12 became a clear solution after 40 min of stirring and remained a clear solution for the rest of the 12 h reaction period. The explanation of this unusual solubility behaviour at pH 12 is the formation of a large proportion of monomethylolurea from *N,N'*-dimethylolurea and urea, as indicated by liquid-sample ^{13}C n.m.r. (*vide infra*), and the larger solubility of monomethylolurea in water at pH 12 in comparison to the solubility of *N,N'*-dimethylolurea in water at pH 12. All the reaction mixtures with 'equivalent' F/U/W molar ratios of 1.00/1.00/105 and 1.90/1.00/107 prepared at all six pH values from the *N,N'*-dimethylolurea reagent, urea and water or from the *N,N'*-dimethylolurea reagent and water became clear solutions in less than 1 min after mixing. All six neutral or basic reaction mixtures with 'equivalent' F/U/W molar ratios of 1.00/1.00/105 or 1.90/1.00/107 remained in a clear solution state for the entire 12 h reaction period. However, all the six reaction systems with the corresponding 'equivalent' F/U/W molar ratios at pH 1, 3 and 5 produced precipitates at various times (see *Table 2*). This behaviour roughly indicates the production of insoluble UF resins containing various kinds of linkages in these reaction systems.

The solubility of paraformaldehyde in water under various conditions has been discussed in detail[19–21]. The plot of the solubility of paraformaldehyde in water vs. pH value has a valley between pH 3 and 5[19]. The establishment of equilibria among methylene glycol and its higher-molecular-weight oligomers is slow between pH 3 and 5 at room temperature[19]. The solubility of paraformaldehyde in water depends not only on pH value and temperature, but also on how the paraformaldehyde was prepared[19]. Room-temperature mixtures of paraformaldehyde and water with an equivalent F/W molar ratio of 2.00/25.0 remain in a milky state even after 33 h of stirring at pH 1 or after 83 h of stirring at pH 3 or 5. With the same equivalent F/W molar ratio of 2.00/25.0, room-temperature mixtures of paraformaldehyde and water become almost clear solutions after 3 h of stirring at pH 9 or after 2 min of stirring at pH 12; at 66°C such mixtures become almost clear after 90 min of stirring at pH 7.

The reaction mixtures of paraformaldehyde and urea in water with equivalent F/U/W molar ratio of 2.00/1.00/25.0 remained in a milky state during the entire 12 h reaction period at pH 1 or during the entire 83 h reaction period at pH 3 or 5. However, the reaction mixture with the same equivalent F/U/W molar ratio became a clear solution after 3 h of stirring at pH 9 and remained in that state for the rest of the 12 h reaction period. The reaction mixture with the same F/U/W molar ratio of 2.00/1.00/25.0 prepared from paraformaldehyde and urea at pH 12 became almost clear after 2 min of stirring and started to form *N,N'*-dimethylolurea precipitates after 1 h of reaction at pH 12. The reaction mixtures prepared from urea and pretreated paraformaldehyde (pretreated with methanol at a paraformaldehyde-to-methanol weight ratio of 37/8 at pH 5 for 6 h or with acid at pH 1 for 33 h) with an equivalent F/U/W molar ratio of 2.00/1.00/25.0 at pH 5 remained in a milky state during the entire 12 h reaction period. As mentioned above, paraformaldehyde dissolves in water (with an equivalent F/W molar ratio of 2.00/25.0) after pretreatment with base at pH 9 for 12 h or at 66°C for 6.5 h. The clear solutions of these pretreated paraformaldehydes started to form precipitates at different times (see *Table 2*) at pH 1, 3 and 5 after mixing with urea at an equivalent F/U/W molar ratio of 2.00/1.00/25.0; the times of appearance of precipitates indicate the times needed to form insoluble UF resin structures in these reaction systems under different acidic conditions.

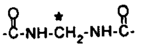
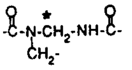
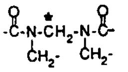
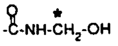
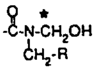
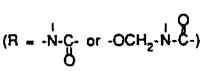
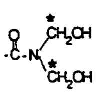
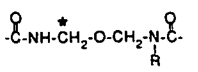
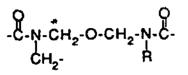
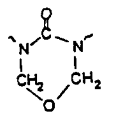
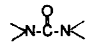
Chemical-shift summary. ^{13}C n.m.r. chemical shifts of some possible or likely structural fragments of UF resins have been discussed in detail in a previous article[7]. The chemical-shift values are based on liquid-state ^{13}C n.m.r. studies of model compounds and UF resin solutions[22–29], ^{13}C c.p.-m.a.s. n.m.r. studies on *N,N'*-dimethylolurea and solid UF resins[6], and ^{13}C c.p.-m.a.s. n.m.r. studies of methylenediurea and various UF resin products[7]. *Table 3* lists the chemical shifts of some of the most important structural fragments that possibly or probably occur in the UF resins discussed in this paper. The chemical shifts of some other less important or less obvious structural choices will be mentioned in pertinent places when

Table 2 The time of appearance of precipitates in some UF resin reaction mixtures prepared under acidic conditions

Equivalent F/U/W molar ratio	Starting material[a]	pH[b]	Time (min)
1.00/1.00/105	*N,N'*-Dimethylolurea[c]	1	1
		3	3
		5	70
1.90/1.00/107	*N,N'*-Dimethylolurea[c]	1	3
		3	6
		5	80
2.00/1.00/25.0	Paraformaldehyde pretreated with base[d]	1	2
		3	13
		5	180

[a] The source of methylols or various CH_2-based linkages in UF resin
[b] Adjusted by addition of 85% phosphoric acid
[c] Contaminated with 10 mol% of monomethylolurea
[d] Aqueous NaOH solution at pH 9 for 12 h

Table 3 ^{13}C n.m.r. chemical shifts of some of the most important structural fragments that possibly or probably appear in the UF resins discussed in this paper

Structural fragment	Name of group[a]	Numerical label[b]	Chemical shift[c] (ppm)
 $-\overset{O}{\overset{\|}{C}}-NH-\overset{*}{C}H_2-NH-\overset{O}{\overset{\|}{C}}-$	Methylene linkage	I	47
 $-\overset{O}{\overset{\|}{C}}-\underset{CH_2-}{\underset{\|}{N}}-\overset{*}{C}H_2-NH-\overset{O}{\overset{\|}{C}}-$	Methylene linkage	II	54
 $-\overset{O}{\overset{\|}{C}}-\underset{CH_2-}{\underset{\|}{N}}-\overset{*}{C}H_2-\underset{CH_2-}{\underset{\|}{N}}-\overset{O}{\overset{\|}{C}}-$	Methylene linkage	III	60
 $-\overset{O}{\overset{\|}{C}}-NH-\overset{*}{C}H_2-OH$	Methylol	IV	65
 $-\overset{O}{\overset{\|}{C}}-\underset{CH_2-R}{\underset{\|}{N}}-\overset{*}{C}H_2OH$  $(R = -\overset{\|}{N}-\underset{O}{\underset{\|}{C}}- \text{ or } -OCH_2-\overset{\|}{N}-\overset{O}{\overset{\|}{C}}-)$	Internal methylol	Va	72
 $-\overset{O}{\overset{\|}{C}}-N(\overset{*}{C}H_2OH)(\overset{*}{C}H_2OH)$	Geminate methylol	Vb	72
 $-\overset{O}{\overset{\|}{C}}-NH-\overset{*}{C}H_2-O-CH_2-\underset{R}{\underset{\|}{N}}-\overset{O}{\overset{\|}{C}}-$ (R = H or $-CH_2-$)	Dimethylene ether linkage	X	69
 $-\overset{O}{\overset{\|}{C}}-\underset{CH_2-}{\underset{\|}{N}}-\overset{*}{C}H_2-O-CH_2-\underset{R}{\underset{\|}{N}}-\overset{O}{\overset{\|}{C}}-$ (R = H or $-CH_2-$)	Dimethylene ether linkage	XI	76
	Disubstituted uron	XIII $-CH_2-$ XX >C=O	79[d] 156[e]
 $>N-\overset{O}{\overset{\|}{C}}-N<$	Carbonyl		155–169

[a] Relevant carbon position labelled by an asterisk

[b] Based on the numbering system used in a previous paper[7]

[c] Relative to TMS; expressed to nearest integer owing to extensive dispersion (see text)

[d] Dimethylene ether linkage

[e] Carbonyl

encountered in the discussion. The numerical system of labelling various species is that adopted in a previous article[7]. Owing to the extensive chemical-shift dispersion associated with amorphous solids, the chemical shifts are expressed to the nearest integer in *Table 3*. Values are given in ppm relative to liquid TMS (tetramethylsilane), with larger numbers corresponding to lower shieldings.

Overview of ^{13}C c.p.-m.a.s. n.m.r. properties. In contrast to the liquid-state ^{13}C n.m.r. studies of UF resins (see refs. 22–29 and the discussion of liquid-state ^{13}C n.m.r. spectra below), the spectral region around 160 ppm does not generally provide a good diagnostic tool for the determination of environments around various carbonyl groups of UF resins. The splitting seen in the signals at about 160 ppm and 65 ppm in the spectra of *N,N'*-dimethylolurea and monomethylolurea are usually due mainly to the residual ^{14}N quadrupolar effect on the ^{13}C spectra via the ^{14}N–^{13}C magnetic dipole–dipole interaction[9–15].

Quantitative aspects of the ^{13}C c.p.-m.a.s. analysis of UF resins were discussed in detail in a previous article[7]. In the ^{13}C c.p.-m.a.s. n.m.r. spectra, an individual peak intensity depends not only on the relative concentration of the corresponding type of carbon environment, but also on the ^{1}H–^{13}C cross-polarization efficiency. By employing variable-contact-time experiments, one can extract values of the ideal (full) cross-polarized ^{13}C magnetization, the ^{1}H–^{13}C cross-polarization rate constant T_{CH}^{-1} and $T_{1\rho}^{H}$ (the rotating-frame spin–lattice relaxation time for the proton type that transfers polarization to the given ^{13}C magnetization component) of each individual peak in the ^{13}C spectrum at a given m.a.s. spinning rate and for a given Hartmann–Hahn r.f. match condition. With these three parameters obtained from variable-contact-time experiments[7], one can calculate the c.p. efficiencies and the 'ideal' c.p. intensity for any c.p. contact time (say, 1 ms) for each individual peak at the given m.a.s. speed. For a 1 ms contact time the maximum difference among the c.p. efficiencies for the peaks of 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. *Within* a given spectrum, differences between the c.p. efficiencies with a 1 ms contact time for carbonyl carbons and 'rigid' hydrogen-bearing carbons were found to range from 0 to 14%, depending on the sample and m.a.s. speed.

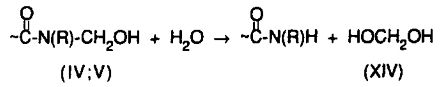
The previously reported variable-contact-time data[7] indicate that quantitative ^{13}C c.p.-m.a.s. comparison *within* a given UF sample can be made directly from raw intensities for more rigid carbon atoms that are directly attached to protons, such as methylene linkages (I, 47 ppm; II, 54 ppm; III, 60 ppm), methylol groups (IV, 65 ppm; V, 72 ppm), dimethylene ether linkages (X, 69 ppm; XI, 76 ppm) and long-chain polyoxymethylene glycols (87–92 ppm). Therefore, ^{13}C intensity interpretations for these moieties can be made directly from the spectra, even with a m.a.s. speed up to 6.7 kHz, at least at a semiquantitative level (say, ±3%).

Systematic variations in the parameters of resin preparation. The factors that affect the final structure of a UF resin include the initial molar concentrations and 'equivalent' molar ratio (*vide infra*) of formaldehyde and urea, pH value, reaction temperature, duration of reaction, and the identities and concentrations of any other relevant substances (e.g. ammonium chloride) present in the reaction mixture[1,2,7]. In a complicated UF resin system, a large variety of functional groups can coexist in equilibrium with each other, and the equilibrium in a reaction mixture presumably can be shifted by varying the parameters mentioned above. To deal with such a complicated system, a systematic approach is needed in order to extract useful trends. One possible way to carry out a systematic study of the UF resin system is to single out a specific factor from the various factors affecting the structure of the UF resin product, e.g. the pH, and then vary this single factor systematically while keeping other factors fixed[7].

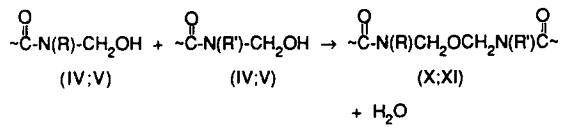
In this paper, this kind of systematic strategy is employed. We single out three parameters, i.e. pH value, concentration and a parameter similar to the formaldehyde-to-urea molar ratio (*vide infra*) called the 'equivalent F/U molar ratio', for the systematic study of UF resin systems. The *starting* materials employed in this study are the *N,N'*-dimethylolurea reagent, urea and various pretreated paraformaldehyde agents. The *N,N'*-dimethylolurea reagent and various pretreated paraformaldehyde agents act as the sources of methylol groups and various CH_2-based linkages in the UF resins.

