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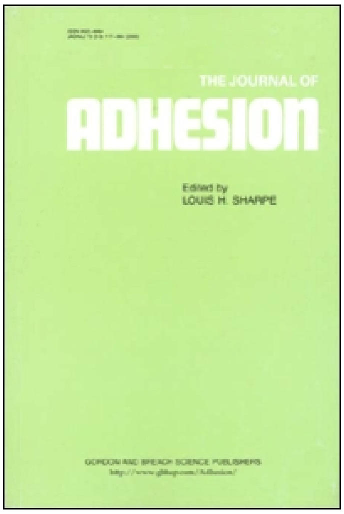

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Richard M. Rammon[a]; William E. Johns[b]; James Magnuson[b]; A. Keith Dunker[b]
[a] Chembond Corporation, Springfield, OR, U.S.A. [b] Washington State University, Pullman, WA, U.S.A.

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The Chemical Structure of UF Resins†

RICHARD M. RAMMON
Chembond Corporation, P.O. Box 270, Springfield, OR 97477, U.S.A.

and

WILLIAM E. JOHNS, JAMES MAGNUSON and A. KEITH DUNKER
Washington State University, Pullman, WA 99164-2262, U.S.A.

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The structure of urea-formaldehyde (UF) resin was studied in light of the influence of various synthesis parameters on the chemical structure of the resulting resin solutions. The structural variability was analyzed by ^{13}C nuclear magnetic resonance spectroscopy (NMR). Using appropriate pulse techniques, quantitative determination of the proportion of various functional groups was obtained.

The parameters of formaldehyde/urea mole ratio, pH control, extent of reaction, and concentration of reactants were shown to affect the final resin structure. Variation of these parameters influenced the extent of branching, the rate of condensation, and the proportion of di-methylene ethers and cyclic uron structures.

KEYWORDS: Adhesives, chemical structure, reaction mechanisms, reaction parameters, synthesis, urea-formaldehyde resins.

INTRODUCTION

When discussing the concept of structure in urea-formaldehyde resins, there are several levels at which structure can be considered. One such level is the chemical structure of the UF resin solution.

Since the discovery in the early 1880s that the reaction of urea and formaldehyde produced a resinous material, the development of urea-

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formaldehyde (UF) resins has gone through many stages. When first commercially produced, these resins were very expensive and primarily used as molding resins. Since then the uses of UF resins have changed dramatically. The major use has shifted to the area of adhesives, particularly for wood products. Along with this change in end-use and an increase in consumption have come changes in resin chemistry as well.

The nature of the changes in UF resin chemistry which have been developed are not well documented. The modification of resin formulations has historically been done by the resin producers, who tend to keep their findings as trade secrets. In general, however, the chemistry of UF resin synthesis has been established as being a two-stage reaction mechanism. The first stage of the reaction, typically conducted at an alkaline pH, involves the initial addition of urea and formaldehyde to form methylol ureas. The second stage, at acid pH, results in the condensation of these methylol ureas to form a polymeric material. Within this general reaction scheme, there lies a great deal of potential for variation in the synthesis of UF resins. The effect of variation of synthesis parameters on the chemical structure of the resin has not been well established. This is due, in part, to the ineffectiveness of classical wet chemistry techniques to elucidate the actual structure of the reaction products. With the development of modern analytical techniques has come the ability to determine the influence of synthesis parameters on resin structure. One of these modern analytical tools which has demonstrated great potential is nuclear magnetic resonance spectroscopy (NMR).

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The use of NMR, and in particular ^{13}C NMR, has been shown to be a valuable tool for the identification of functional groups in UF resins[1,2,3,4]. The major objective of this study was to utilize ^{13}C NMR to correlate the influence of various synthesis parameters on the structure of the resulting resin solution. These parameters were:

1. Final mole ratio (MR) of the resin
2. MR during resin advancement
3. pH control
4. Extent of reaction
5. Concentration during the cook

By systematically varying each of these parameters in a series of parallel cooks, the effect of each factor can be determined.

EXPERIMENTAL

The resins in this study were made in approximately 500 ml batches utilizing urea-formaldehyde concentrate (UFC) as a starting material. The reaction vessel used allowed for insertion of pH and temperature probes, a condenser and for addition of acid and base for pH control. Heating and agitation were accomplished by using a laboratory hot plate equipped with a magnetic stirrer. The standard cook procedure involved starting with 300 grams of UFC and the appropriate amount of water to result ultimately in a 65% solids concentration resin. Heating and agitation were begun and solid urea was added to reduce the F:U mole ratio (MR) to 2.2:1. The reaction mixture was heated to 80 degrees centigrade and adjusted to a pH between 7.5 and 8.0 with 1N NaOH. For the alkaline phase of the reaction, the mixture was held at these conditions for 30 minutes. At this point the pH was adjusted to 5.0 with 1N H_2SO_4. Temperature and pH were monitored continuously and were adjusted when necessary to maintain the reaction conditions. The acid phase of the reaction was continued until the appropriate viscosity had been reached. The reaction mixture was then neutralized and additional urea added to a MR of 1.1. The resin was then cooled, placed in a closed container and refrigerated for storage. Appropriate modifications of this procedure were done, as will be discussed, to determine the effect of the factors of interest.

The NMR analysis of the resins was generally conducted within one to two days from the time of synthesis. This was deemed necessary since prolonged storage, even at reduced temperatures, results in a change in the resin structure, primarily from the standpoint of increased resin viscosity.

Resin solutions at 65% solids were used without further dilution. A 4 ml sample was pipetted into the NMR sample tube and 1.5 ml of D_2O was added. The D_2O was added to obtain the deuterium signal for adjustment of field homogeneity. Four drops of dioxane were also added to act as an internal reference in assigning peak resonance positions. The chemical shift of dioxane was set to 67.4 ppm in accordance with the assignment of Tomita.[1] The identification of the various UF resonance positions was also done utilizing the assignments of Tomita.[1] The UFC solutions, because of their high viscosity, were diluted with water to 65% and then treated in the same manner as the resins.

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The NMR spectra were obtained on a Nicolet NT 200 FT-NMR instrument. The qualitative survey spectra were done using a 45 degree pulse and broad-band proton decoupling. The high concentration of the samples allowed very good signal-to-noise ratios to be obtained with 2000 scans. Acquisition of quantitative spectra required a different pulse technique.

