Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Solid-State ^{13}C-NMR Studies of Uncured Urea-Formaldehyde Resins

Sivananda S. Jada[a]
[a] Manville Technical Center, Denver, Colorado

To cite this Article Jada, Sivananda S.(1990) 'Solid-State ^{13}C-NMR Studies of Uncured Urea-Formaldehyde Resins', Journal of Macromolecular Science, Part A, 27: 3, 361 — 375
To link to this Article: DOI: 10.1080/00222339009349559
URL: http://dx.doi.org/10.1080/00222339009349559

J. MACROMOL. SCI.—CHEM., A27(3), pp. 361–375 (1990)

SOLID-STATE ^{13}C-NMR STUDIES OF UNCURED UREA-FORMALDEHYDE RESINS*

SIVANANDA S. JADA

Manville Technical Center
Denver, Colorado 80217

ABSTRACT

^{13}C solid-state NMR has been used for quantitative determination of the proportion of various functional groups present in uncured urea-formaldehyde (UF) resins. The quantitative interpretation of the structural units present in UF resins synthesized in different pH conditions was made possible by using appropriate rotors and pulse techniques. Resin prepared in acid medium showed more methylene units in the polymer branch and less methylol moieties in the polymer chain compared to resin prepared in alkaline condition. Plausible mechanistic routes are proposed to explain the structural differences due to pH change.

INTRODUCTION

The urea-formaldehyde (UF) resins have been in use for many decades, but the saga of chemical and structural understanding of their formation and crosslinking mechanism, hydrolytic instability, and formaldehyde release from cured composites over a long service period is still continuing. There are a few reasons to account for such a continued interest in this "age-old" amino resin: 1) for economic reasons these UF resins occupy a dominant position within the aminoplast resins group; 2) their major applications in the areas of textile and paper auxiliaries, coatings, adhesives, castings, fertilizers, and molding compounds; 3) the complexity arising from the different synthetic routes utilized in manufacturing the commercial resins; and 4) a

---

*Research was conducted at the Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio.

need to understand and eliminate the mechanism or cause for formaldehyde emission from cured products so they will meet the federal regulations of formaldehyde emission controls. Progress in accomplishing such critical tasks will not occur until more complete knowledge regarding the structure of low molecular weight reactive intermediates formed during the condensation of urea with formaldehyde, the reaction kinetics, and the mechanism of resin formation and cure are obtained. A large number of analytical tools have already been applied to gain such insight, both qualitatively and quantitatively, including Fourier transform infrared (FT-IR) [1], ^{15}N nuclear magnetic resonance (NMR) [2, 3], solution ^{13}C NMR [4–10], solid-state ^{13}C NMR [11, 12] using cross-polarization and magic angle spinning (CP/MAS), and Raman [13] spectroscopies. Until recently, high resolution ^{13}C-NMR spectra of UF prepolymers were obtained in solution—the widths of these resonances frequently being on the order of a few hertz. In contrast, the spectra of solid polymers (cured UF resins) showed lines tens of kilohertz in width, with no resolvable fine structure. The dipolar and anisotropy interactions responsible for these broad lines are averaged to zero in a normal solution by rapid molecular motion. Such motion is restricted in glassy polymers. It was assumed that quantitative data on the proportion of various functional groups obtained by ^{13}C solution NMR for *uncured* resin could be erroneous if correlated with data obtained on cured resin by ^{13}C solid-state NMR.

The objective of this study is to utilize ^{13}C NMR (CP/MAS) to correlate the proportion of functional groups present in UF resins before and after cure. In this paper the influence of pH on the structure and functional group content of "uncured" resin using solid-state NMR is discussed.

EXPERIMENTAL

Several model compounds whose presence was identified in resin formation or during curing by other analytical techniques were synthesized or purchased. Two UF prepolymers were prepared at different pH conditions, but the urea and formaldehyde mole ratio, synthesis temperature, and time were kept constant. The acid-catalyzed prepolymer had pH 3.0 ± 0.2 (Resin A) at the end of the synthesis, and the second prepolymer had pH 8.0 ± 0.2 (Resin B). The general method of resin preparation and the source of model compounds have been reported elsewhere [1]. After preparation, both resins were freeze-dried and stored cold over desiccant.