The N,N'*-dimethylolurea reagent as a source of methylols and* CH_2*-based linkages*

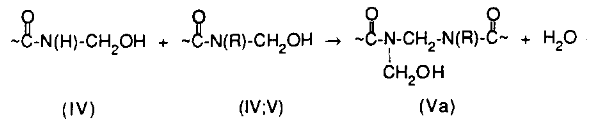
In these systems, 'equivalent' formaldehyde-to-urea molar ratios and related 'equivalent' formaldehyde/urea/water molar ratios (F/U/W) are computed on the basis of the $-CH_2O-$ and $>NC(O)N<$ moieties present in the starting material. Three new aspects emerge when *N,N'*-dimethylolurea is used instead of 37% formalin (containing 8% methanol)[7]. These new aspects are: (1) no methanol is present (a Cannizzaro reaction[18] is not a feasible reaction under conditions employed in this study); (2) there are no unreacted methylene glycol or polyoxymethylene glycols present at the beginning of reaction; and (3) initially there are always precisely two methylol groups per urea unit. Some possible reactions that can be undergone by a methylol group attached to the amide group of a urea unit in the UF resins or *N,N'*-dimethylolurea are shown below:



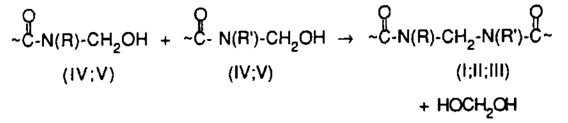
$$\underset{(IV;V)}{\sim\overset{O}{\overset{\|}{C}}\text{-N(R)-CH}_2\text{OH}} + H_2O \rightarrow \sim\overset{O}{\overset{\|}{C}}\text{-N(R)H} + \underset{(XIV)}{\text{HOCH}_2\text{OH}} \qquad (1)$$



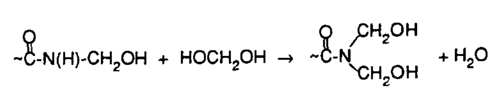
$$\underset{(IV;V)}{\sim\overset{O}{\overset{\|}{C}}\text{-N(R)-CH}_2\text{OH}} + \underset{(IV;V)}{\sim\overset{O}{\overset{\|}{C}}\text{-N(R')-CH}_2\text{OH}} \rightarrow \underset{(X;XI)}{\sim\overset{O}{\overset{\|}{C}}\text{-N(R)CH}_2\text{OCH}_2\text{N(R')}\overset{O}{\overset{\|}{C}}\sim} + H_2O \qquad (2)$$



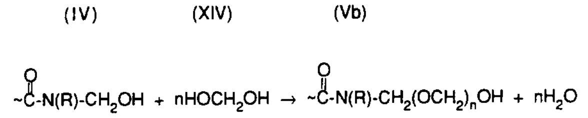
$$\underset{(IV)}{\sim\overset{O}{\overset{\|}{C}}\text{-N(H)-CH}_2\text{OH}} + \underset{(IV;V)}{\sim\overset{O}{\overset{\|}{C}}\text{-N(R)-CH}_2\text{OH}} \rightarrow \underset{(Va)}{\sim\overset{O}{\overset{\|}{C}}\text{-}\underset{\text{CH}_2\text{OH}}{\underset{|}{\text{N}}}\text{-CH}_2\text{-N(R)-}\overset{O}{\overset{\|}{C}}\sim} + H_2O \qquad (3)$$



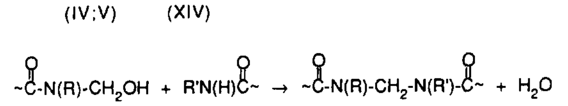
$$\underset{(IV;V)}{\sim\overset{O}{\overset{\|}{C}}\text{-N(R)-CH}_2\text{OH}} + \underset{(IV;V)}{\sim\overset{O}{\overset{\|}{C}}\text{- N(R')-CH}_2\text{OH}} \rightarrow \underset{(I;II;III)}{\sim\overset{O}{\overset{\|}{C}}\text{-N(R)-CH}_2\text{-N(R')-}\overset{O}{\overset{\|}{C}}\sim} + \text{HOCH}_2\text{OH} \qquad (3')$$



$$\underset{(IV)}{\sim\overset{O}{\overset{\|}{C}}\text{-N(H)-CH}_2\text{OH}} + \underset{(XIV)}{\text{HOCH}_2\text{OH}} \rightarrow \underset{(Vb)}{\sim\overset{O}{\overset{\|}{C}}\text{-N}\begin{matrix}\diagup\text{CH}_2\text{OH}\\ \diagdown\text{CH}_2\text{OH}\end{matrix}} + H_2O \qquad (4)$$



$$\underset{(IV;V)}{\sim\overset{O}{\overset{\|}{C}}\text{-N(R)-CH}_2\text{OH}} + \underset{(XIV)}{n\text{HOCH}_2\text{OH}} \rightarrow \sim\overset{O}{\overset{\|}{C}}\text{-N(R)-CH}_2\text{(OCH}_2)_n\text{OH} + nH_2O \qquad (4')$$



$$\underset{(IV;V)}{\sim\overset{O}{\overset{\|}{C}}\text{-N(R)-CH}_2\text{OH}} + \text{R'N(H)}\overset{O}{\overset{\|}{C}}\sim \rightarrow \underset{(I;II;III)}{\sim\overset{O}{\overset{\|}{C}}\text{-N(R)-CH}_2\text{-N(R')-}\overset{O}{\overset{\|}{C}}\sim} + H_2O \qquad (5)$$

In these reactions R and R' can be H or CH_2-. The relative importance of these possible methylol reactions in determining the structures of UF resins prepared from the *N,N'*-dimethylolurea reagent under various reaction conditions is explored below.

Equivalent F/U molar ratio 1.00/1.00. By mixing the *N,N'*-dimethylolurea reagent (which is 'contaminated' by 8 wt% (10 mol%) of monomethylolurea) with the equivalent molar quantity of urea (relative to the molar quantity of *N,N'*-dimethylolurea), one can synthesize a UF resin from a reaction mixture with an equivalent F/U molar ratio of 1.00/1.00. By adding certain amounts of water to this type of mixture, the following three different equivalent formaldehyde/urea/water (F/U/W) molar ratios were obtained: 1.00/1.00/2.48, 1.00/1.00/12.5 and 1.00/1.00/105. Resin-forming reactions were performed at six different pH values (1, 3, 5, 7, 9 and 12) at room temperature for a 12 h reaction period.

Figure 1 shows six rather similar ^{13}C c.p.-m.a.s. n.m.r. spectra of six UF resins prepared at pH 1 and 3. The amounts of unreacted methylol groups (IV, 65 ppm) evident from these spectra are small in all six of these UF resins prepared at pH 1 and 3 from mixtures with an equivalent F/U molar ratio of 1.00/1.00, with only slightly elevated amounts of these methylols in the particular resins designated 1.00/1.00/2.48(3) and 1.00/1.00/105(3). Even with the limited solubility of *N,N'*-dimethylolurea in water (12 g/100 g)[7] and with even smaller solubilities of UF resins containing methylene linkages formed under acidic conditions, the reactions between *N,N'*-dimethylolurea reagent and urea in water

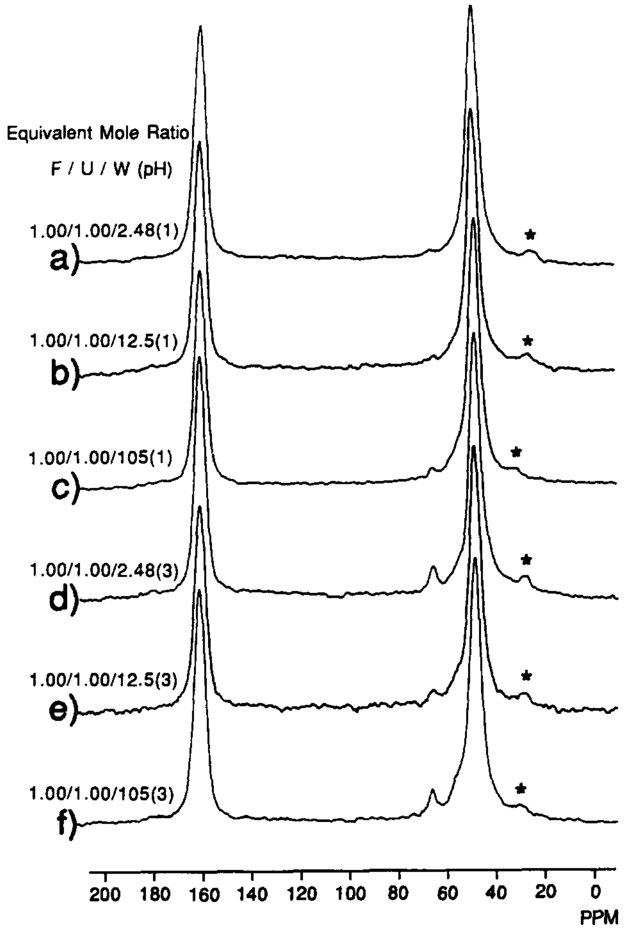
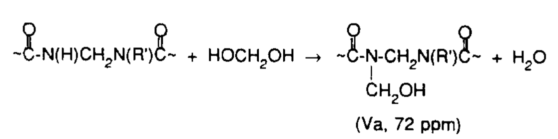


Figure 1 The 50.3 MHz ^{13}C c.p.-m.a.s. n.m.r. spectra of six UF resin samples prepared from the *N,N'*-dimethylolurea reagent, urea and water. C.p. contact time = 1 ms; repetition time = 1 s. Sample prepared from a mixture with an equivalent F/U/W molar ratio of : (a) 1.00/1.00/2.48 at pH 1; (b) 1.00/1.00/12.5 at pH 1; (c) 1.00/1.00/105 at pH 1; (d) 1.00/1.00/2.48 at pH 3; (e) 1.00/1.00/12.5 at pH 3; (f) 1.00/1.00/105 at pH 3. Spinning sidebands are indicated by asterisks

with equivalent F/U/W molar ratios of 1.00/1.00/2.48 and 1.00/1.00/12.5 managed to proceed almost to completeness, as witnessed by the very small amounts of unreacted methylols (IV, 65 ppm) remaining in the corresponding four resin samples. The higher proportions of unreacted methylol groups (IV, 65 ppm) present in the samples designated 1.00/1.00/2.48(3) and 1.00/1.00/105(3), relative to the 1.00/1.00/12.5(3) sample, are attributed to the limited soubility of *N*,*N*′-dimethylolurea in the case of the concentrated 1.00/1.00/2.48 sample and to the lower reactivity of methylols at lower concentrations in the dilute 1.00/1.00/105 case.

Consulting the spectra shown in *Figure 1*, the amounts of crosslinking methylene linkages (II, 54 ppm) are slightly higher in the 1.00/1.00/105(3) sample than for the other five cases shown. The similarities of those six spectra shown in *Figure 1*, with predominant peaks at 160 and 47 ppm (I, straight-chain methylene linkages), indicate that either (1) within the 12 h reaction period the entire UF resin system prepared at pH 1 or 3 from a mixture with an equivalent F/U molar ratio of 1.00 achieves an equilibrium state that favours the formation of straight-chain methylene linkages, or (2) the reactions described by equations (5) and/or (3′) with both R and R′ equal to H are by far the most favoured one(s) among the possible reactions (equations (1)–(5)) of methylol groups attached to the amide group of a urea unit. Judging from the similarities among the ^{13}C c.p.-m.a.s. spectra (*Figure 1*) of the six UF resins prepared at pH 1 and 3 from mixtures with three different concentrations and comparisons among the ^{13}C c.p.-m.a.s. spectra of resins prepared from the *N*,*N*′-dimethylolurea reagent and from 37% formalin and urea (*vide infra*), we favour the second of those two possibilities. Additional experiments described below are required to confirm this interpretation and to separate the contributions from reactions corresponding to equations (3′) and (5). With both R and R′ equal to H, the reactions described by equations (5) and/or (3′) can lead only to straight-chain methylene linkages (I, 47 ppm). Therefore, the occurrence of crosslinking methylene linkages (II, 54 ppm), which amount to about 14% of the total methylene linkages in the six UF resins mentioned above (see *Figure 1*), requires other explanations.

With R and/or R′ representing methylene linkages (I, 47 ppm) or dimethylene ether linkages (X, 69 ppm), the reactions described by equations (5) and/or (3′) can lead to crosslinking methylene linkages (II, 54 ppm). There are two possible routes for the case in which R represents methylene linkages in equations (5) and/or (3′): the first route is the reaction between methylol groups and a secondary amide attached to a methylol group, as described by equation (3) (the R in equation (3) can be H or CH_2–); the second route is the methylolation by methylene glycol of a secondary amide nitrogen that is connected to a carbonyl group and a methylene linkage as described by the following equation:



$$-\overset{O}{\overset{\|}{C}}-N(H)CH_2N(R')\overset{O}{\overset{\|}{C}}- + HOCH_2OH \rightarrow -\overset{O}{\overset{\|}{C}}-\underset{\underset{CH_2OH}{|}}{N}-CH_2N(R')\overset{O}{\overset{\|}{C}}- + H_2O \qquad (6)$$

(Va, 72 ppm)

On the basis of similarities among the ^{13}C c.p.-m.a.s. spectra shown in *Figure 1* and the observation of a slightly higher proportion of crosslinking methylene linkages (II, 54 ppm) in the resins prepared at pH 3 and at lower concentration, the possbility described by equation (6) is favoured at this time. The methylene glycol that appears in equation (6) can come from the demethylolation reaction described by equation (1) or from the reaction described by equation (3′). At the present time, it is difficult to attribute the formation of methylols (Va, 72 ppm) to either route.

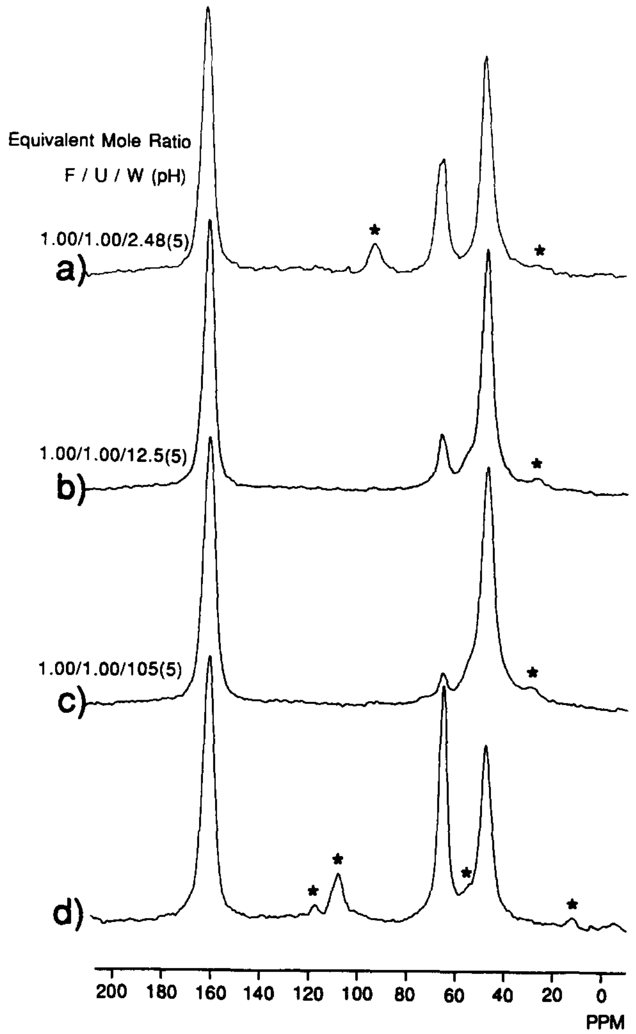


Figure 2 The 50.3 MHz ^{13}C c.p.-m.a.s. n.m.r. spectra of four UF resin samples prepared from the *N*,*N*′-dimethylolurea reagent, urea and water at pH 5. C.p. contact time = 1 ms; repetition time = 1 s. Sample prepared from a mixture with an equivalent F/U/W molar ratio of: (a) 1.00/1.00/2.48; (b) 1.00/1.00/12.5; (c) 1.00/1.00/105 (the precipitates); (d) 1.00/1.00/105 (solids obtained by vacuum drying of the liquid portion after neutralization to pH 7). Spinning sidebands are indicated by asterisks

With the same equivalent F/U/W molar ratios of 1.00/1.00/2.48, 1.00/1.00/12.5 and 1.00/1.00/105 as represented in *Figure 1*, UF resins were also prepared at pH 5 from the *N*,*N*′-dimethylolurea reagent, urea and water. *Figure 2* shows the ^{13}C c.p.-m.a.s. n.m.r. spectra of the three UF resin samples prepared at pH 5. This figure also shows the spectrum of a solid sample obtained by neutralizing and then vacuum drying (10^{-2} Torr, $-5°C$) the liquid portion of the reaction mixture prepared with an equivalent F/U/W molar ratio of 1.00/1.00/105 at pH 5 (*Figure 2d*). The spectrum given in *Figure 2d* shows that the water-soluble components of the resin prepared with an equivalent F/U/W molar ratio of 1.00/1.00/105 at pH 5 are $HOCH_2NHC(O)NHCH_2NHC(O)NHCH_2OH$ and/or $NH_2C(O)NHCH_2NHC(O)NHCH_2OH$, urea, monomethylolurea and *N*,*N*′-dimethylolurea. Because the formation of methylene linkages from corresponding methylol groups is catalysed by acid[1,2,7], one expects lower reactivities in reactions described by equations (3), (3′) and (5) between urea and *N*,*N*′-dimethylolurea and between *N*,*N*′-dimethylolurea molecules at pH 5, in comparison to corresponding reactivities at pH 1 and pH 3. The limited solubility of *N*,*N*′-dimethylolurea in water and the formation of even less soluble[7] UF resins containing methylene linkages enter the picture in the preparation of UF resin from urea and the *N*,*N*′-dimethylolurea reagent with an equivalent F/U/W molar ratio of 1.00/1.00/2.48 at pH 5, owing to the low reactivities of various methylol groups in UF resin at pH 5. Substantial amounts of unreacted *N*,*N*′-dimethylolurea exist in the reaction mixture, as evidenced by the strong intensity and the ^{14}N splitting pattern (even more apparent in the spectrum, not shown, without line broadening applied) around 65 ppm in the spectrum shown in *Figure 2a*.