To obtain quantitative peak intensities from a ^{13}C NMR spectra, a sufficient delay time between pulses must be used to allow total relaxation of all carbon resonances. This requires a knowledge of the range of spin-lattice relaxation times, T_1, found in the sample. An inversion recovery experiment was done to determine the T_1s for the UF resins.

The inversion recovery experiment indicated that the longest T_1 in the methylene region was approximately three seconds for free methylene glycol. Since the methylene region is the area of the spectrum of interest for determination of resin variability, a pulse delay of 20 seconds was used. In addition to the modified pulse timing, an interrupted decoupling technique was also used. This decoupling procedure removes all the proton-carbon coupling without introducing the variable nuclear Overhauser effect on peak intensities. The quantitative spectra were obtained from 2000 scans and took approximately 12 hours to collect.

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RESULTS AND DISCUSSION

Analysis of UFC

The UFC used as a starting material for the synthesis of resins in this study was obtained from the Borden Chemical Company. The quantitative ^{13}C NMR spectra of this UFC is presented in Figure 1. The resonance position of the urea carbonyl indicates the urea to be almost entirely tri-substituted. Expansion of the methylene region in Figure 2 indicates that besides the simple methylols associated with the initial reaction of formaldehyde and urea, there are also present dimethylene ether structures and free formaldehyde. The free formaldehyde is present as methylene glycol and higher molecular weight paraformaldehyde as indicated. Also indicated in the spectrum is the presence of methanol and methoxy groups resulting from the reaction of the methanol with the methylene glycol. The relative percentages of the various functional groups can be determined by integration of the quantitative peak

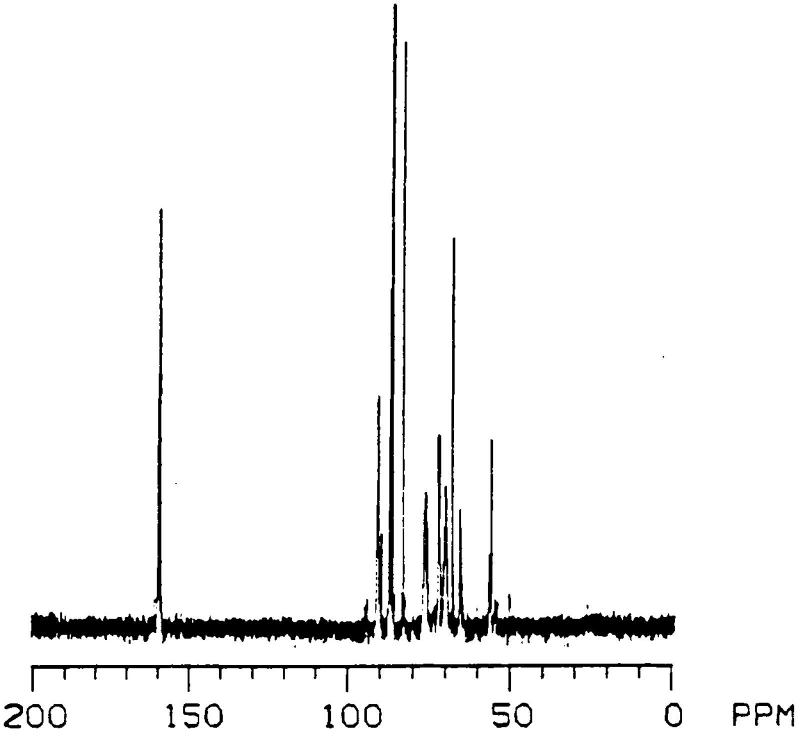

FIGURE 1 ^{13}C NMR spectrum of urea-formaldehyde concentrate (UFC).

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intensities in the spectrum. A summary of these percentages is presented in the functional group analysis in Table I.

With a clear picture of the structual makeup of the UFC starting material, we can begin to ascertain the influence of the various cook parameters on the structure of the UF resins produced.

Effects of Cook Parameter Modifications

Final Resin Mole Ratio

The trend in the industry has been toward lower F:U mole ratios. This change in resin formulation has primarily been the result of efforts to reduce formaldehyde emissions from panel products bonded with UF resin. Currently, commercial resins are being produced with MRs as low as 1.05:1. More typically the MR is in the range of 1.1 to 1.2. In

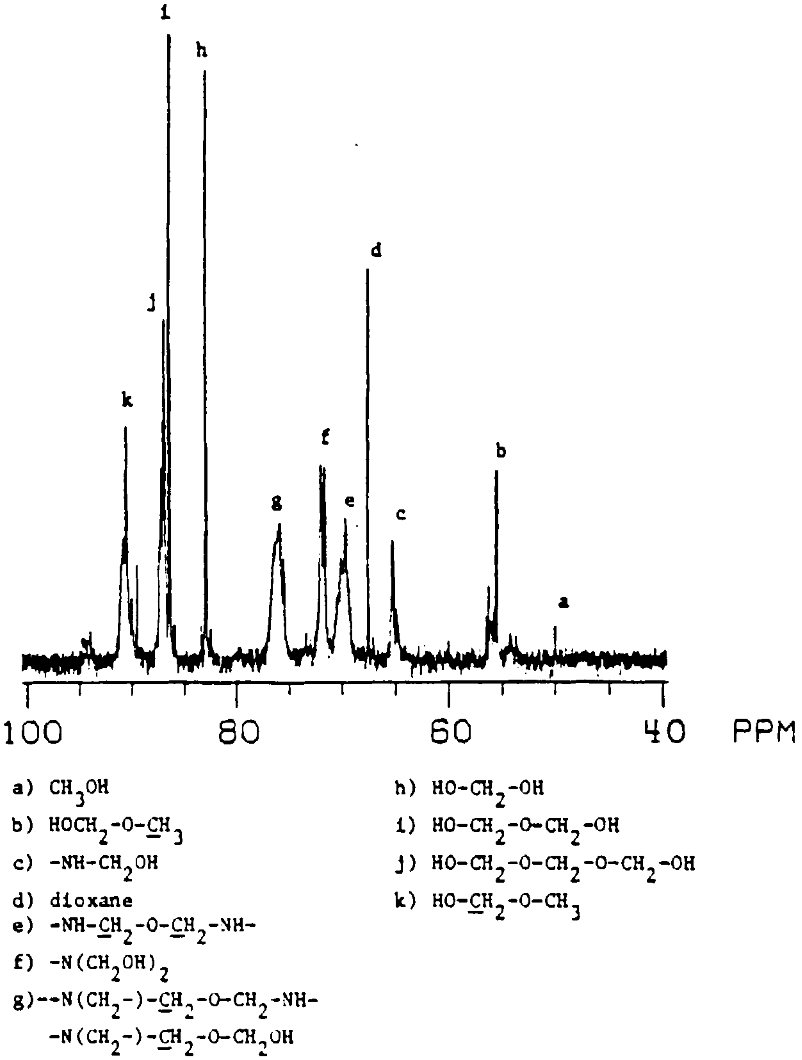

FIGURE 2 The methylene region of the ^{13}C NMR spectrum of UFC.

this study, a MR of 1.1 was chosen as a standard for comparison purposes.