Instrumentation

The solid-state ^{13}C-NMR spectra of model compounds and the freeze-dried UF prepolymers were recorded using a Nicolet NT-150 spectrometer fitted with a cross-polarization accessory. Radio-frequency amplifiers delivering 550 W at 150 MHz and 1000 W at 37.7 MHz were adjusted to satisfy the Hartman-Hahn condition at roughly 68 kHz. Cross-polarization experiments (CP/MAS) were recorded with a single 1.0 ms contact time, and the typical delay between pulse sequences was 2.0 ms.

In all these CP/MAS experiments the magic angle of 54.7° was set by maximizing the intensity of the carbonyl peak of glycine. To improve the S/N ratio in the ^{13}C-NMR spectra of solid samples, 10 000 transients were collected.

The resonance of the Delrin (89 ppm downfield from tetramethylsilane) was used as a reference. The spin-temperature alteration was used to eliminate various artifacts [14]. The static field was not locked during accumulations of transients. Beam-Andrew-type rotors were used in this study. These rotors were machined from Delrin and also from Kel-F materials. Delrin rotors were spun at 3.5–4.0 kHz and Kel-F at 2.0–2.2 kHz. The resulting spectra were deconvoluted to give approximate relative concentrations of various chemical group moieties present in the final resin. In addition, the percentage of the carbons of each observed chemical group in the resin was also calculated based on the total number of carbons in the system.

RESULTS

Solid-State ^{13}C-NMR Data Analysis

Under the conditions set (see Experimental Section) to record the spectra of model compounds and the experimental prepolymers, the resultant resonance peaks are broad and overlapped, which makes analysis difficult. However, by utilizing high power proton decoupling and magic angle sample spinning, the resonance peaks are narrowed considerably. Nevertheless, the recorded peaks are still broad, and this residual line width may be due to the quadrupolar interactions of the ^{14}N-^{13}C type and also from the unaveraged chemical shift anisotropy. Similar problems were encountered by other authors while studying the amino resin curing mechanism using similar techniques [12]. The magic angle spinning may not average these additional ^{14}N-^{13}C interactions caused by the nitrogens attached to the ^{13}C atoms [15–18]. In other words, the overlap peaks have to be deconvoluted to find the areas of each peak for quantitative analysis.

Spectra of Model Compounds

The model compounds were made use of in the assignments of the ^{13}C-NMR chemical shifts of freeze-dried resins. These model compounds are useful in understanding the complex nature of the UF resins. For example, there is a wide distribution of methylene resonances between ~40–90 ppm in the ^{13}C-NMR (solid) spectrum of prepolymer in the aliphatic region, see Fig. 1. These are the methylene carbons

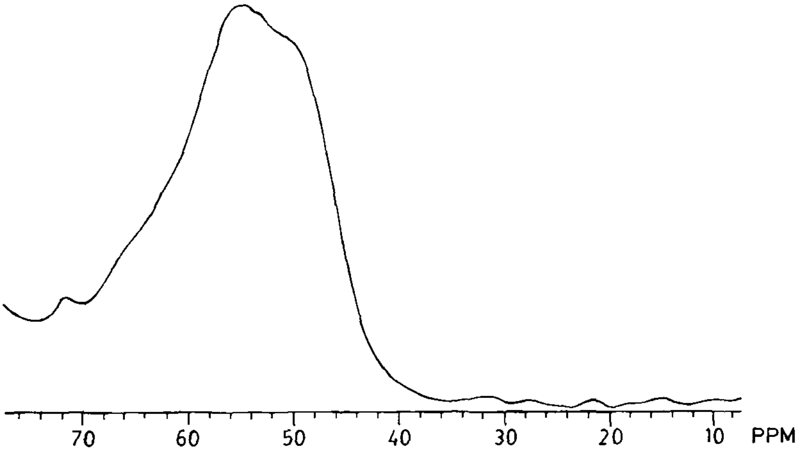


FIG. 1. ^{13}C CP/MAS spectrum of Resin A (pH 3.0); aliphatic region.

attached to primary, secondary, and tertiary nitrogens and the oxygen atoms. Model compounds having such methylene carbon units are most useful to identify the various structures of intermediate complexes formed during the condensation of urea with formaldehyde under different pH conditions.