With modest dilution to an equivalent F/U/W molar ratio of 1.00/1.00/12.5 at pH 5, the limited solubility of *N*,*N*′-dimethylolurea in water exerts only a small constraint on the reaction between urea and the *N*,*N*′-dimethylolurea reagent, as witnessed by the small proportion of unreacted methylols (IV, 65 ppm) remaining in the resulting UF resin system (see *Figure 2b*). A composite spectrum was constructed from the spectra of *Figures 2c* and *2d*, with weighting according to their relative amounts in the *total* UF resin obtained from the precipitate and liquid portion of the reaction mixture prepared from an equivalent F/U/W molar ratio of 1.00/1.00/105 at pH 5; this composite spectrum (not shown) is very similar to the spectrum in *Figure 2b*, showing slightly higher proportions of unreacted methylols (IV, 65 ppm) and of crosslinking methylene linkages (II, 54 ppm) appearing in the composite spectrum than in *Figure 2b*. As mentioned above for the case of a UF resin prepared at pH 3 from an equivalent F/U/W molar ratio of 1.00/1.00/105, even though all the *N*,*N*′-dimethylolurea is easily dissolved (within 1 min) in the reaction system prepared with an equivalent F/U/W molar ratio of 1.00/1.00/105 at pH 5, the reaction between urea and the *N*,*N*′-dimethylolurea reagent was slowed by dilution at this higher pH, and more unreacted urea and *N*,*N*′-dimethylolurea remain in the solution.

Both of the UF resin samples designated 1.00/1.00/12.5(5) and 1.00/1.00/105(5) have higher proportions of crosslinking methylene linkages (II, 54 ppm) than in the four UF samples prepared with the same equivalent F/U/W molar ratios at pH 1 and pH 3. Judging from the very limited extent of the reaction between methylol groups described by equation (3) (see discussion below on UF resins prepared from the *N*,*N*′-dimethylolurea reagent with an equivalent F/U molar ratio of 1.90 at pH 5) and the slightly higher proportion of crosslinking methylene linkages (II, 54 ppm) in the UF resins prepared at pH 5 under more dilute conditions with an equivalent F/U molar ratio of 1.00 (*vide supra*), we favour the following route to crosslinking methylene linkages in UF resins prepared at pH 5 from a mixture of the *N*,*N*′-dimethylolurea reagent and urea in water with an equivalent F/U molar ratio of 1.00: the liberation of methylene glycol according to equation (1), followed by the methylolation of a secondary amide site connected between a methylene linkage (I, 47 ppm) and a carbonyl group, as described by equation (6) (with R′ = H), and finally a condensation between the methylol group thereby formed (Va, 72 ppm) and a primary amide, as described by equation (5) (with R′ = H). One expects the rates of the reactions between methylols and urea units described by equations (3), (3′) and (5) at pH 5 to be lower than at lower pH values (*vide supra*), permitting a longer time for the competitive demethylolation described by equation (1) to occur. Therefore, more crosslinking methylene linkages (II, 54 ppm) are formed at pH 5 than at pH 1 and pH 3 and under more dilute conditions than that under more concentrated conditions at either pH 3 or pH 5. The same scheme for the formation of crosslinking methylene linkages was espoused above for the case of pH 3.

Figures 3a and *3b* show the 50 μs interrupted-decoupling ^{13}C c.p.-m.a.s. n.m.r. spectra of UF resins 1.00/1.00/2.48(5) and 1.00/1.00/12.5(5). *Figure 3c* shows the corresponding spectrum of the solid obtained by vacuum drying of the liquid portion of the reaction mixture prepared at pH 5 from a mixture of the *N*,*N*′-dimethylolurea reagent and urea in water with an equivalent F/U/W molar ratio of 1.00/1.00/105. Both *Figures 3a* and *3c* show small surviving peaks at 47 ppm, which implies substantial mobilities of some methylene linkages (I, 47 ppm) in those two UF resin samples; this level of mobility is probably due to short-chain components in the UF resins. The 50 μs interrupted-decoupling ^{13}C c.p.-m.a.s. spectra (not shown here) of all six UF resin samples prepared at pH 1 and 3 from mixtures of the *N*,*N*′-dimethylolurea reagent and urea in water with an equivalent F/U molar ratio

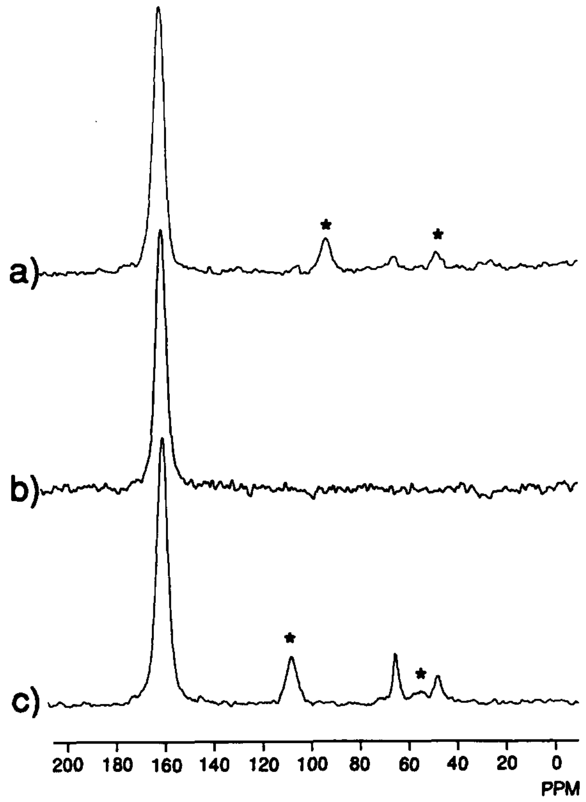
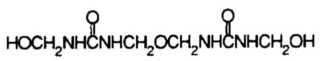


Figure 3 The 50.3 MHz interrupted-decoupling ^{13}C c.p.-m.a.s. n.m.r. spectra of three UF samples prepared at pH 5. C.p. contact time = 1 ms; repetition time = 1 s; interrupted-decoupling period = 50 μs. Sample prepared from a mixture with an equivalent F/U/W molar ratio of: (a) 1.00/1.00/2.48; (b) 1.00/1.00/12.5; (c) 1.00/1.00/105 (obtained by vacuum drying of the liquid portion after neutralization to pH 7). Spinning sidebands are indicated by asterisks

of 1.00 and of the 1.00/1.00/105(5) resin are all similar to the spectrum shown in *Figure 3b*; all these interrupted-decoupling ^{13}C c.p.-m.a.s. spectra indicate that the methylene linkages (I, 47 ppm; II, 54 ppm) in these UF resin samples are rather immobile, so ^{13}C magnetization components corresponding to these methylene linkages cannot survive the 50 μs dipolar-dephasing period.

It has been shown previously[7] that, under neutral or basic conditions at room temperature, the main products from the reaction between 37% formalin and urea are methylolureas without any linkages (other than dimethyl ether linkages (X)) between two urea units. It is interesting to observe what happens when the same number of moles of urea and *N*,*N*′-dimethylolurea are put together at different concentrations under neutral or basic conditions at room temperature.

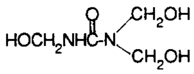
UF resins were prepared at pH 7, 9 and 12 from mixtures of the *N*,*N*′-dimethylolurea reagent, urea and water with the equivalent F/U/W molar ratios of 1.00/1.00/2.48, 1.00/1.00/12.5 and 1.00/1.00/105. All three 1.00/1.00/2.48 samples and those two 1.00/1.00/12.5 samples prepared at pH 7 and 9 remained in a slushy rather than solid state during the entire 12 h reaction period. The 1.00/1.00/12.5 sample prepared at pH 12 became a clear solution after stirring for 40 min, whereas all three 1.00/1.00/105 samples prepared at pH 7, 9 and 12 became clear solutions after stirring for 1 min. The 125.8 MHz liquid-state ^{13}C n.m.r. spectrum of the 1.00/1.00/12.5 sample prepared at pH 12 for 12 h is shown in *Figure 4*. This spectrum indicates that the major components in the solution of 1.00/1.00/12.5 prepared at pH 12 are monomethylolurea, *N*,*N*′-dimethylolurea and urea, in order of decreasing proportion. The liquid-state ^{13}C n.m.r. signal of the methylol group in monomethylolurea appears at slightly lower shielding[23,26] (higher frequency) than the signal of the two methylol groups in *N*,*N*′-dimethylolurea, as seen in the expanded spectrum of the 62–68 ppm region in *Figure 4*. The two small shoulders at about 65.3 and 65.5 ppm in the expanded spectrum in *Figure 4* are assigned[23,26] to the methylol groups of an ether-bridged species (XXI) and trimethylolurea (XXII):



$HOCH_2NH\overset{O}{\overset{\|}{C}}NHCH_2OCH_2NH\overset{O}{\overset{\|}{C}}NHCH_2OH$

(XXI)

and



$HOCH_2NH\overset{O}{\overset{\|}{C}}N(CH_2OH)_2$

(XXII)

The dimethylene ether linkage (X) of ether XXI has a ^{13}C n.m.r. signal at 69 ppm, whereas the geminate methylol groups (Vb) of trimethylolurea appear at 72 ppm. The 83 ppm peak in the spectrum of *Figure 4* is assigned to methylene glycol (XIV). The three peaks at about 160 ppm in the spectrum of *Figure 4* are assigned to carbonyl groups of urea, monomethylolurea and *N*,*N*′-dimethylolurea in order of increasing shielding (decreasing frequency); the intensities of these three peaks reflect the relative proportions of these three species in the 1.00/1.00/12.5(12) solution. In contrast to the solid-state ^{13}C c.p.-m.a.s. n.m.r. spectra, the spectral region around 160 ppm in the liquid-state ^{13}C n.m.r. spectra provides a good diagnostic tool for the determination of various groups attached to the carbonyl groups of UF resins. The liquid-state ^{13}C n.m.r. spectrum (not shown here) of a sample prepared at pH 7 from a 1.00/1.00/105 mixture indicates that the amount of monomethylolurea is only about one-eighth of the amount of *N*,*N*′-dimethylolurea in the sample.

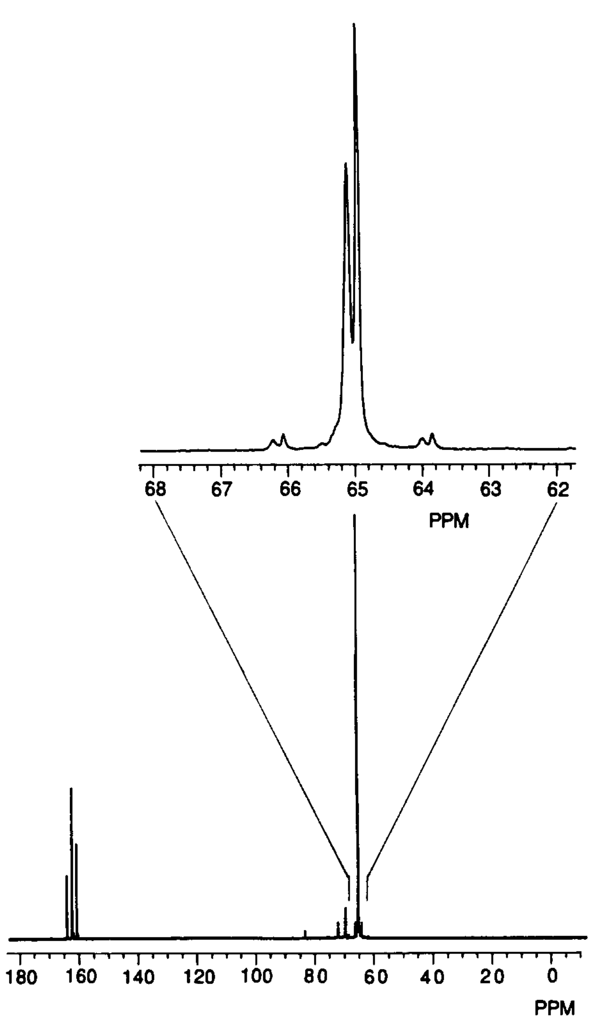


Figure 4 The 125.8 MHz liquid-sample ^{13}C n.m.r. spectrum of a UF resin sample prepared at pH 12 from the *N*,*N*′-dimethylolurea reagent, urea and water with an equivalent F/U/W molar ratio of 1.00/1.00/12.5. Top: expanded spectrum of 65 ppm region; bottom: entire spectrum

Figure 5a shows the solid-state ^{13}C c.p.-m.a.s. n.m.r. spectrum of a mixture of the unreacted *N*,*N*′-dimethylolurea reagent, consisting of 0.9 mole fraction of *N*,*N*′-dimethylolurea and 0.1 mole fraction of monomethylolurea. *Figures 5b* and *5c* are the spectra of samples prepared from mixtures of the *N*,*N*′-dimethylolurea reagent, urea and water with equivalent F/U/W molar ratios of (*5b*) 1.00/1.00/2.48 at pH 7 and (*5c*) 1.00/1.00/12.5 at pH 9, respectively. All three *Figures 5a*, *5b* and *5c* show the splitting patterns around 160 and 65 ppm regions due to residual ^{14}N–^{13}C dipolar interactions arising from the quadrupolar effect[9–15] of ^{14}N. The lower-shielding side (at 69 ppm) of the doublet around 65 ppm arising from the methylol groups of *N*,*N*′-dimethylolurea strongly overlaps with the signal from dimethyl ether linkages (X). *Figure 5d* shows the ^{13}C c.p.-m.a.s. spectrum of a solid obtained by vacuum drying (10^{-2} Torr, -5°C) the clear solution resulting from reaction of a 1.00/1.00/12.5 mixture at pH 12. The main component represented by *Figure 5d* is dimethyl ether linkage (X, 69 ppm) and is formed by condensation of monomethylolurea and/or *N*,*N*′-dimethylolurea of 1.00/1.00/12.5 mixture at pH 12 during the vacuum drying process at -5°C and pH 12.