Quantitative spectra have been obtained for resins with final MRs of 1.1, 1.43, and 2.0. The 1.1 MR resin was prepared by the standard cook precedure described in the experimental section. The spectrum of

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TABLE I
Functional group analysis for UFC

Functional Group		Resonance Position (ppm)	Amount of Each Group as a Percentage of Total Formaldehyde
$\mathrm{-NH-CH_2OH}$		64.8	6.6
$\mathrm{-N(CH_2OH)_2}$		71.6	12.8
$\mathrm{-NH-CH_2-O-CH_2-NH-}$ $\mathrm{-NH-CH_2-O-CH_2OH}$		69.6	12.6
$\mathrm{-N(CH_2-)-CH_2-O-CH_2-NH-}$ $\mathrm{-N(CH_2-)-CH_2-O-CH_2OH}$		76.2	19.4
$\mathrm{-NH-CH_2-NH-}$		47.2	0.0
$\mathrm{-N(CH_2-)-CH_2-NH-}$		53.5	0.0
$\mathrm{HO-CH_2-OH}$		82.9	10.5
$\mathrm{HOCH_2-O-CH_2OH}$		86.3	8.2
$\mathrm{HOCH_2-O-CH_2-O-CH_2OH}$		86.8	18.3
$\mathrm{HO-CH_2-OCH_3}$	1)	90.5	11.5
(1) (2)	2)	55.4	from methanol

this resin is presented in Figure 3. The other two resins were prepared by the same procedure. The variation in MR was achieved by varying the amount of urea added during the final stage of the cook. The variability of these three resins can most accurately be evaluated from the integrated peak intensitities for the different functionalities. A summary of this evaluation is given in the functional group analysis in Table II.

The extent of condensation was relatively constant as indicated by the total methylene percentages. The mole ratio did have an effect on the rate of branching. The extent of branching in the UF polymer can be determined from the ratio of linear to branch-point methylenes. For the standard cook with a MR of 1.1, this ratio was 0.82:1. In the 1.43 MR resin the ratio dropped to 0.76:1 and at a MR of 2.0 the ratio was 0.57:1. When examining these branching ratios to determine the extent of branching, care must be taken in assigning the number of branches. The branch-point methylene intensity accounts not only for the branch methylene, but also for the linear methylene on the nitrogen to which the branch is attached. To correct for this, half of the branch-point intensity was subtracted and added to the linear intensity and the ratio recalculated. Making this correction for the 1.1 MR resin resulted in a linear-to-branched methylene ratio of 2.64:1. This ratio predicts an average of one branch occurring for every 2.64 linear methylenes. Making the same correction for the other two resins gave ratios of 2.51:1 for the 1.43 MR and 2.15:1 for the 2.0 MR. The trend in these

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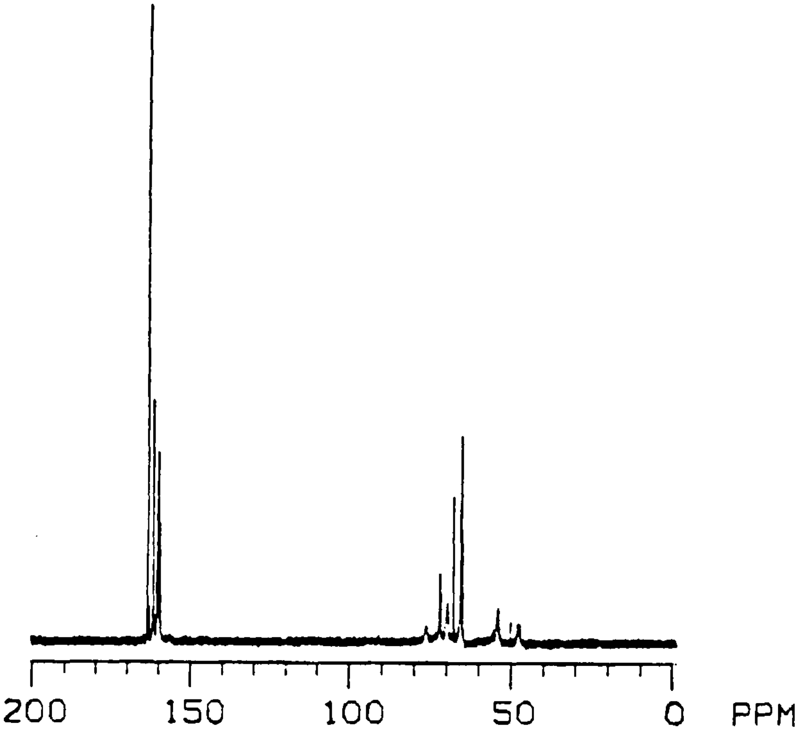

FIGURE 3 ^{13}C NMR spectrum of the standard 1.1 MR UF resin.

ratios supports the common thought that a higher MR resin would be more highly branched.

The other factor evident from the NMR spectra was that at the higher MRs there was a portion of the formaldehyde present as free methylene glycol. At a MR of 1.43 there was 1% free formaldehyde and at 2.0 this increases to 5.1%. This trend in free formaldehyde content shows that the urea added in the final step of the cook does react with the formaldehyde available at that point in the synthesis. The level of formaldehyde remaining as free methylene glycol was inversely related to the amount of urea added in the final stage of the cook procedure.

The final MR of the resin does have an effect on the structure of the resin, even when the MR during the condensation phase is held constant. A greater influence on resin structure, however, is obtained by varying the MR during the condensation phase of the cook.

TABLE II
Functional group analysis for resins with different final mole ratios

Functional Group	Resonance Position (ppm)	Amount of Each Group as a Percentage of Total Formaldehyde		
		*Resin: A	B	C
—NH—$\mathrm{CH_2OH}$	64.8	44.1	50.6	36.6
—N$\mathrm{(CH_2OH)_2}$	71.6	14.0	10.4	13.4
—NH—$\mathrm{CH_2}$—O—$\mathrm{CH_2}$—NH— —NH—$\mathrm{CH_2}$—O—$\mathrm{CH_2OH}$	69.6	15.6	13.7	17.1
—N($\mathrm{CH_2}$—)$\mathrm{CH_2}$—O—$\mathrm{CH_2}$—NH— —N($\mathrm{CH_2}$—)—$\mathrm{CH_2}$—O—$\mathrm{CH_2OH}$	76.2	7.8	5.7	9.6
—NH—$\mathrm{CH_2}$—NH—	47.2	8.3	8.1	6.6
—N($\mathrm{CH_2}$—)—$\mathrm{CH_2}$—NH—	53.5	10.1	10.7	11.5
HO—$\mathrm{CH_2}$—OH	82.9	0.0	1.0	5.1
$\mathrm{HOCH_2}$—O—$\mathrm{CH_2OH}$	86.3	0.0	0.0	0.0
$\mathrm{HOCH_2}$—O—$\mathrm{CH_2}$—O—$\mathrm{CH_2OH}$	86.8	0.0	0.0	0.0

*Resin description
A—1.1 MR (standard cook)
B—1.43 MR
C—2.0 MR

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Mole Ratio During Resin Advancement

In addition to the final MR of the resin, there was an opportunity to develop resin variability by changing the MR during the acid condensation phase of the cook. The resins studied in this phase of the investigation all had a final MR of 1.1. The standard resin for comparison was acidified and advanced at a 2.2 MR. After the appropriate level of condensation had been reached, as determined by viscosity, additional urea was added to achieve the final 1.1 MR. Changing the MR during advancement produced resins with significantly different structural makeup.

For comparison to the standard cook, resins were synthesized where the acid advancement was initiated at MRs of 3.0 and 1.1. The functional group analysis obtained from integration of quantitative peak intensities is presented in Table III.

At a 3.0 MR the rate of advancement was very slow. In the time frame used for the standard cook, there was little condensation observed. After an intermediate urea addition to lower the MR to 2.2 the resin did advance, but still at a lower rate. The final resin had a lower extent of condensation as indicated by the percentages for total methylene. The resin with the acid advancement initiated at a 3.0 MR had 15.5% of the formaldehyde as methylene linkages compared to 18.4% for the

TABLE III
Functional group analysis for resins advanced at different mole ratios

Functional Group	Resonance Position (ppm)	*Resin:	Amount of Each Group as a Percentage of Total Formaldehyde A	B	C
$-NH-CH_2OH$	64.8		65.2	44.1	31.7
$-N(CH_2OH)_2$	71.6		5.4	14.0	10.7
$-NH-CH_2-O-CH_2-NH-$ $-NH-CH_2-O-CH_2OH$	69.6		13.8	15.6	20.4
$-N(CH_2-)-CH_2-O-CH_2-NH-$ $-N(CH_2-)-CH_2-O-CH_2OH$	76.2		0.0	7.8	8.2
$-NH-CH_2-NH-$	47.2		10.9	8.3	19.2
$-N(CH_2-)-CH_2-NH-$	53.5		4.6	10.1	9.6
$HO-CH_2-OH$	82.9		0.0	0.0	0.0
$HOCH_2-O-CH_2OH$	86.3		0.0	0.0	0.0
$HOCH_2-O-CH_2-O-CH_2OH$	86.8		0.0	0.0	0.0

* Resin description
A—acid advance begun at 3.0 MR
B—acid advance done at 2.2 MR (standard cook)
C—acid advance done at 1.1 MR

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standard resin. There is also a much higher percentage of residual methylol; 70.6% compared to 58.1% for the standard. There was an effect on the degree of branching as well. The high MR advancement resulted in no branched ethers and fewer branched methylenes. The ratio of linear methylene to branched methylene was 2.57:1, while the standard cook had a ratio of 0.82:1.

Making the adjustment of the methylene ratio for the high MR advancement gave a ratio of 5.74:1 compared to the 2.64:1 ratio for the standard cook. This indicates a more linear polymer resulting from a higher MR reaction.

This result was very unexpected since a high MR should produce a highly branched polymer. This high linearity was presumably due to the intermediate urea addition. As indicated, the extent of condensation was very low at the 3.0 MR and an intermediate urea addition was made under acid conditions. The addition of this urea at an acid pH would not allow the high degree of methylolation which would occur if the urea had been added under alkaline conditions. The urea added under acid conditions, once initially methylolated, would immediately undergo a condensation reaction to form a methylene linkage. This would ultimately result in the formation of a linear polymer. This is analogous to the acid novolak procedure for making a linear phenolformaldehyde polymer. The slow rate of advancement and the low degree of condensation at the high MR indicates that the presence of excess formaldehyde inhibits the condensation reaction.

This inhibition effect is illustrated in the series of spectra obtained using the variable temperature control unit of the NMR. The acid condensation phase of the cook was monitored as it occurred at 70 degrees C for both the 2.2 MR advance and the 3.0 MR advance. The spectra obtained are presented in Figures 4–7. These spectra could not be obtained under quantitative conditions because of the time factor involved. The condensation reaction can be monitored by observing the development of the methylene resonances at 47 ppm and 53 ppm.

At 8 minutes into the reaction, as seen in Figure 4, neither mixture had developed methylene linkages. At 16 minutes the 2.2 MR mixture had begun to form linear methylenes. Observing the spectra at 32 minutes, the 2.2 MR mixture shows the development of branched methylenes, and the 3.0 MR shows a slight indication of linear linkages. The final spectra, in Figure 7, shows that the 2.2 MR mixture had developed strong methylene resonances while the 3.0 MR mixture had just begun to condense. These spectra clearly show the inhibiting effect of the high formaldehyde content. This experiment also indicated that the linear condensation reactions occur to a noticeable extent before any branch point condensations occur.