The ^{13}C c.p.-m.a.s. n.m.r. spectrum (not shown here)

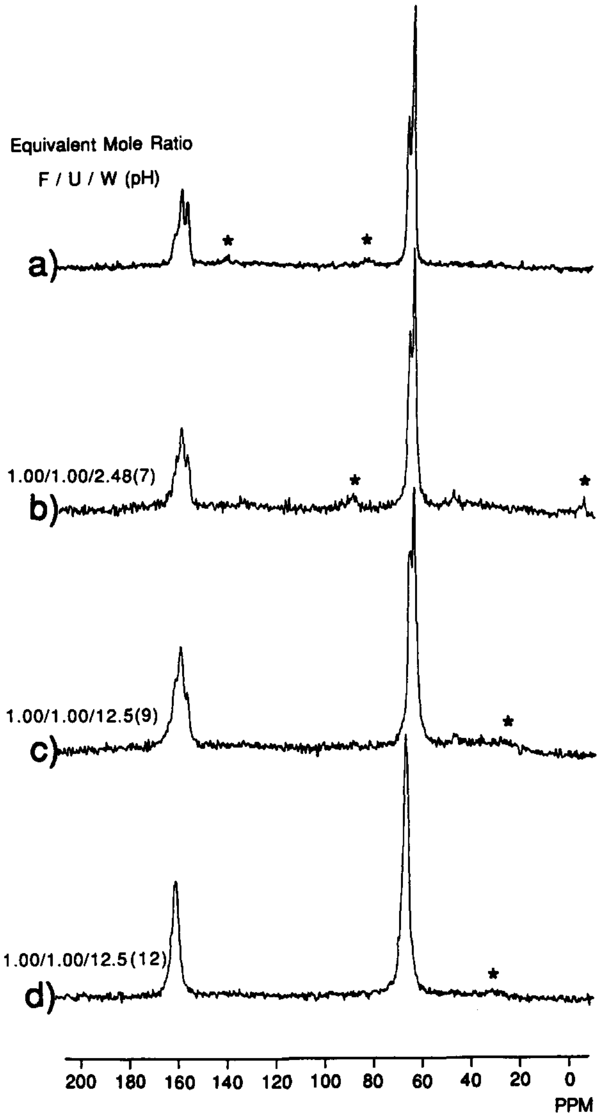
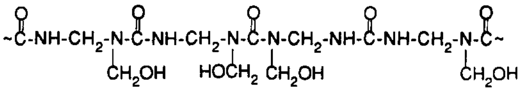


Figure 5 The 50.3 MHz ^{13}C c.p.-m.a.s. n.m.r. spectra of *N*,*N*′-dimethylolurea reagent (with the accompanying 10 mol% of monomethylolurea) and three UF resin samples prepared from the *N*,*N*′-dimethylolurea reagent, urea and water. C.p. contact time = 1 ms; repetition time = 1 s. (a) The *N*,*N*′-dimethylolurea reagent. (b) Resin prepared from a mixture with an equivalent F/U/W molar ratio of 1.00/1.00/2.48 at pH 7. (c) Resin prepared from a mixture with an equivalent F/U/W molar ratio of 1.00/1.00/12.5 at pH 9. (d) Resin prepared from a mixture with an equivalent F/U/W molar ratio of 1.00/1.00/12.5 at pH 12. Spinning sidebands are indicated by asterisks

of a sample prepared at pH 7 from a mixture of the *N*,*N*′-dimethylolurea reagent, urea and water with an equivalent F/U/W molar ratio of 1.00/1.00/12.5 is very similar to the spectrum shown in *Figure 5b*. The spectrum (not shown) of a solid obtained by vacuum drying (10^{-2} Torr, -5°C) the clear solution prepared at pH 7 from a reacted mixture of the *N*,*N*′-dimethylolurea reagent, urea and water with an equivalent F/U/W molar ratio of 1.00/1.00/105 looks very similar to the spectrum shown in *Figure 5c*. The spectrum (not shown) of a solid sample obtained in a similar manner by vacuum drying at -5°C the clear 1.00/1.00/105 solution obtained at pH 9 has characteristics that are intermediate between the spectra shown in *Figures 5c* and *5d*. The liquid-sample ^{13}C n.m.r. results (not shown here) indicate that basic conditions and higher dilution favour the demethylolation of *N*,*N*′-dimethylolurea to form monomethylolurea and methylene glycol, as described by equation (1) with R equal to H. At pH 12, the demethylolation of *N*,*N*′-dimethylolurea is probably assisted by the reaction of urea with liberated methylene glycol to shift the equilibrium corresponding to equation (1). During vacuum drying of these three 1.00/1.00/105 solutions of pH 7, 9 and 12, some methylolureas condense to form dimethyl ether linkages (X, 69 ppm). The formation of dimethyl ether linkages is most likely to happen at pH 12 among these three pH values, as indicated by the spectra (not shown here) of these three solids.

Equivalent F/U molar ratio 1.90/1.00. With a starting material that contains 0.9 mole fraction of *N*,*N*′-dimethylolurea and 0.1 mole fraction of monomethylolurea, the equivalent F/U molar ratio is 1.90/1.00. UF resins were prepared at the six different pH values of 1, 3, 5, 7, 9 and 12 at room temperature (23 ± 2°C) from mixtures with three sets of concentrations expressed by equivalent F/U/W molar ratios of 1.90/1.00/4.96, 1.90/1.00/25.0 and 1.90/1.00/107.

The possible reactions between two *N*,*N*′-dimethylolurea molecules are described by equations (2), (3) and (3′) with all R and R′ in these equations representing H. Equation (2) describes the formation of dimethylene ether linkages (X, 69 ppm) from *N*,*N*′-dimethylolurea. Equation (3) shows how a methylene linkage (II, 54 ppm) that is 'a precursor of crosslinking' (*vide infra*) is formed from *N*,*N*′-dimethylolurea, while equation (3′) represents the formation of a straight-chain methylene linkage (I, 47 ppm) together with the liberation of methylene glycol from *N*,*N*′-dimethylolurea. If the type of reaction described by equation (3) (with R = H) prevails, the initial product would be of the following type:

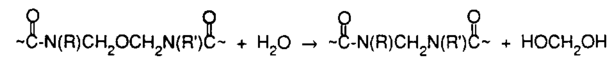


$$\sim\overset{O}{\overset{\|}{C}}-NH-CH_2-\underset{CH_2OH}{N}-\overset{O}{\overset{\|}{C}}-NH-CH_2-\underset{HOCH_2}{N}-\overset{O}{\overset{\|}{C}}-\underset{CH_2OH}{N}-CH_2-NH-\overset{O}{\overset{\|}{C}}-NH-CH_2-\underset{CH_2OH}{N}-\overset{O}{\overset{\|}{C}}\sim$$

(XXIII) (XXIV) (XXV)

In such a structure there are three types of urea units, which contain one methylol (XXIII), two methylols (XXIV) or no methylol groups (XXV) per urea unit. The methylol groups in XXIII and XXIV are capable of undergoing those reactions described by equations (1) to (5).

The starting *N*,*N*′-dimethylolurea reagent in the systems represented in *Figures 6*, *7* and *8* contains 10 mol% of monomethylolurea relative to 90 mol% of *N*,*N*′-dimethylolurea; therefore, each mole of *N*,*N*′-dimethylolurea reagent contains 1.9 mol of $-NHCH_2OH$ (methylol) groups and 0.1 mol of $-NH_2$ groups. If all the methylol groups in the starting material eventually formed methylene linkages, without any side products other than water, each mole of *N*,*N*′-dimethylolurea reagent would produce 1.9 mol of methylene linkages; in other words, each nitrogen atom on average would be attached to 1.9 methylene linkages. If all the methylol groups in the starting materials ended up as methylene linkages without any side products except water, one would expect at least 90% of the methylene linkages to be double crosslinked (III, 60 ppm) and at most 5.3% (0.1 mol out of 1.9 mol) of methylene linkages to be straight-chain moieties. If the proportion of straight-chain methylene linkages is higher than 5.3% of the total methylene linkages formed, then various side reactions must be significant (see *Figures 6* and *7c*), and/or a large quantity of unreacted methylol groups must be present (see *Figures 7a, 7b, 8b* and *8c*). The possible side reactions that could diminish the proportion of methylol groups ending up in methylene linkages and ultimately lead to an increase in the proportion of straight-chain methylene linkages in the resin are: formation of dimethylene ether linkages (X, 69 ppm; XI, 76 ppm) through equation (2); formation of uronic rings (XII, XIII, XIX, XX) from species XXIV; and various demethylolation reactions. The most obvious demethylolation reactions are described by equations (1) and (3'). Another possible route to demethylolation is the formation of dimethylene ether linkages (X, XI) described by equation (2), followed by the demethylolation of the dimethylene ether linkages described by the following equation:



$$\sim\overset{O}{\overset{\|}{C}}\text{-N(R)CH}_2\text{OCH}_2\text{N(R')}\overset{O}{\overset{\|}{C}}\sim + H_2O \rightarrow \sim\overset{O}{\overset{\|}{C}}\text{-N(R)CH}_2\text{N(R')}\overset{O}{\overset{\|}{C}}\sim + HOCH_2OH \qquad (7)$$

Demethylolations described by equations (1), (3') and (7), formation of dimethylene ether linkages (X, XI) and uronic rings (XXII, XXIII, XIX, XX), and steric or other geometrical effects could all favour the formation of straight-chain methylene linkages (I, 47 ppm) and single crosslinking methylene linkages (II, 54 ppm) instead of double crosslinking methylene linkages (III, 60 ppm).

Figures 6a, 6b and *6c* present the ^{13}C c.p.-m.a.s. spectra of three samples prepared from mixtures of water and the *N,N'*-dimethylolurea reagent (with its accompanying 10 mol% of monomethylolurea) at pH 1 with equivalent F/U/W molar ratios of 1.90/1.00/4.96, 1.90/1.00/25.0 and 1.90/1.00/107, respectively. The major constituents of all three samples represented in *Figure 6* are seen to be carbonyl groups (155–169 ppm), the three types of methylene linkages (I, 47 ppm; II, 54 ppm; III, 60 ppm), methylols (IV, 65 ppm; V, 72 ppm), substituted uronic rings (XIII, 79 ppm; XX, 156 ppm) and some dimethylene ether linkages (X, 69 ppm; XI, 76 ppm). The spectra in *Figure 6* indicate that the amount of substituted uronic rings formed from species XXIV decreases with increasing dilution. The peaks at about 65 and 72 ppm in the spectra shown in *Figure 6* indicate the amounts of unreacted methylol groups (IV, V). These spectra show that not only the amount of uronic rings (XIII, XX) but also the amounts of unreacted methylol groups (IV, V) and of the dimethylene ether linkages (X, XI) decrease with increasing dilution in these UF resin samples. The proportion of double crosslinking methylene linkages (III) is seen to decrease with increasing dilution, as indicated by the intensities of the shoulder around 60 ppm. All three samples prepared at pH 1 from mixtures of the *N,N'*-dimethylolurea reagent and water with an equivalent F/U molar ratio of 1.90 are seen to contain substantial amounts of crosslinking methylene linkages of both type II (54 ppm) and type III (60 ppm), with a higher proportion of single crosslinking methylene linkages (II) in comparison to double crosslinking methylene linkages (III) in all three of these UF resin samples.

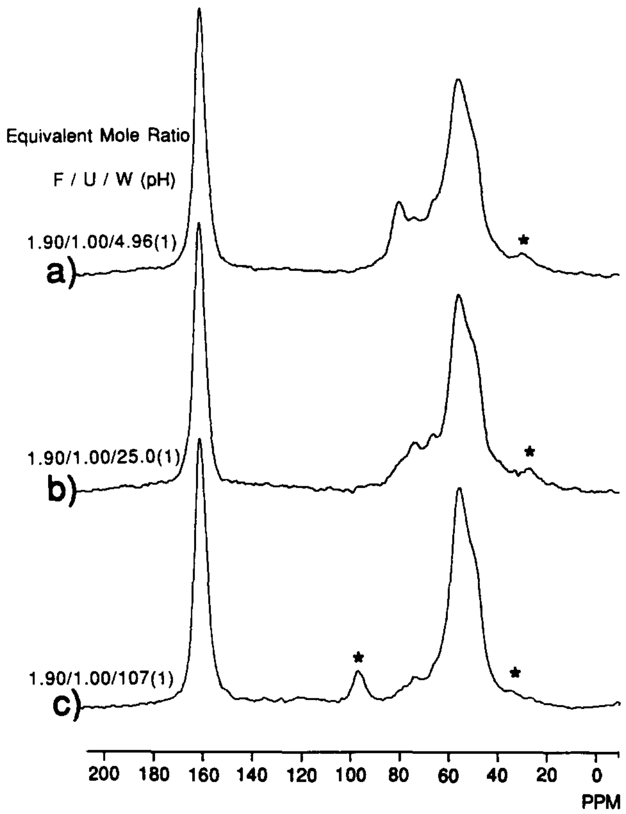


Figure 6 The 50.3 MHz ^{13}C c.p.-m.a.s. n.m.r. spectra of three UF resin samples prepared from the *N,N'*-dimethylolurea reagent and water at pH 1. C.p. contact time = 1 ms; repetition time = 1 s. Sample prepared from a mixture with an equivalent F/U/W molar ratio of: (a) 1.90/1.00/4.96, (b) 1.90/1.00/25.0 and (c) 1.90/1.00/107. Spinning sidebands are indicated by asterisks

The proportions of straight-chain methylene linkages (I, 47 ppm) in all three of these 1.90/1.00 samples prepared at pH 1 far exceed the 5.3% limit mentioned above. For the most concentrated reaction mixture investigated in this series of samples, i.e. with an equivalent F/U/W molar ratio of 1.90/1.00/4.96, the formation of a substantial amount of uronic rings (XIII, 79 ppm; XX, 156 ppm) and some dimethylene ether linkages (X, 69 ppm; XI, 76 ppm) and the existence of substantial amounts of unreacted methylol groups (IV, 65 ppm; V, 72 ppm) can partially explain the higher proportion of straight-chain methylene linkages in this resin. Formation of the first two of these species competes with the formation of methylene linkages from methylols and therefore makes the systems behave like a system with a lower F/U molar ratio (*vide supra*). However, *Figure 6* indicates that the proportions of all these uronic rings, dimethylene ether linkages and unreacted methylols decrease with increasing dilution of the reaction mixture; this trend is especially evident for the smallest concentration employed here, i.e. with an equivalent F/U/W molar ratio of 1.90/1.00/107, at pH 1. In this case, there are more methylene linkages (I, 47 ppm; II, 54 ppm; III, 60 ppm) formed and more demethylolation reactions apparently occur (equations (1), (3') and (7)) to produce straight-chain methylene linkages (I, 47 ppm) than in the other cases represented by *Figure 6*.