When the advancement was done at the final MR of 1.1 the condensation reaction was very rapid. The effect of this rapid condensation is apparent in the functional group analysis, Table III, from the percentage of total methylenes. The total methylene intensity was 28.8% compared to 18.4% for the standard cook. This higher extent of reaction is also evident in the percentage of residual methylols. A residual methylol content of 42.4% was computed for the resin advanced at 1.1 while the standard cook had a 58.1% residual methylol content. The low MR advancement also resulted in a more linear polymer than the standard cook. For the methylene intensities the ratio of linear to branched was 2.0:1 as compared to the standard resin with a ratio of 0.82:1. Making the appropriate adjustments to these intensities gave a ratio of 4.80:1 compared to 2.64:1 for the standard cook.

These results indicated that the MR at which the acid condensation is initiated had an effect on the linearity of the resin and on the rate and extent of condensation. The effect on the extent of condensation is evident from the total methylene intensities and from the percentages of dimethylene ether linkages as well.

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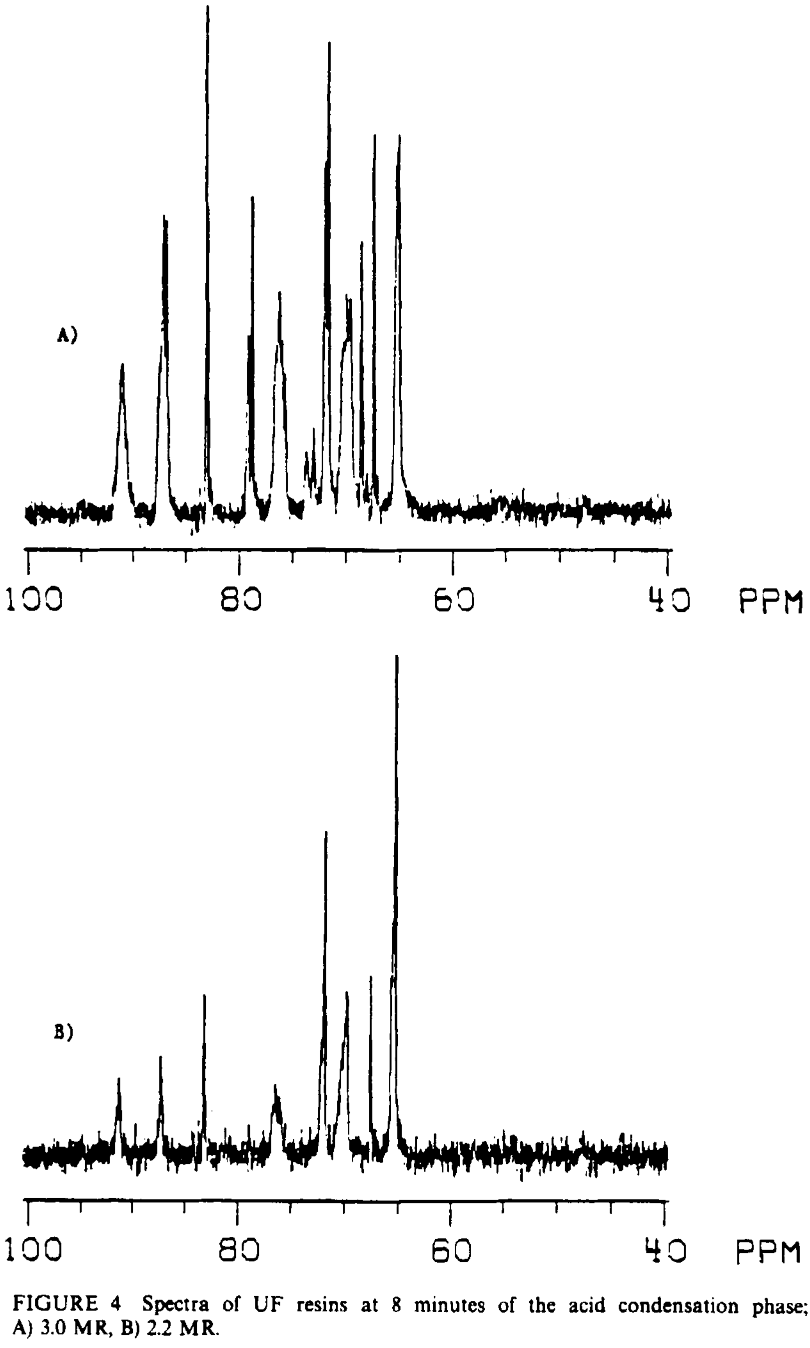

FIGURE 4 Spectra of UF resins at 8 minutes of the acid condensation phase; A) 3.0 MR, B) 2.2 MR.

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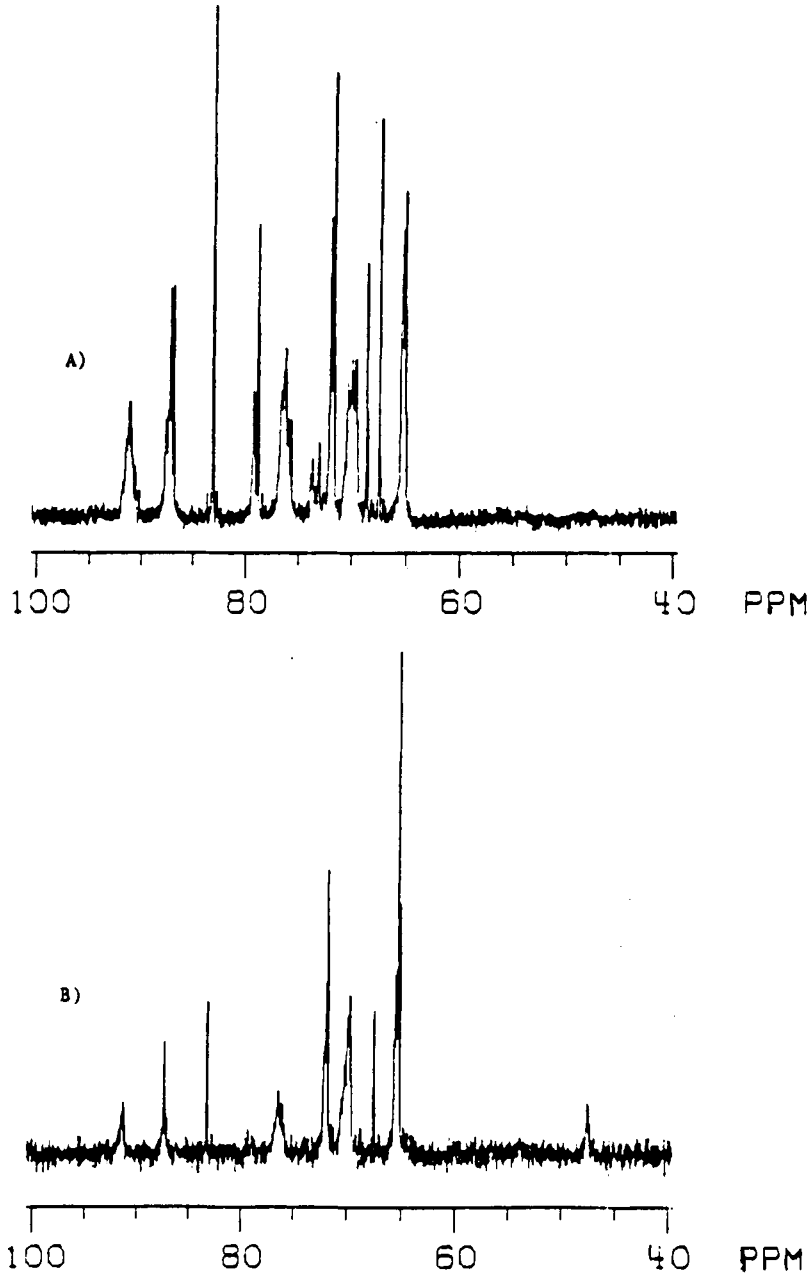

FIGURE 5 Spectra of UF resins at 16 minutes of the acid condensation phase; A) 3.0 MR, B) 2.2 MR.

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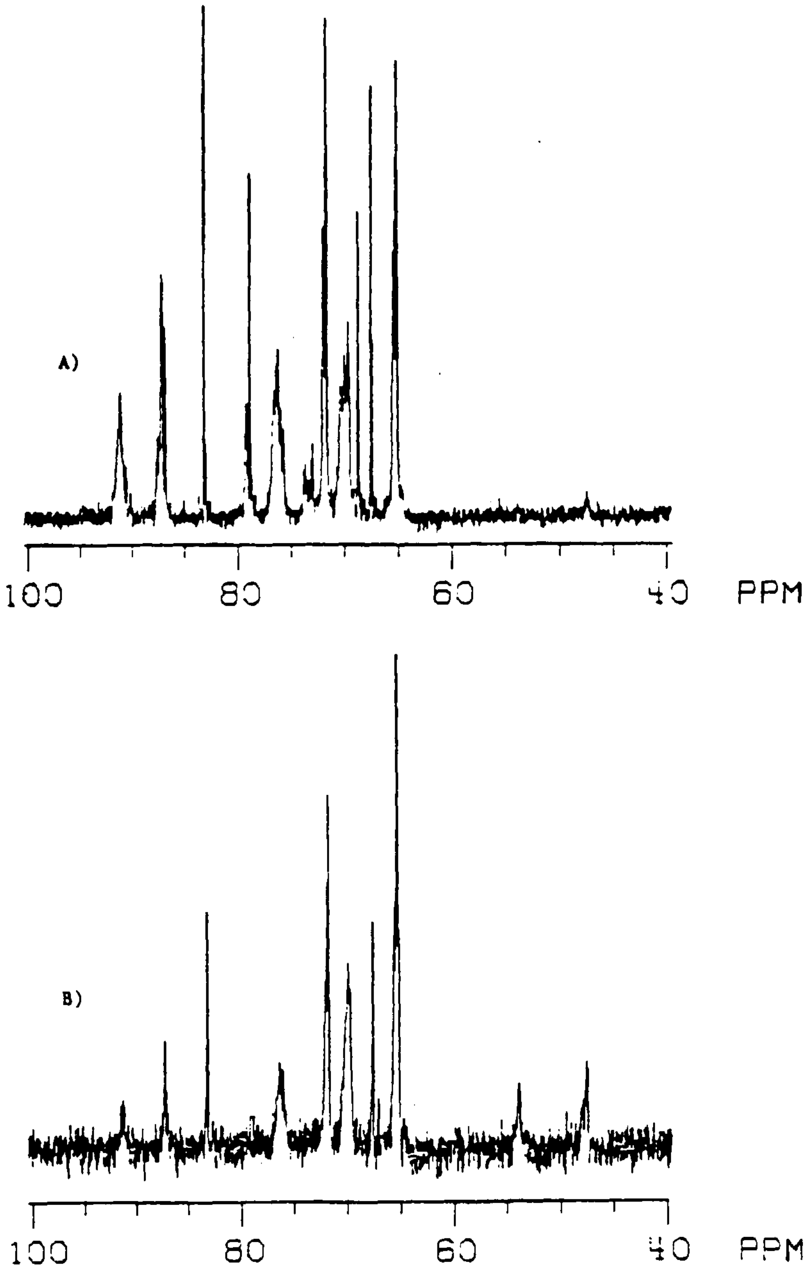

FIGURE 6 Spectra of UF resins at 32 minutes of the acid condensation phase; A) 3.0 MR, B) 2.2 MR.