Figures 6a and *6b* show that a substantial amount of methylol groups (IV, 65 ppm; V, 72 ppm) are present at pH 1 in the two concentrated reaction mixtures with equivalent F/U/W molar ratios of 1.90/1.00/4.96 and 1.90/1.00/25.0. Methylol groups attached to tertiary amides (V, 72 ppm) are the products of reaction of *N,N'*-dimethylolurea, as described by equations (3) or (4), and only part of the methylol groups (IV, 65 ppm) represented in the spectra of *Figures 6a* and *6b* belong to unreacted *N,N'*-dimethylolurea. This reflects the fact that some of the methylol groups can be at the ends of long chains (IV) and therefore can be viewed as the products of reacted *N*,*N*′-dimethylolurea. Based on the above arguments and the spectra of *Figure 6*, one can see that a large proportion of the *N*,*N*′-dimethylolurea molecules undergo various reactions at pH 1 over the 12 h reaction period. The limited solubility of *N*,*N*′-dimethylolurea in water (12 g/100 g)[7] plays some part in determining the structures of the final UF resin products prepared at pH 1 from reaction mixtures of the *N*,*N*′-dimethylolurea reagent with an equivalent F/U molar ratio of 1.90; this behaviour stands in contrast to the case of UF resin products prepared from mixtures with an equivalent F/U molar ratio of 1.00 (*vide supra*; cf. *Figure 1a*). The formation of large amounts of uronic rings (XIII, 79 ppm; XX, 156 ppm), some dimethylene ether linkages (X, 69 ppm; XI, 76 ppm) and the existence of substantial amounts of unreacted methylol groups (IV, 65 ppm; V, 72 ppm) probably can partially be attributed to the lack of water in the two concentrated mixtures prepared from the *N*,*N*′-dimethylolurea reagent at pH 1.

The ^{13}C c.p.-m.a.s. spectra of three UF resin samples prepared at pH 3 from mixtures of the *N*,*N*′-dimethylolurea reagent and water with the equivalent F/U/W molar ratios of 1.90/1.00/4.96, 1.90/1.00/25.0 and 1.90/1.00/107 are shown in *Figures 7a, 7b* and *7c*, respectively. In contrast to the pH 3 cases with a F/U molar ratio of 1.00 discussed above (see *Figures 1d, 1e* and *1f*), the limited solubility of *N*,*N*′-dimethylolurea in water plays a large role in determining the final UF resin structures represented in *Figure 7*. This difference is due to the much lower extent of reaction between *N*,*N*′-dimethylolurea molecules themselves in the F/U = 1.90 case in comparison to the reaction between *N*,*N*′-dimethylolurea and urea in mixtures with an equivalent F/U molar ratio of 1.00 discussed above. When the reaction between *N*,*N*′-dimethylolurea and urea is sufficiently fast and favoured, then the limited solubility of *N*,*N*′-dimethylolurea in water becomes an unimportant factor in determining the structure of final UF resin products (*vide supra*). *Figure 7a* clearly shows that the reaction between *N*,*N*′-dimethylolurea and the accompanying 10 mol% of monomethylolurea to form straight-chain methylene linkages (I, 47 ppm) proceeds quite well at pH 3 even in the most concentrated F/U = 1.9 reaction mixture employed in this investigation (F/U/W = 1.90/1.00/4.96). Part of these straight-chain methylene linkages are formed from those reactions mentioned above (see the discussion for an equivalent F/U molar ratio of 1.90 at pH 1). That there is some reaction between *N*,*N*′-dimethylolurea molecules themselves in the 1.90/1.00/4.96(3) case is witnessed by the intense peaks at 54 ppm (II, methylene linkages) and 72 ppm (Va, internal methylol groups) and possibly at 69 ppm (X, dimethylene ether linkages) in the spectrum of *Figure 7a*, even though the spectrum also reveals that there is a predominant amount of unreacted methylol groups (IV, 65 ppm; V, 72 ppm) remaining. A possible structural candidate to explain the peaks at 54 and 72 ppm in the spectrum of *Figure 7a* has already been mentioned above, i.e. the structure XXIII–XXIV–XXV.

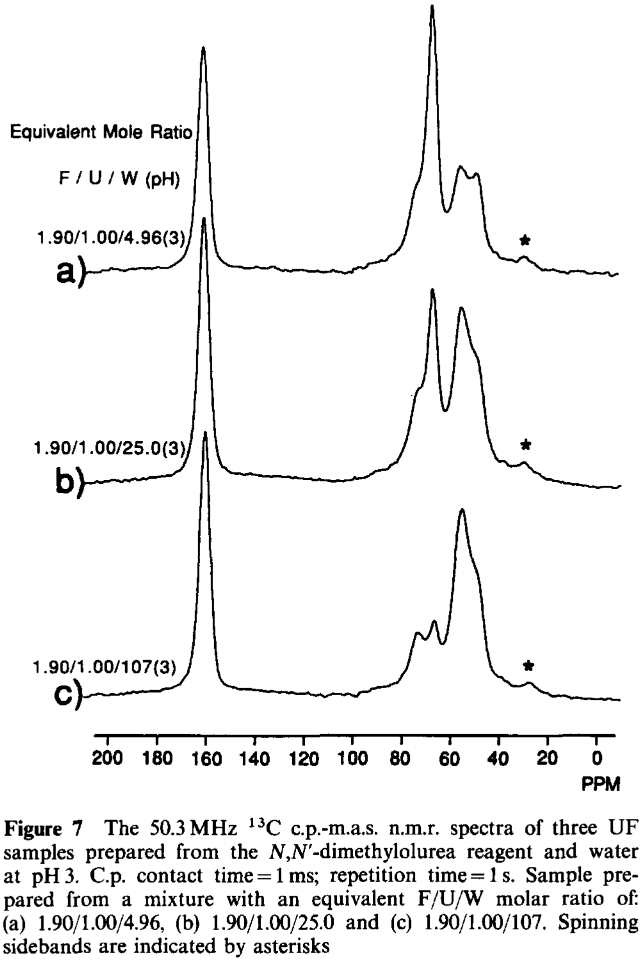


Figure 7 The 50.3 MHz ^{13}C c.p.-m.a.s. n.m.r. spectra of three UF samples prepared from the *N*,*N*′-dimethylolurea reagent and water at pH 3. C.p. contact time = 1 ms; repetition time = 1 s. Sample prepared from a mixture with an equivalent F/U/W molar ratio of: (a) 1.90/1.00/4.96, (b) 1.90/1.00/25.0 and (c) 1.90/1.00/107. Spinning sidebands are indicated by asterisks

Methylene linkages (II, 54 ppm) in the structure XXIII–XXIV–XXV are referred to here as 'precursors of crosslinking', because the accompanying methylol groups (Va, 72 ppm) are capable of forming crosslinks through various kinds of linkages (II, III, X, XI). Of course, some of the methylol groups can be expelled from a resin as a result of the demethylolation reaction described by equation (1), thereby favouring the production of straight-chain methylene linkages by eliminating these crosslinking possibilities. Judging from the relative intensities of the 54 ppm peak and the 72 ppm peak in the spectrum of *Figure 7a*, it appears that most of the methylene linkages (II, 54 ppm) and most of the methylol groups (Va, 72 ppm) are present as *precursors* of crosslinking, without undergoing further reaction in the 1.90/1.00/4.96(3) sample. There is also some portion of 60 ppm methylene linkages (III) in this 1.90/1.00/4.96(3) resin sample.

With additional water added to give a mixture with an equivalent F/U/W molar ratio of 1.90/1.00/25.0 at pH 3, the amount of *N*,*N*′-dimethylolurea that dissolves in water, as well as the extent of the various reactions undergone by dissolved *N*,*N*′-dimethylolurea, increase. In comparison to the 1.90/1.00/4.96(3) sample, in this 1.90/1.00/25.0(3) sample there is a higher proportion of internal methylol groups (Va, 72 ppm) undergoing further reaction to produce more crosslinking methylene linkages (II, 54 ppm). This trend is indicated by a higher intensity of the 54 ppm peak relative to the 72 ppm peak in the spectrum of *Figure 7b* in comparison to the spectrum in *Figure 7a*. Nevertheless, there is still a substantial amount of unreacted methylol groups of both kinds (IV, 65 ppm, Va, 72 ppm) remaining in the 1.90/1.00/25.0(3) sample.

With further dilution at pH 3 to an equivalent F/U/W molar ratio of 1.90/1.00/107, the trends discussed above are seen to continue (*Figure 7c*), i.e. more extensive dissolution and reactions of *N*,*N*′-dimethylolurea, and a larger fraction of methylol groups (IV, 65 ppm; Va, 72 ppm) undergoing reaction to produce methylene linkages (I, 47 ppm; II, 54 ppm; III, 60 ppm). Nevertheless, one notes in *Figure 7c* that there is still a substantial quantity of unreacted methylol groups remaining, even though all the *N*,*N*′-dimethylolurea has dissolved at this concentration.

In comparison to the situation at pH 1 discussed earlier in this paper, the reactivities of methylol groups (IV, 65 ppm; Va, 72 ppm) to produce various linkages, such as methylene linkages (II, 54 ppm; III, 60 ppm) and uronic rings (XIII, 79 ppm; XX, 156 ppm), are lower at pH 3 (compare *Figures 6* and *7*); this behaviour is consistent with observations that the formation of methylene linkages[1,2,7] and uronic rings[7,23,26] from corresponding methylol groups are catalysed by acid.

Figure 8 presents the ^{13}C c.p.-m.a.s. spectra of three resin samples prepared at pH 5 from mixtures of the *N*,*N*′-dimethylolurea reagent and water with equivalent F/U/W molar ratios of 1.90/1.00/4.96, 1.90/1.00/25.0 and 1.90/1.00/107. The spectra in *Figures 8a* and *8b* were plotted without applying any line broadening in order to emphasize chemical-shift differences among peaks in the 65 ppm region. *Figure 8a* indicates that *N*,*N*′-dimethylolurea and the accompanying 10 mol% of monomethylolurea remain almost intact at pH 5 in the most concentrated reaction mixture employed here, i.e. with an equivalent F/U/W molar ratio of 1.90/1.00/4.96. With some dilution at pH 5 to an equivalent F/U/W molar ratio of 1.90/1.00/25.0, some methylene linkages (I, 47 ppm; II, 54 ppm) are formed, as indicated in the spectrum of *Figure 8b*. Methylene linkages (II, 54 ppm) in the 1.90/1.00/25.0(5) sample (*Figure 8b*) appear to be present as potential crosslinking sites, judging from the fact that the shoulder at about 72 ppm has about the same intensity as that at 54 ppm in the spectrum of *Figure 8b*. In a resin prepared at pH 5 from a mixture with an equivalent F/U/W molar ratio of 1.90/1.00/25.0, some of the dissolved *N*,*N*′-dimethylolurea molecules react with each other to form potential crosslinking sites (II, 54 ppm; Va, 72 ppm); some of the *N*,*N*′-dimethylolurea molecules lose one of their methylol groups, as described by equation (1), to form monomethylolurea, some fraction of which leads eventually to straight-chain methylene linkages (I, 47 ppm). Of course, straight-chain methylene linkages can be formed by demethylolation of the crosslinking precursors or from the original 10 mol% of monomethylolurea that accompanies *N*,*N*′-dimethylolurea in the starting material. As indicated in the spectrum of *Figure 8b*, the predominant portion of methylol groups (IV, 65 ppm) remain intact in the 1.90/1.00/25.0(5) sample. In the most dilute pH 5 reaction mixture of the *N*,*N*′-dimethylolurea reagent, 1.90/1.00/107(5), all of the *N*,*N*′-dimethylolurea dissolved within 1 min and about 5% of the total starting material was collected as a precipitate after 12 h of reaction. As indicated in the spectrum of *Figure 8c*, the precipitate obtained from the 1.90/1.00/107(5) sample consists mainly of methylene linkages (I, 47 ppm; II, 54 ppm), methylol groups (IV, 65 ppm; V, 72 ppm), dimethylene ether linkages (X, 69 ppm), methylene glycol (XIV, 83 ppm) and its polymeric oligomers (87–92 ppm) and carbonyl groups (around 160 ppm). Those methylene linkages (II) contributing to the ^{13}C n.m.r. signal at 54 ppm in the spectrum of *Figure 8c* are very likely to be part of the crosslinking precursors (II, 54 ppm; Va, 72 ppm); part of the 72 ppm peak in the spectrum of *Figure 8c* is likely to arise from geminate methylol groups (Vb), because the intensity at about 72 ppm in *Figure 8c* is higher than that of the 54 ppm peak in the same spectrum. The formation of these geminate methylols is described by equation (4).

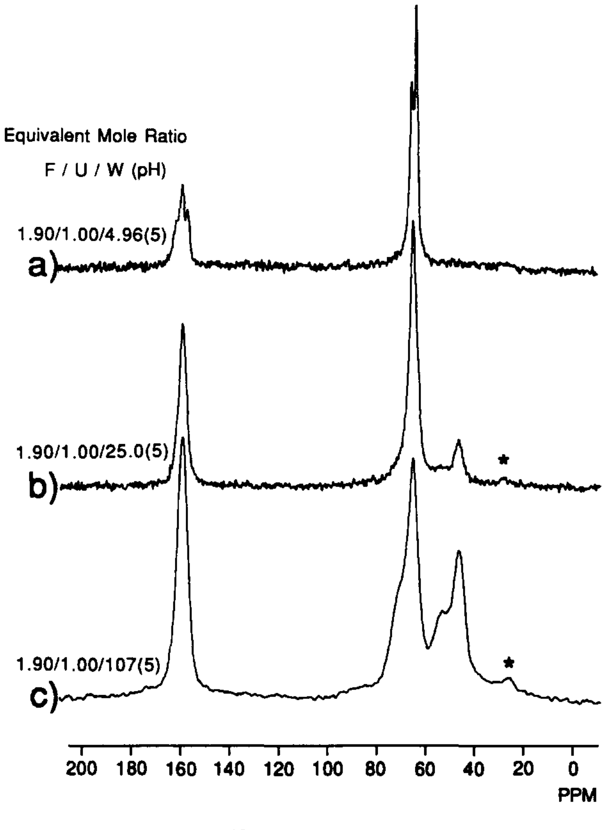


Figure 8 The 50.3 MHz ^{13}C c.p.-m.a.s. n.m.r. spectra of three UF samples prepared from the *N*,*N*′-dimethylolurea reagent and water at pH 5. C.p. contact time = 1 ms; repetition time = 1 s. Sample prepared from a mixture with an equivalent F/U/W molar ratio of: (a) 1.90/1.00/4.96, (b) 1.90/1.00/25.0 and (c) 1.90/1.00/107. Spinning sidebands are indicated by asterisks

Similar to the case discussed above for a UF resin prepared at pH 5 from a reaction mixture of the *N*,*N*′-dimethylolurea reagent and urea with an equivalent F/U/W molar ratio of 1.00/1.00/105 (*Figure 2c*), some of the straight-chain methylene linkages (I, 47 ppm) in the 1.90/1.00/107(5) sample are part of short UF resin chains that are rich in methylols (IV, 65 ppm). These short-chain UF structures are soluble in water in the most dilute mixtures employed in this study.

Resin samples were synthesized at pH 7, 9 and 12 from mixtures of the *N*,*N*′-dimethylolurea reagent and water with equivalent F/U/W molar ratios of 1.90/1.00/4.96, 1.90/1.00/25.0 and 1.90/1.00/107. ^{13}C c.p.-m.a.s. spectra of the three solid samples prepared at pH 12 are presented in *Figure 9*. The spectra in this figure clearly show that the proportion of dimethyl ether linkages (X, 69 ppm) relative to *N*,*N*′-dimethylolurea in these resins increases with increasing dilution at pH 12 (note the change in lineshape of the 65–69 ppm region, as discussed above for *Figure 5*). The liquid-state ^{13}C n.m.r. spectrum (not shown here) of a solution of the 1.90/1.00/107 sample prepared at pH 12 indicates that small amounts of dimethylene ether linkages (X, 69 ppm) and trimethylolurea (IV, 65 ppm; Vb, 72 ppm) and substantial amounts of monomethylolurea and methylene glycol (XIV, 83 ppm) are also formed. *Figure 9c* indicates that, during the

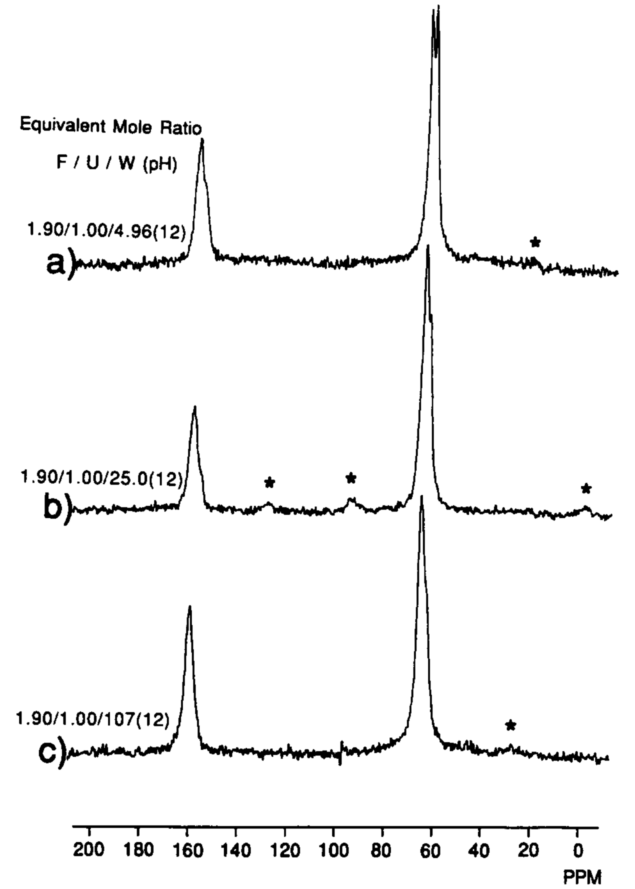


Figure 9 The 50.3 MHz ^{13}C c.p.-m.a.s. n.m.r. spectra of three UF samples prepared from the *N,N'*-dimethylolurea reagent and water at pH 12. C.p. contact time = 1 ms; repetition time = 1 s. Sample prepared from a mixture with an equivalent F/U/W molar ratio of: (a) 1.90/1.00/4.96, (b) 1.90/1.00/25.0 and (c) 1.90/1.00/107. Spinning sidebands are indicated by asterisks

vacuum drying at −5°C, most methylolureas condense to form dimethyl ether linkages at pH 12. The signal arising from trimethylolurea is observed in the spectra shown in *Figure 9*; the signal arising from methylene glycol (XIV, 83 ppm) is absent, presumably because of evaporation during the period of sample drying. The ^{13}C c.p.-m.a.s. spectra (not shown here) of samples obtained at pH 7 and pH 9 from reaction mixtures at the three concentrations, 1.90/1.00/4.96, 1.90/1.00/25.0 and 1.90/1.00/107, indicate that formation of dimethyl ether linkages (X, 69 ppm) during vacuum drying at −5°C increases with increasing dilution and with increasing pH value under neutral or basic conditions.

Paraformaldehyde as a source of methylols and CH_2-based linkages in the UF resins

Because of the limited water solubility of paraformaldehyde and the slowness of establishment of the equilibria among various oligomers of methylene glycol[19–21], it is of interest to study the structures of UF resins prepared from urea and paraformaldehyde. In some of the cases studied, paraformaldehyde has undergone some pretreatment reaction before reacting with urea; in other cases there was no pretreatment.

Figure 10 shows the ^{13}C c.p.-m.a.s. spectra of three UF resin samples prepared at pH 1 from urea and three different paraformaldehyde mixtures (see below) with an equivalent F/U/W molar ratio of 2.00/1.00/25.0 with 12 h of reaction at 23±2°C. One resin sample, DA1, was prepared by the reaction of a mixture of untreated paraformaldehyde, urea and water with an equivalent F/U/W molar ratio of 2.00/1.00/25.0. The major constituents of this sample, as indicated by the spectrum shown in *Figure 10a*, are carbonyl groups (ca. 160 ppm), straight-chain methylene linkages (I, 47 ppm), some crosslinking methylene linkages (II, 54 ppm; III, 60 ppm), methylol groups (IV, 65 ppm; V, 72 ppm), uronic rings (XIII, 79 ppm; XX, 156 ppm) and a small quantity of unreacted paraformaldehyde (89 ppm). The spectrum of *Figure 10a* is very similar to the spectrum[7] of a resin sample prepared at pH 1 from a mixture of 37% formalin and urea with a F/U/W molar ratio of 1.00/1.00/12.5, except that *Figure 10a* indicates the appearance of uronic rings, unreacted paraformaldehyde and 72 ppm methylols (V) in the sample. As expected, with the limited solubility of paraformaldehyde in water and the slowness of the equilibria among various oligomers of methylene glycol[19–21], the reaction mixture of paraformaldehyde and urea with an equivalent F/U molar ratio of 2.00/1.00 behaves somewhat like a system with a lower F/U molar ratio. After 12 h of reaction at pH 1, there is still a large portion of unreacted paraformaldehyde left in the reaction mixture (*vide infra*).

The nature of the resulting resin prepared at pH 1 from urea and untreated paraformaldehyde with an equivalent F/U/W molar ratio of 2.00/1.00/25.0 depends substantially on the drying processes that follow the 12 h of reaction; details of this dependence will be given elsewhere[8]. During the drying period at pH 1 at room

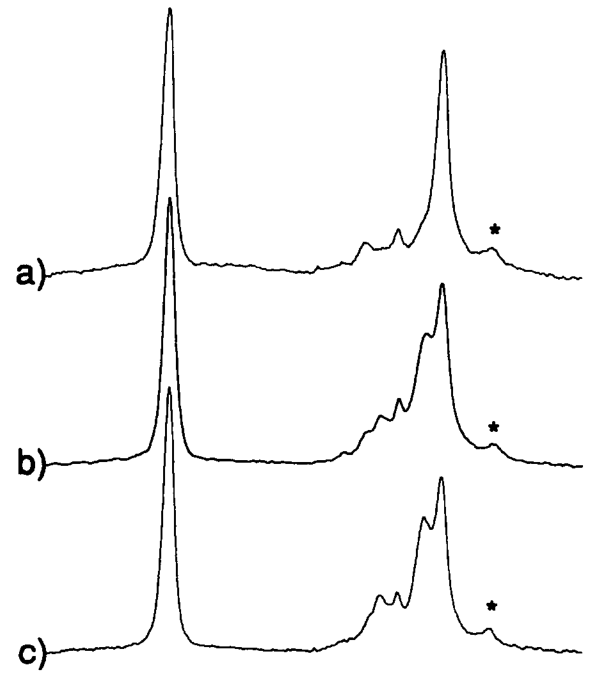


Figure 10 The 50.3 MHz ^{13}C c.p.-m.a.s. n.m.r. spectra of UF resin samples prepared at pH 1 from mixtures of urea and different paraformaldehyde reagents with an equivalent F/U/W molar ratio of 2.00/1.00/25.0. C.p. contact time = 1 ms; repetition time = 1 s. Samples prepared from: (a) untreated paraformaldehyde (DA1); (b) paraformaldehyde pretreated at 66°C for 6.5 h at pH 7 (HA1); (c) paraformaldehyde pretreated with an aqueous sodium hydroxide solution at pH 9 for 12 h (BA1). Spinning sidebands are indicated by asterisks

temperature, paraformaldehyde continues to decompose to its lower-molecular-weight oligomers, including methylene glycol. After comparing *Figure 10a* and the spectra of three other samples obtained from the same reaction mixture by different separation processes following the 12 h of reaction at pH 1[8], we concluded that some of the methylene glycol formed during the room-temperature drying period reacts with urea at pH 1 to produce more straight-chain methylene linkages (I, 47 ppm), crosslinking methylene linkages (II, 54 ppm; III, 60 ppm) and methylols (IV, 65 ppm; V, 72 ppm); but the major portion of methylene glycol escapes (probably as formaldehyde). In some cases, pairs of methylol groups (Va, 72 ppm) produced during the drying period at pH 1 become attached to the two nitrogen atoms of a urea unit (species XXIV) and subsequently condensed to form uronic rings (XIII, 79 ppm; XX, 156 ppm).

It is known that the solubility of paraformaldehyde and the rates of establishing equilibria among the various oligomers of methylene glycol are increased at higher temperature[19], or in strongly acidic conditions or basic conditions. When a mixture of paraformaldehyde and water with an equivalent F/W molar ratio of 2.00/25.0 was heated at 66°C and pH 7, almost all the paraformaldehyde dissolved within 90 min. When the resulting solution was maintained at 66°C for another 5 h, and then cooled and maintained at room temperature for 2 h, it remained clear. After acidification of that solution with 85% phosphoric acid to pH 1, urea was added, yielding a solution with an equivalent F/U/W molar ratio of 2.00/1.00/25.0. The added urea dissolved within 1 min; and the reaction between the paraformaldehyde solution and added urea proceeded fast, as indicated by the appearance of a UF resin precipitate within 2 min of mixing. The temperature increased spontaneously to 40°C before the reaction mixture cooled down to room temperature. After 12 h of reaction at 23 ± 2°C and at pH 1, one portion of the reaction mixture was spread out without neutralization on a watch glass for drying after decantation of the liquid portion; the ^{13}C c.p.-m.a.s. spectrum of the resulting solid, labelled here as HA1, is shown in *Figure 10b*. This spectrum is very similar to the ^{13}C c.p.-m.a.s. spectrum of a UF resin sample prepared at pH 1 from a mixture of 37% formalin and urea with a F/U/W molar ratio of 2.00/1.00/25.0[7]. The major group components of this HA1 sample are carbonyl (155–169 ppm), straight-chain methylene linkages (I, 47 ppm), crosslinking methylene linkages (II, 54 ppm; III, 60 ppm), methylols (IV, 65 ppm; V, 72 ppm), dimethylene linkages (X, 69 ppm; XI, 76 ppm), substituted urons (XIII, 79 ppm; XX, 156 ppm) and polyoxymethylene glycols (88–92 ppm)[7].

As mentioned above, the solubility of paraformaldehyde and the rates of its decomposition to the lower oligomers are increased under basic conditions[19]. By adjusting the pH of a mixture of paraformaldehyde and water with an equivalent F/W molar ratio of 2.00/25.0 to pH 9 by adding 5.0 M aqueous NaOH solution, the mixture became almost clear within 3 h; this mixture was stirred for 12 h before acidification to pH 1 and adding sufficient urea to yield an equivalent F/U/W molar ratio of 2.00/1.00/25.0. As in the case of the reaction mixture of urea and a heat-treated paraformaldehyde solution, the added urea dissolved in the base-treated paraformaldehyde solution quickly (within 1 min); the reaction mixture became cloudy and warm within 2 min, with the highest temperature (40°C) attained within 4 min, before cooling down to room temperature. After 12 h at room temperature, one portion of the reaction mixture was spread out for drying on a watch glass without neutralization after decantation of the liquid portion from the reaction mixture; the ^{13}C c.p.-m.a.s. spectrun of the resulting solid, labelled here as BA1, is shown in *Figure 10c*. This spectrum is similar to *Figure 10b*, with slightly higher intensity at 72 ppm and lower intensity at 79 ppm in comparison to *Figure 10b*. The major ^{13}C n.m.r. spectral difference between samples HA1 and BA1 is associated with the formation of a large amount of uronic rings (XIII, 79 ppm; XX, 156 ppm) in the HA1 sample from neighbouring internal methylol group (Va, 72 ppm). From a comparison of the three ^{13}C c.p.-m.a.s. spectra shown in *Figure 10* and the related discussion, it appears that paraformaldehyde without pretreatment is a poor source, even at pH 1, for methylene glycol (or formaldehyde), which is required in the synthesis of UF resins. However, when pretreated with base or at elevated temperature, the paraformaldehyde solution functions as an efficient supplier of methylene glycol or formaldehyde for the reaction with urea.

Owing to the fast reaction at pH 1 between urea and the methylene glycol supplied by untreated paraformaldehyde to form methylol groups, the limited solubility of paraformaldehyde in water and the slow nature of the equilibria among methylene glycol and its higher oligomers[19] render the reaction system deficient in methylene glycol; then, because of the high formation rate of methylene linkages (I) from methylols at pH 1, as described by equation (5), the major components of the resulting UF resins should be straight-chain methylene linkages and carbonyl groups. Owing to the very low water solubility of UF resins that contain methylene linkages[7], the methylene glycol formed from the continuous decomposition of paraformaldehyde in the later stages of the resin formation reaction, or during the drying period, can methylolate only a very small portion of the solid UF resin to produce more methylol groups and crosslinking methylene linkages (II, III); hence the major portion of this later-formed methylene glycol is separated along with the liquid portion from the resulting resin. When pretreated with base or at elevated temperatures, paraformaldehyde depolymerized considerably to produce a high enough concentration of methylene glycol to react with urea at pH 1 to form all three types of methylols, IV (65 ppm), Va (72 ppm) and Vb (72 ppm), and consequently to form all three types of methylene linkages indicated by equation (3′) and (5) — I (47 ppm), II (54 ppm) and III (60 ppm).

The reaction between urea and untreated paraformaldehyde was also carried out at pH 1 in a mixture having an equivalent F/U/W molar ratio of 2.00/1.00/107; the ^{13}C c.p.-m.a.s. spectrum (not shown here) of the resulting UF resin is almost identical to the spectrum of *Figure 10a*, except with slightly lower intensities at about 79 ppm (uronic rings, XIII) and 54 ppm (crosslinking methylene linkages, II) relative to *Figure 10a*.

The pH dependence of the solubility of paraformaldehyde in water and the rates of establishing the equilibria among methylene glycol and its higher oligomers all have flat minima between pH 3 and 5[19]. Therefore, it is of interest to investigate the reaction between urea and paraformaldehyde under different conditions in this pH range. *Figures 11a* and *11b* show the ^{13}C c.p.-m.a.s.