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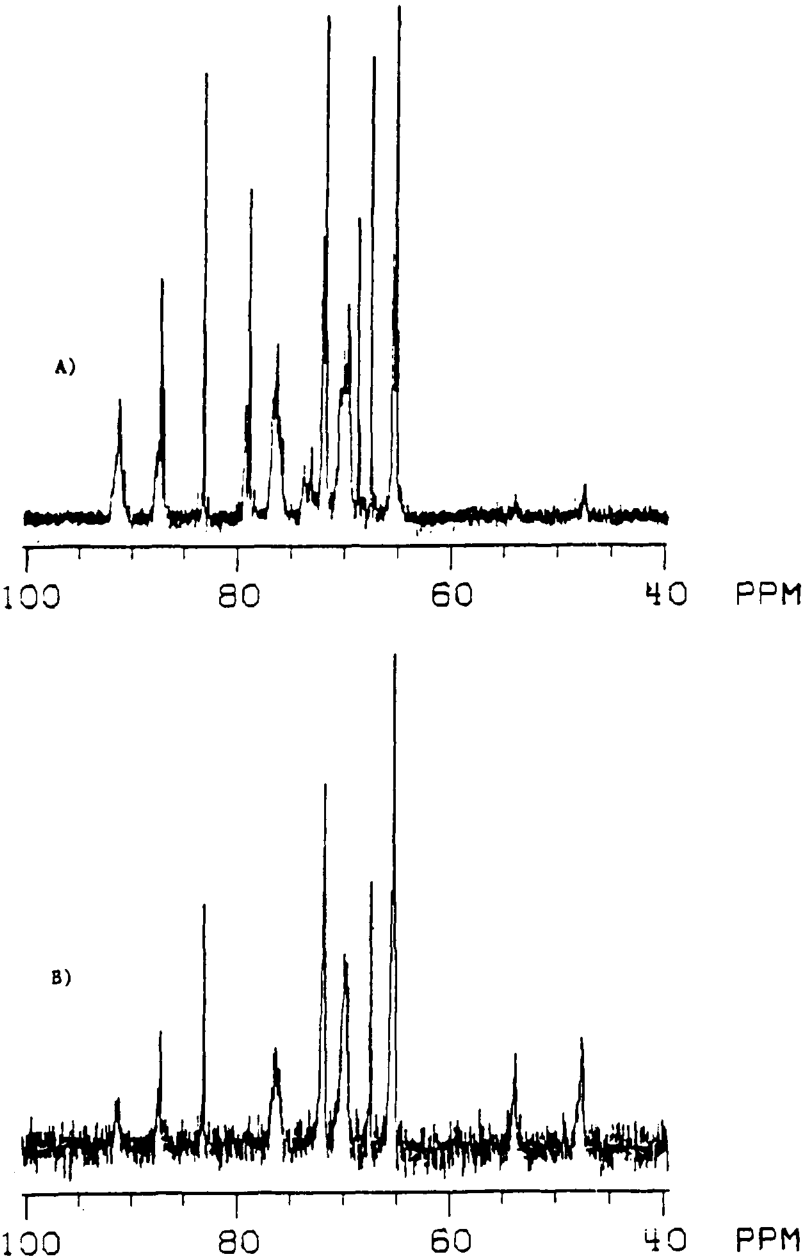

FIGURE 7 Spectra of UF resins at 32 minutes of the acid condensation phase; A) 3.0 MR, B) 2.2 MR.

Effect of pH Control

The pH of the reaction mixture had to be continuously monitored and frequently adjusted to maintain the proper conditions. This was particularly true during the alkaline phase of the cook. At alkaline conditions the pH of the Cook tended to drift down toward the acid side and had to be continuously adjusted. This may have been due to the decomposition of formaldehyde by a Cannizzaro reaction to form formic acid and methanol.

$$2\ CH_2O + H_2O \longrightarrow HCOOH + CH_3OH$$

Producting resin variability by modification of the pH during the acid condensation phase of the cook has limited potential. The range over which pH can be varied for the condensation phase of the cook is small. Typically the condensation is conducted at a pH between 4.5 and 5.0. Below pH 4.5 the rate of condensation is too rapid to maintain control of the reaction. A higher pH does not allow sufficient condensation to occur and no viscosity increase is observed.

The pH during the alkaline phase of the cook does have an effect on resin structure. Modifying the standard procedure by increasing the pH to 9.5 and extending the time to 1 hour resulted in an unique resin structure. In this cook, after the extended alkaline treatment, the MR was reduced to 1.1 and acidified for rapid advancement. This allowed the best opportunity to maintain the structural modification established by the alkaline treatment. The influence of the treatment is demonstrated in the function group analysis in Table IV.

The literature indicates that alkaline pH conditions promote the formation of ethers.[5] This may be true under normal cook conditions, but the results of this study suggest that the more severe and extended alkaline treatment yields fewer ether linkages. It is commonly believed that the ether linkages are hydrolyzed under acid conditions to form a methylene linkage and formaldehyde. This is supported by the fact that all the resins produced which underwent an acid phase show fewer ethers than the UFC they were produced from. The substantially fewer ether structures in the resin with the modified alkaline treatment suggests that a portion of the original ethers were hydrolyzed while in the alkaline phase of the cook. This hydrolysis may have been catalyzed by an increased amount of formic acid resulting from the Cannizzaro reaction of formaldehyde. The fact that a significantly greater amount of formic acid was produced is suggested by the resonance intensity

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TABLE IV
Functional group analysis for resins with different alkaline phase treatments

Functional Group		Resonance Position (ppm)	Amount of Each Group as a Percentage of Total Formaldehyde *Resin: A	B
$—NH—CH_2OH$		64.8	24.1	31.7
$—N(CH_2OH)_2$		71.6	2.2	10.7
$—NH—CH_2—O—CH_2—NH—$ $—NH—CH_2—O—CH_2OH$		69.6	4.3	20.4
$—N(CH_2—)—CH_2—O—CH_2—NH—$ $—N(CH_2—)—CH_2—O—CH_2OH$		76.2	0.0	8.2
$—NH—CH_2—NH—$		47.2	29.3	19.2
$—N(CH_2—)—CH_2—NH—$		53.5	12.0	9.6
$HO—CH_2—OH$		82.9	0.0	0.0
$HOCH_2—O—CH_2OH$		86.3	0.0	0.0
$HOCH_2—O—CH_2—O—CH_2OH$		86.8	0.0	0.0
$NH—CO—NH$ $\vert \quad\quad \vert$ $CH_2—O—CH_2$		74.8	11.1	0.0
$NH—CO—N—CH_2OH$ $\vert \quad\quad \vert(1)$ $CH_2—O—CH_2$ (2)	(1)	68.6	5.3	0.0
	(2)	78.9	8.9	0.0

*Resin description
A—modified alkaline treatment (higher pH and longer time)
B—standard alkaline treatment
(both resins were advanced at 1.1 MR)

for the methanol. The integration of the methanol peak indicates there to be 28.5% more methanol in the resin with the modified alkaline treatment than the resin with the standard alkaline treatment.

In addition to the reduced number of ether linkages, the modified alkaline treatment promotes the formation of cyclic ethers resulting from ring-closure reactions. The influence on the ethers and the formation of the cyclic uron structures indicates that the alkaline phase of the cook does have a significant effect on the final resin structure.

Extent of Reaction In order to isolate the effect of extent of reaction, the standard cook parameters were used but the acid condensation phase of the reaction was lengthened. The final viscosity was approximately 3.4 times the viscosity of the standard cook.