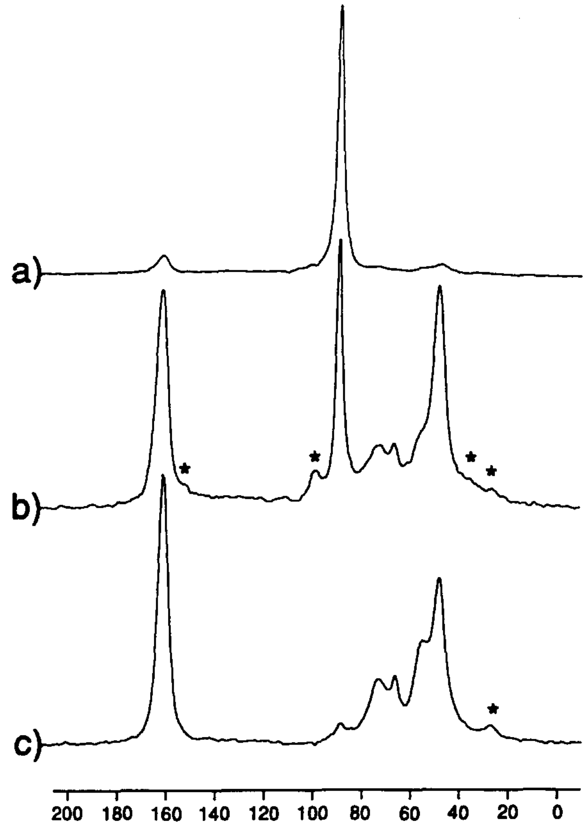


Figure 11 The 50.3 MHz ^{13}C c.p.-m.a.s. n.m.r. spectra of three UF resin samples prepared at pH 3 from mixtures of urea and different paraformaldehyde reagents. Each mixture had an equivalent F/U/W molar ratio of 2.00/1.00/25.0. C.p. contact time = 1 ms; repetition time = 1 s. Samples prepared from: (a) untreated paraformaldehyde, 12 h reaction time; (b) untreated paraformaldehyde, 83 h reaction time; (c) paraformaldehyde pretreated with an aqueous NaOH solution at pH 9 for 12 h, 12 h reaction time. Spinning sidebands are indicated by asterisks

spectra of UF resins prepared at room temperature and pH 3 directly from a mixture of urea, untreated paraformaldehyde and water with an equivalent F/U/W molar ratio of 2.00/1.00/25.0, using 12 and 83 h of reaction time, respectively. *Figure 11c* shows the ^{13}C c.p.-m.a.s. spectrum of a UF resin sample prepared during a 12 h period at room temperature and pH 3 from a mixture of urea, water and pretreated paraformaldehyde (treated with base at pH 9 for 12 h in water as described above) with an equivalent F/U/W molar ratio of 2.00/1.00/25.0. *Figure 11a* clearly indicates that most of the paraformaldehyde (89 ppm region) remains unchanged at pH 3 during the 12 h reaction period and subsequent 24 h drying period on a watch glass; only a small portion of the paraformaldehyde had decomposed to methylene glycol, which then reacts with urea to form structures containing carbonyl groups (160 ppm region), straight-chain methylene linkages (I, 47 ppm), and very small amounts of methylol groups (IV, 65 ppm) and precursors of crosslinking (equal amounts of II, 54 ppm and Va, 72 ppm). With an 83 h reaction time at pH 3 (*Figure 11b*), a large amount of paraformaldehyde still remains intact; however, a much larger portion of paraformaldehyde undergoes decomposition to methylene glycol, which subsequently reacts with urea to form substantial amounts of structures with carbonyl groups (160 ppm region), straight-chain methylene linkages (I, 47 ppm), small amounts of crosslinking methylene linkages (II, 54 ppm; III, 60 ppm), precursors of crosslinking (equal amounts of II, 54 ppm and Va, 72 ppm), methylols (IV, 65 ppm) and dimethylene ether linkages (X, 69 ppm; XI, 76 ppm).

In comparison to the pH 1 conditions represented by *Figure 10a*, the untreated paraformaldehyde is an even poorer supplier of methylene glycol at pH 3, as expected. However, because of the slower pace of formation of methylene linkages from methylol groups (as described by equation (5)) at pH 3, there is a larger relative portion of unreacted methylols (IV, 65 ppm; Va, 72 ppm) remaining or dimethylene ether linkages (X, 69 ppm; XI, 76 ppm) formed, in comparison to the case at pH 1. The 50 μs interrupted-decoupling ^{13}C c.p.-m.a.s. spectra (not shown here) corresponding to *Figures 11a* and *11b* show peaks at about 89 ppm that have a very similar dipolar dephasing behaviour to that of paraformaldehyde; therefore, it is reasonable to assume that the species responsible for the peaks at about 89 ppm in *Figures 11a* and *11b* are very similar to long-chain polyoxymethylene glycols, which are the main constituents of paraformaldehyde. Such species have low mobilities, so that the signals arising from these species do not survive the 50 μs dipolar dephasing period well.

Figure 11c shows the ^{13}C c.p.-m.a.s. spectrum of a UF resin prepared at 23 ± 2°C in a 12 h reaction time at pH 3 from a 2.00/1.00/25.0 mixture prepared using paraformaldehyde that was pretreated at pH 9 for 12 h. Upon examination of this spectrum, one can make the following observations: (1) In contrast to untreated paraformaldehyde, paraformaldehyde that has been pretreated in this manner provides a sufficient amount of available methylene glycol to react with urea and the intermediate UF resins formed to produce large proportions of methylols (IV, 65 ppm; V, 72 ppm); some of these methylols in turn condense with amide groups of urea units to form all three types of methylene linkages (I, 47 ppm; II, 54 ppm; III, 60 ppm); some of these methylols form dimethylene ether linkages (X, 69 ppm; XI, 76 ppm) and small amounts of uronic rings (XIII, 79 ppm; XX, 156 ppm); and the rest of these methylols remain unreacted. (2) The spectrum of *Figure 11c* is very similar to the ^{13}C c.p.-m.a.s. spectrum of a resin sample prepared at pH 3 from a mixture of 37% formalin and urea with a F/U/W molar ratio of 2.00/1.00/25.0[7]; the major difference between these two spectra is the proportion of crosslinking precursors (equal amounts of II, 54 ppm and Va, 72 ppm), which is higher in the resin sample prepared from treated paraformaldehyde and urea at pH 3.

The ^{13}C c.p.-m.a.s. spectrum (not shown here) of a UF resin sample prepared at pH 3 from a mixture of urea and untreated paraformaldehyde with an equivalent F/U/W molar ratio of 2.00/1.00/107 is similar to the spectrum of *Figure 11a*, but with smaller relative intensities at 160, 72, 65, 54 and 47 ppm in comparison to *Figure 11a*.

Five different reaction schemes were used to synthesize UF resins at pH 5 from mixtures prepared with an equivalent F/U/W molar ratio of 2.00/1.00/25.0 from paraformaldehyde and urea. In the first reaction scheme, paraformaldehyde was pretreated with methanol (13/37 weight ratio with respect to paraformaldehyde, similar to 37% formalin) and water (yielding an equivalent F/W molar ratio of 2.00/25.0) at pH 5 and room temperature for 6 h before addition of urea to give a mixture with an equivalent F/U/W molar ratio of 2.00/1.00/25.0; this mixture was allowed to react at pH 5 and 23 ± 2°C for 12 h. The second and third reaction schemes were the direct room-temperature reactions between untreated paraformaldehyde and urea at pH 5 in mixtures with an equivalent F/U/W molar ratio of 2.00/1.00/25.0 for 12 and 83 h, respectively. The fourth scheme involved a paraformaldehyde pretreatment in which a paraformaldehyde and water mixture with an equivalent F/W molar ratio of 2.00/25.0 was stirred at pH 1 and 23 ± 2°C for 33 h, at the end of which the mixture still looked milky. (However, a considerable amount of paraformaldehyde had depolymerized during this 33 h period, as will be seen in the discussion below.) In the fourth reaction scheme this pretreated paraformaldehyde mixture was brought to pH 5 with a 5.0 M aqueous NaOH solution before introducing urea to yield a mixture with an equivalent F/U/W molar ratio of 2.00/1.00/25.0; this mixture was allowed to react at pH 5 and 23 ± 2°C for 12 h. In the fifth reaction scheme, the paraformaldehyde mixture with an equivalent F/W molar ratio of 2.00/25.0 was first brought to pH 9 with 5.0 M aqueous NaOH solution and stirred at 23 ± 2°C for 12 h before acidifying to pH 5 with 85% phosphoric acid and introducing urea to yield a mixture with an equivalent F/U/W molar ratio of 2.00/1.00/25.0; this mixture was allowed to react at pH 5 at 23 ± 2°C for 12 h.

Figure 12 shows the ^{13}C c.p.-m.a.s. spectra of five UF resin samples prepared from the five 2.00/1.00/25.0(5) mixtures described above. *Figures 12a* and *12b* show that the spectra of samples prepared from the first and second reaction schemes are very similar to each other, with the 89 ppm peak (unreacted paraformaldehyde) as the predominant peak. The ^{13}C c.p.-m.a.s. spectrum of *Figure 12c*, obtained on a sample prepared with 83 h of reaction time between urea and untreated paraformaldehyde at pH 5, shows that there is a substantial amount of UF resin formed in this case, as witnessed by the high intensities in the regions of 160 ppm (carbonyls), 72 ppm (methylols, V), 65 ppm (methylols, IV), 54 ppm (methylene linkages, II) and 47 ppm (methylene linkages, I); however, a substantial amount of paraformaldehyde (89 ppm) still remains intact in this sample. Most of the 72 ppm methylol groups (Va) and 54 ppm methylene linkages (II) probably belong to crosslinking precursors, judging from the roughly equal intensities of these two peaks in the spectrum of *Figure 12c*. The predominant paraformaldehyde peak (89 ppm) and weak crosslinking methylene peaks (V, 54 ppm; III, 60 ppm) and methylol peaks (IV, 65 ppm; V, 72 ppm) in all three spectra of *Figures 12a, 12b* and *12c* indicate that the products were formed under a deficiency of methylene glycol during the course of reaction, as discussed above.

Figures 12d and *12e* correspond to samples that were prepared with large quantities of methylene glycol present in the solutions mixed with urea by virtue of paraformaldehyde pretreatment with acid at pH 1 or with base at pH 9. These figures display the results of methylolations of urea at pH 5 to form monomethylolurea (carbonyl, 160 ppm; methylol IV, 65 ppm), *N,N'*-dimethylolurea (carbonyl, 160 ppm; methylol IV, 65 ppm) and trimethylolurea (carbonyl, 160 ppm; methylol IV, 65 ppm; methylol Vb, 72 ppm). Some of the methylolurea moieties formed in the reaction mixture have proceeded to form straight-chain methylene linkages (I, 47 ppm), crosslinking precursors (equal amounts of II, 54 ppm and Va, 72 ppm; or V, 60 ppm and a double amount of Va, 72 ppm) and dimethylene ether linkages (X, 69 ppm; X, 72 ppm); and some of these methylols remained unreacted, as indicated by the strong intensities in the regions of 72 ppm (Va and/or Vb, 72 ppm) and 65 ppm (IV, 65 ppm) in the spectra of *Figures 12d* and *12e*. Even with the extension to 33 h of the pH 1 dissolution/pretreatment step (with an equivalent F/W molar ratio of 2.00/25.0), substantial amounts of paraformaldehyde or long-chain polyoxymethylene glycols still remained undissolved, as witnessed by the strong peak at about 89 ppm in the spectrum of *Figure 12d*. In contrast, the weak intensity around 89 ppm in the spectrum of *Figure 12e* shows that only small amounts of unreacted paraformaldehyde or long-chain polyoxymethylene glycols remained in the UF resin system made at pH 5 from a reaction mixture with an equivalent F/U/W molar ratio of 2.00/1.00/25.0, prepared from urea and paraformaldehyde pretreated with aqueous NaOH at pH 9. Other differences between *Figures 12d* and *12e* are the higher intensities on the 156 ppm shoulder

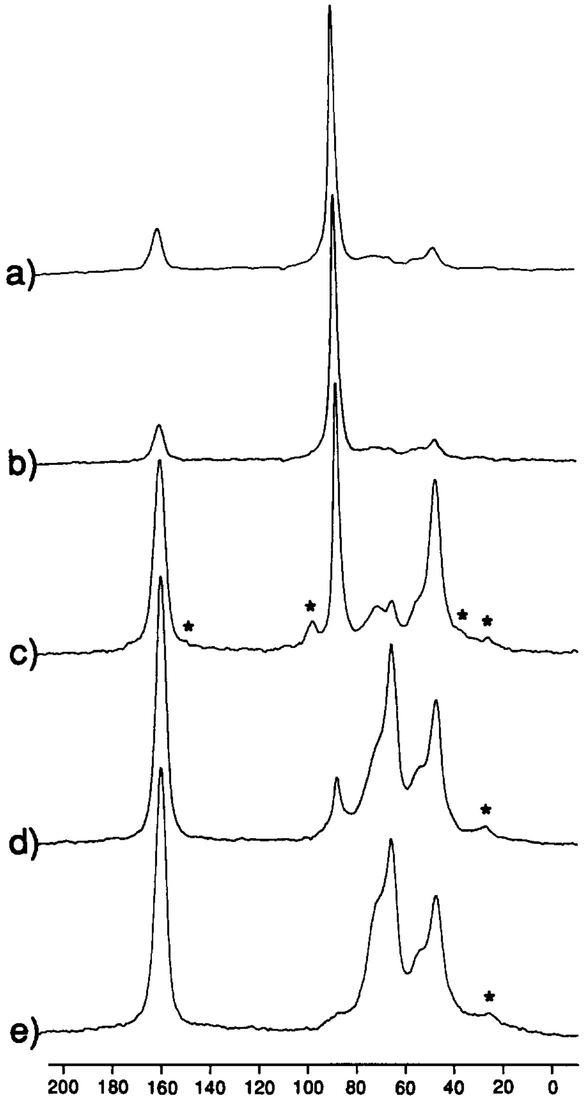


Figure 12 The 50.3 MHz ^{13}C c.p.-m.a.s. n.m.r. spectra of five UF resin samples prepared at pH 5 from mixtures of urea and different paraformaldehyde reagents. Each mixture had an equivalent F/U/W molar ratio of 2.00/1.00/25.0. Contact time = 1 ms; repetition time = 1 s. Samples prepared from: (a) paraformaldehyde pretreated with methanol at pH 5 for 6 h, 12 h reaction time; (b) untreated paraformaldehyde, 12 h reaction time; (c) untreated paraformaldehyde, 83 h reaction time; (d) paraformaldehyde pretreated with an aqueous phosphoric acid solution at pH 1 for 33 h, 12 h reaction time; (e) paraformaldehyde pretreated with an aqueous sodium hydroxide solution at pH 9 for 12 h, 12 h reaction time. Spinning sidebands are indicated by asterisks

and 79 ppm peak (uronic rings: XX and XIII) and the 72 ppm shoulder (probably attributable to trimethylolurea: Vb) in *Figure 11e*, a result of the higher concentration of methylene glycol. This occurs because of more extensive depolymerization of paraformaldehyde in the paraformaldehyde solution that has been pretreated with base, in comparison to the paraformaldehyde solution pretreated with acid, even though a roughly threefold longer period was employed for the pretreatment at pH 1.

It is of interest to compare the spectra in *Figures 10c, 11c* and *12e* corresponding to the three samples prepared at pH 1, 3 and 5 from 2.00/1.00/25.0 mixtures of urea and paraformaldehyde that had been pretreated with base at pH 9 for 12 h in mixtures with an equivalent F/W molar ratio of 2.00/25.0. In each of these cases large amounts of methylene glycol are available in the pretreated paraformaldehyde mixtures. The largest extent of formation of various methylene linkages (I, 47 ppm; II, 54 ppm; III, 60 ppm) from methylol groups (IV, 65 ppm; V, 72 ppm), e.g. according to equation (5), is seen to occur at pH 1 (*Figure 10c*) among these three pH values.

The ^{13}C c.p.-m.a.s. spectrum (not shown here) of a sample prepared at pH 5 from a mixture of urea and untreated paraformaldehyde with an equivalent F/U/W molar ratio of 2.00/1.00/107 is very similar to the spectrum shown in *Figure 12b*, with only slightly lower intensities at 160 ppm (carbonyls), 72 ppm (V, methylols), 65 ppm (IV, methylols), 54 ppm (II, methylene linkages) and 47 ppm (I, methylene linkages) in the spectrum of the sample from the more dilute 2.00/1.00/107 system.

The low and roughly equal fractions of the untreated paraformaldehyde consumed by the room-temperature formation of UF resins at pH 3 and pH 5 (see *Figures 11a* and *12b, 11b* and *12c*) is consistent with the reported observation[19] of flat minima in the pH dependences of the solubility and the rates of establishing equilibria among methylene glycol and its higher oligomers in the pH region from 3 to 5[19]. Judging from the proportion of paraformaldehyde that is consumed by the formation of UF resins represented in *Figures 12a* and *12b*, it appears that methanol provides no assistance in the room-temperature formation of UF resins from urea and paraformaldehyde at pH 5.

The ^{13}C c.p.-m.a.s. spectra (not shown here) of UF samples prepared at pH 9 and pH 12 from mixtures of urea and untreated paraformaldehyde with an equivalent F/U/W molar ratio of 2.00/1.00/25.0 are very similar to the ^{13}C c.p.-m.a.s. spectra[7] of UF samples prepared at pH 9 and pH 12 from mixtures of 37% formalin and urea with the same equivalent F/U/W molar ratio; these spectra indicate that the main constituent in the sample prepared at pH 9 is *N,N'*-dimethylolurea, while the main constituents in the sample prepared at pH 12 are *N,N'*-dimethylolurea, monomethylolurea and dimethylene ether linkages (X, 69 ppm).

Comparison among UF resins prepared from the N,N'*-dimethylolurea reagent, formalin or paraformaldehyde*

The formation of straight-chain methylene linkages is the predominant reaction under acidic conditions in mixtures of urea and *N,N'*-dimethylolurea with an equivalent F/U molar ratio of 1.00. This is probably due to the high rate of the reaction between a methylol group and a primary amide nitrogen of a urea unit (equation (5) with both R and R' equal to H), in comparison to the overall rate of the following combined process: decomposition of *N,N'*-dimethylolurea (equation (1) with R = H) to produce methylene glycol, the methylolation of a secondary amide group connected to a methylene linkage (equation (6)) and subsequent formation of crosslinking methylene linkages. Except for the three small differences discussed below, the UF resins prepared from formalin and urea[7] are very similar to UF resins prepared from a mixture generated from the *N,N'*-dimethylolurea reagent and urea with the same equivalent F/U molar ratio of 1.00 at the same three concentrations and same three (acidic) pH values.

One difference is that a substantial amount of unreacted *N,N'*-dimethylolurea remains in the reaction mixture prepared at pH 5 from the *N,N'*-dimethylolurea reagent and urea with an equivalent F/U/W molar ratio of 1.00/1.00/2.48. This difference is due to the limited solubility of *N,N'*-dimethylolurea in water (12 g/100 g)[7] and the slow rate of the reaction between *N,N'*-dimethylolurea and urea at pH 5. Therefore, the proportion of unreacted methylol groups (IV) in this system is much higher than that in the reaction mixture prepared from a mixture of formalin and urea with the same F/U/W ratio and pH. Because of the high rate of the reaction between *N,N'*-dimethylolurea and urea at pH 1 and pH 3, the limited water solubility of *N,N'*-dimethylolurea plays almost no role in determining the structure of the UF resins prepared from the *N,N'*-dimethylolurea reagent and urea at pH 1 and pH 3, even in the most concentrated reaction mixture (1.00/1.00/2.48); therefore, the proportions of methylol groups (IV) in these two UF resins are similar to that in the 1.00/1.00/2.48 resin samples prepared from 37% formalin and urea at pH 1 and pH 3[7]. A second difference arises from the presence of 8% (by weight) of methanol in 37% formalin; this methanol gives rise to small amounts of methyl ether groups[7] in the UF resins prepared from mixtures of formalin and urea with a F/U/W molar ratio of 1.00/1.00/2.48 at pH 1, 3 and 5. On the other hand, there is apparently no methyl ether formation in the UF resins prepared from the *N,N'*-dimethylolurea reagent and urea. A third difference is that there are somewhat higher proportions of crosslinking methylene linkages (II, III) in the UF resins prepared from mixtures of formalin and urea with a F/U molar ratio of 1.00 under acidic conditions in comparison to the UF resins prepared from the *N,N'*-dimethylolurea reagent and urea at the same concentrations and at the same pH values. This observation is consistent with the view that equation (6) is a favoured route to produce crosslinking methylene (II). As mentioned above, the reason for the lower proportion of crosslinking methylene linkages in the resins prepared under acidic conditions from the *N,N'*-dimethylolurea reagent and urea with an equivalent F/U molar ratio of 1.00 probably can be attributed to the very high rate of the reaction between the primary amide moiety of a urea unit and a methylol group (equation (5) with R, R' = H) in comparison to other reactions, especially the demethylolation (equations (1) and (3')), which provides methylene glycol to produce crosslinking methylene linkages (equation (6)).

Owing to the limited solubility of paraformaldehyde in water and the slowness in establishment of the equilibria among methylene glycol and its oligomers[19], the UF resins prepared at pH 1 from mixtures of untreated paraformaldehyde and urea with equivalent

F/U/W molar ratios of 2.00/1.00/25.0 and 2.00/1.00/107 are much like the resins prepared from 37% formalin and urea at pH 1 with equivalent F/U/W molar ratios of 1.00/1.00/12.5 and 1.00/1.00/105[7]; the most notable chemical structural difference between these two sets of reaction mixtures is the occurrence of small amounts of uronic rings (XIII, XX) in the two resins prepared from untreated paraformaldehyde and urea. The reactions between untreated paraformaldehyde and urea in mixtures with equivalent F/U/W molar ratios of 2.00/1.00/25.0 and 2.00/1.00/107 at pH 3 and pH 5 proceed much more slowly than in the corresponding reaction mixtures at pH 1, partly due to the solubility minimum of paraformaldehyde in water between pH 3 and pH 5[19]. Therefore, most of the paraformaldehyde remains intact at pH 3 or 5, even after 12 h of reaction at room temperature, whereas the reactions between urea and 37% formalin in mixtures with F/U/W molar ratios of 2.00/1.00/25.0 and 2.00/1.00/107 at these pH values proceed readily, leaving only small quantities of unreacted formalin after 12 h of reaction at room temperature[7].

After paraformaldehyde pretreatment with base (at pH 9 for 12 h) or heating at 66°C at pH 7 for 6.5 h, depolymerization of paraformaldehyde produces enough methylene glycol to react with urea, and the UF resin prepared at pH 1 from pretreated paraformaldehyde and urea in a mixture with an equivalent F/U/W molar ratio of 2.00/1.00/25.0 is very similar to the resin prepared from 37% formalin and urea with the same F/U/W molar ratio at pH 1[7]. UF resins that were prepared at pH 3 and pH 5 from 2.00/1.00/25.0 mixtures of urea and paraformaldehyde that had been pretreated with base at pH 9 are similar to the UF resins prepared from urea and 37% formalin at the same F/U/W molar ratio and corresponding pH values[7], except that a larger proportion of unreacted methylols (IV, V) remain in the resins prepared from urea and treated paraformaldehyde. These differences are probably associated with the fact that the final pH values of the reaction mixtures after 12 h of reaction at room temperature differed in the two different schemes (pH 3.0 and pH 5.0 for the resins prepared from pretreated paraformaldehyde, and pH 2.8 and pH 4.5 for the resins prepared from 37% formalin) and the higher rate of formation of various methylene linkages (I, II, III) from the corresponding methylols, as described by equations (3′) and (5), at lower pH values[1,2,7].

There is a high degree of crosslinking in UF resins prepared at pH 1 from *N*,*N*′-dimethylolurea (with the accompanying 10 mol% of monomethylolurea) in mixtures with an equivalent F/U molar ratio of 1.90 because of the large rate of reaction between methylol groups and secondary amide moieties of a urea unit at pH 1, as described by equations (3) and (5), and the fact that there are two methylol groups per urea unit in *N*,*N*′-dimethylolurea to begin with. Such resins, which are represented in *Figures 6a, 6b* and *6c*, were prepared from mixtures with equivalent F/U/W molar ratios of 1.90/1.00/4.96, 1.90/1.00/25.0 and 1.90/1.00/107. In comparison to UF resins prepared at pH 1 from 37% formalin and urea with a F/U molar ratio of 2.00[7], the effects of concentrations on the UF resin structures in reaction mixtures prepared at pH 1 from the *N*,*N*′-dimethylolurea reagent with an equivalent F/U molar ratio of 1.90 are much smaller because we already start with two methylol groups per urea unit in *N*,*N*′-dimethylolurea at those three concentrations employed and because of the high reactivity of methylols (IV, V) at pH 1. For the resins prepared from the *N*,*N*′-dimethylolurea reagent, increased dilution produces moderate decreases in the proportions of uronic rings (XIII, XX), unreacted methylols (IV, V) and dimethylene ether linkages (X, XI), and slight decreases in the proportion of crosslinking methylene linkages (II), an indication that the reactions of methylols to produce uronic rings, dimethylene ether linkages and especially crosslinking methylene linkages decreases only slightly with dilution at pH 1. However, increased dilution produces dramatic decreases in the amounts of uronic rings, unreacted methylols (only V) and crosslinking methylene linkages (II) in the corresponding resins prepared at pH 1 from 37% formalin and urea[7], an indication that the methylolation of amide moieties of urea units decreases with increasing dilution[7]. It may be noteworthy that the resins prepared at pH 1 from the *N*,*N*′-dimethylolurea reagent at the smaller F/U molar ratio of 1.90 have much more extensive crosslinking methylene linkages (II, III) than the corresponding resins prepared at the slightly higher F/U molar ratio of 2.00 from mixtures of 37% formalin and urea at pH 1 with the same equivalent F/W molar ratio; this result reflects the fact that there are two methylol groups per urea unit in *N*,*N*′-dimethylolurea to begin with and the high reactivity of these methylol groups at pH 1. This kind of difference in the extent of crosslinking methylene linkages relative to straight-chain methylene linkages (I) between the resins prepared from the *N*,*N*′-dimethylolurea reagent and from formalin-based mixtures increases understandably with increasing dilution owing to the decrease in the formation of methylols from formalin with increasing dilution.

From a comparison of the ^{13}C c.p.-m.a.s. spectra presented in *Figures 6a, 6b* and *6c* with those reported earlier[7], one can conclude that the proportions of uronic rings (XIII, 79 ppm; XX, 156 ppm) and unreacted methylols (IV, 65 ppm; V, 72 ppm) are higher in the resins prepared at pH 1 from mixtures of 37% formalin and urea with a F/U molar ratio of 2.00[7] in comparison to the resins prepared at the same pH from the *N*,*N*′-dimethylolurea reagent with the equivalent F/U molar ratio of 1.90 and the same equivalent F/W molar ratio; this difference is presumably at least in part due to a higher F/U molar ratio in the resins prepared from formalin and in part due to the methylolation of amides at a later stage of the reaction. Such later-stage methylolations may prohibit the alternative reaction of the methylols to form crosslinking methylene linkages for geometric reasons and/or because of the low solubility of the resins prepared from 37% formalin at pH 1. Therefore, a higher proportion of methylol groups that are attached to urea moieties bearing additional methylol groups (species XXIV) accumulate in the reaction mixture and eventually form uronic rings.

If comparisons are made for the samples prepared at pH 3 at the same two dilution levels (i.e. with F/W molar ratios of 2.00/4.96 and 2.00/25.0) one can draw the following conclusion: presumably because of the limited solubility of *N*,*N*′-dimethylolurea in water (12 g/100 g)[7] and the limited reactivity of methylol groups in reacting with secondary amide moieties of urea units (equations (3) and (5)) at pH 3, there are substantially larger portions of unreacted methylol groups (IV, V) remaining in the UF resins prepared at pH 3 from the *N*,*N*′-dimethylolurea reagent with an equivalent F/U molar ratio of 1.90 than in the UF resins prepared at the same pH from mixtures of 37% formalin and urea with an equivalent F/U molar ratio of 2.00. In contrast, the difference in the portion of unreacted methylol groups present in corresponding resins prepared at pH 3 from the most dilute mixtures (with F/W molar ratio of 2.00/107) is very small. However, the amounts of the methylene linkages (II, III) involved in crosslinking or in crosslinking precursors, relative to the portions of straight-chain methylene linkages (I), are higher in all three UF resins prepared at pH 3 from the *N,N'*-dimethylolurea reagent in mixtures with an equivalent F/U molar ratio of 1.90, in comparison to the corresponding three resins prepared at pH 3 from mixtures of 37% formalin and urea with an equivalent F/U molar ratio of 2.00 and at the same overall concentrations[7].

For the same general reasons given in the preceding paragraph (concerned with pH 3), the 'UF resin' material prepared at pH 5 from the *N,N'*-dimethylolurea reagent with an equivalent F/U/W molar ratio of 1.90/1.00/4.96 is essentially the starting material. In contrast, the UF resin prepared at pH 5 from a mixture of 37% formalin and urea with a F/U/W molar ratio of 2.00/1.00/4.96 was reported[7] to contain carbonyl groups, polyoxymethylene glycols, dimethylene ether linkages (X, XI), methylol groups (IV, V) and methylene linkages (I, II, III), as well as methoxy groups.

With some water dilution, to an equivalent F/U/W molar ratio of 1.90/1.00/25.0, *N,N'*-dimethylolurea at pH 5 exhibits some reactivity in processes leading to formation of small amounts of methylene linkages, although the proportion of methylene linkages formed is far less than in the UF resin prepared at pH 5 from a mixture of 37% formalin and urea with a F/U/W molar ratio of 2.00/1.00/25.0[7]. The precipitates formed from the pH 5 reaction mixture prepared from the *N,N'*-dimethylolurea reagent with an equivalent F/U/W molar ratio of 1.90/1.00/107 (*Figure 8c*) consist primarily of carbonyl groups (160 ppm), unreacted methylols (IV, 65 ppm; V, 72 ppm), crosslinking precursors (equal amounts of II, 54 ppm and Va, 72 ppm) and straight-chain methylene linkages (I, 47 ppm), even though the main portion (~80%) of *N,N'*-dimethylolurea remained dissolved in the liquid portion of the reaction mixture. In contrast, the precipitates[7] of the reaction mixture prepared from 37% formalin and urea with a F/U/W molar ratio of 2.00/1.00/107 at pH 5 are reported to be mainly straight-chain methylene linkages (I) between two urea units, some portion of crosslinking methylene linkages (II, III) and small portions of methylol groups (IV, V)[7].

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