Extent of Reaction

In order to isolate the effect of extent of reaction, the standard cook

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TABLE V
Functional group analysis for resins with different extent of condensation (final resin viscosity)

Functional Group	Resonance Position (ppm)	Amount of Each Group as a Percentage of Total Formaldehyde	
		*Resin: A	B
$\mathrm{-NH-CH_2OH}$	64.8	44.1	35.2
$\mathrm{-N(CH_2OH)_2}$	71.6	14.0	11.4
$\mathrm{-NH-CH_2-O-CH_2-NH-}$ $\mathrm{-NH-CH_2-O-CH_2OH}$	69.6	15.6	9.9
$\mathrm{-N(CH_2-)-CH_2-O-CH_2-NH-}$ $\mathrm{-N(CH_2-)-CH_2-O-CH_2OH}$	76.2	7.8	5.9
$\mathrm{-NH-CH_2-NH-}$	47.2	8.3	15.7
$\mathrm{-N(CH_2-)-CH_2-NH-}$	53.5	10.1	22.0
$\mathrm{HO-CH_2-OH}$	82.9	0.0	0.0
$\mathrm{HOCH_2-O-CH_2OH}$	86.3	0.0	0.0
$\mathrm{HOCH_2-O-CH_2-O-CH_2OH}$	86.8	0.0	0.0

*Resin description
A—standard cook (final viscosity—210 cps.)
B—high extent of reaction (final viscosity—715 cps.)

parameters were used but the acid condensation phrase of the reaction was lengthened. The final viscosity was approximately 3.4 times the viscosity of the standard cook.

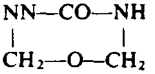
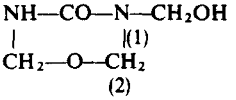
A higher level of condensation is apparent from the total methylene content of 37.7% compared to 18.4% for the standard cook as shown in the functional group analysis of Table V. The integrated peak intensities also demonstrate that the extended acid condensation phase resulted in substantially fewer methylene ether linkages. This supports the contention that the hydrolysis of the ether linkages is primarily acid catalyzed.

There was also a much greater proportion of branched methylenes. The total methylene content was just over twice that of the standard while the viscosity was 3.4 times the standard. This may be due to a loss of solubility of the linear polymer. The limited solubility of the linear UF polymer could be the result of the development of a highly ordered intramolecular and intermolecular hydrogen bonding network. The possibility of a highly ordered hydrogen bonding system suggests the potential for the development of crystallinity.

Concentration of Reactants During the Cook

The majority of the resin cooks done in this study were conducted at

TABLE VI
Functional group analysis for resins cooked at different concentrations

Functional Group	Resonance Position (ppm)	Amount of Each Group as a Percentage of Total Formaldehyde	
		*Resin: A	B
$-NH-CH_2OH$	64.8	44.1	83.5
$-N(CH_2OH)_2$	71.6	14.0	5.1
$-NH-CH_2-O-CH_2-NH-$ $-NH-CH_2-O-CH_2OH$	69.6	15.6	4.3
$-N(CH_2-)-CH_2-O-CH_2-NH-$ $-N(CH_2-)-CH_2-O-CH_2OH$	76.2	7.8	0.0
$-NH-CH_2-NH-$	47.2	8.3	2.8
$-N(CH_2-)-CH_2-NH-$	53.5	10.1	0.0
$HO-CH_2-OH$	82.9	0.0	1.2
$HOCH_2-O-CH_2OH$	86.3	0.0	0.0
$HOCH_2-O-CH_2-O-CH_2OH$	86.8	0.0	0.0
 $\begin{array}{l} NN-CO-NH \\ \mid \qquad\quad \mid \\ CH_2-O-CH_2 \end{array}$	75.0	0.0	0.6
 $\begin{array}{l} NH-CO-N-CH_2OH \\ \mid \qquad\quad \mid(1) \\ CH_2-O-CH_2 \\ \qquad\quad (2) \end{array}$	(1) 68.4	0.0	1.0
	(2) 78.8	0.0	1.2

*Resin description
A—standard cook (cooked at 65% solids)
B—dilute cook (cooked at 5% solids and condensed to 30% by vacuum distilation)

high concentrations. The nature of the resin resulting from synthesis at very low concentration was studied to determine the effect on resin structure. The same reaction conditions (pH, temperature, MR and timing) as the standard cook were utilized. The functional group analysis comparing it to the standard cook is given in Table VI.

The classic kenetics studies of DeJong and DeJonge[6,7,8] indicate that the rate of consumption of formaldehyde in the initial addition reaction is independent of concentration. A major difference, however, was found with respect to the condensation reaction. At a low concentration a very low extent of condensation was observed. The total methylene content was only 2.8%. These were entirely linear, no branch point methylenes were indicated. A large portion of the formaldehyde (83.5%) remained as linear methylol and 1.2% as free formaldehyde. This suggests that the kenetics of the reactions are influenced by concentration.

The NMR analysis of this resin also indicated the presence of a small

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amount of cyclic uron structures. The presence of these cyclic ethers in this resin and their absence in the more advanced standard cook, suggests that the ring closure reactions occur early in the condensation process and are hydrolyzed in the later stages of condensation.

CONCLUSIONS

The results of this study have demonstrated the influence of various production parameters on the structure of the final resin solution. It is evident that the structural features most dramatically affected are the extent of branch point development, extent of condensation and the percentages of methylene ethers and methylol groups maintained in the final solution. All the cook parameters studied had an influence on the final resin structure, although some were more effective than others.

The conclusions drawn from this study can best be summarized as follows:

1. The final mole ratio of the resin does have an effect on the number of branch points developed in the resin. The extent of branching increased with increased formaldehyde:urea mole ratio.

2. The mole ratio during the acid condensation phase of the cook had an even greater impact on the resin synthesis and the final resin structure. At a high mole ratio the excess formaldehyde has an inhibiting effect on the rate of condensation. When the resin is advanced at a low mole ratio the condensation is very rapid. The low mole ratio advancement also yields a more linear polymer than the standard cook.

3. An extended and more severe alkaline phase treatment results in the formation of cyclic uron structures. The high pH also tends to promote the formaldehyde Cannizzaro reaction. The formic acid generated seems to catalyze the hydrolysis of the methylene ether linkages. The resulting resin has fewer ethers, fewer residual methylols and more methylene linkages.

4. Increasing the time of the acid condensation phase of the cook results in a resin with a higher degree of condensation. This is apparent in a reduced number of residual methylols and more methylene linkages. There are also more branch points observed. This may be due to the limited solubility of highly condensed linear UF polymer.

5. The concentration of reactants during the cook has an effect on the kinetics of the reaction. At low concentration, very little condensa-

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tion is observed in the time frame of the standard cook.

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