The solid-state CP/MAS ^{13}C-NMR spectrum of paraformaldehyde is shown in Fig. 2. It has a single ^{13}C resonance of the methylene ether carbons $-(CH_2-O-)_n$ at 88.9 ppm. This assignment is in agreement with methylene units in polyoxymethylene (89 ppm) [19]. Solid-state ^{13}C chemical shifts of model compounds having various chemical groups are shown in Table 1. For comparison, the chemical shifts of similar groups in the solution state and the peak assignments from the literature on the solid state are listed in the same table.

Spectra of UF Resins

(A) Acid-Catalyzed Prepolymer (Resin A)

The CP/MAS spectrum of acid-catalyzed prepolymer is shown in Fig. 3. This spectrum was recorded with a Kel-F rotor. The use of this rotor made it possible to see the additional resonances not seen when the sample was recorded using a Delrin rotor, see Fig. 4. The observed overlap may be due to the resonance of polyoxymethylene with which the Delrin rotor is made. The ^{13}C resonance peak at 48 ppm

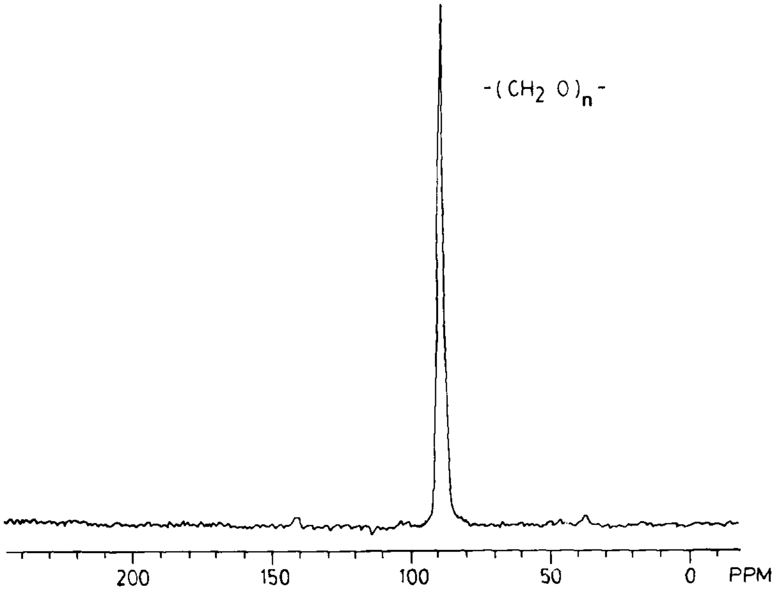


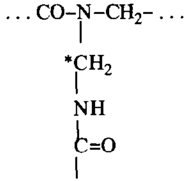
FIG. 2. ^{13}C CP/MAS spectrum of paraformaldehyde.

is assigned to the methylene units between two secondary nitrogens $-(NH-CH_2-NH)-$ in the linear chain, see Peak A in Fig. 3. These $-NH-CH_2-NH-$ units in such model compounds as methylolmethylenediurate, dimethylenetriureate, and methylenediureate [8, 11] appear at ~47 ppm. The resonance Peak B (54.5 ppm) is assigned to the methylene units between the tertiary and secondary nitrogens of the branched chain.

The methylol groups on the secondary nitrogens $(-NH-CH_2OH)$ appear at ~65 ppm in the monomethylolurea and dimethylolurea model compounds, Table 1. In prepolymer the Peak C appears at chemical shift 65.3 ppm, see Fig. 3 and Table 1. So, based on the model compound peak assignments, Peak C is assigned to methylol units in the polymer branch or at the polymer chain end. The resonance of the methylene groups on the tertiary nitrogen which appears at 72.6 ppm is assigned to Peak D. The ^{13}C resonance of the methylene carbons between nitrogen and oxygen atoms, Peak E, appear at ~77 ppm.

The carbonyl resonances appear at ~160 ppm. This resonance is very strong and broad. No attempt was made to resolve the different carbonyl resonance peaks

TABLE 1. ^{13}C-NMR Chemical Shifts of Model Systems

Chemical group		Resonance position, ppm		
Name	Structure	Author's work	Ref. 12	Solution
Methylene units in linear chain	$\ldots OCH_2\text{-}HN\text{-}CO\text{-}NH\text{-}{}^*CH_2\text{-}NH\text{-}CO\text{-}NH\text{-}\ldots$	48.3	46.3–47.4	47
Methylene units in the branch	 $\ldots CO\text{-}N(\text{-}{}^*CH_2\text{-}NH\text{-}C{=}O)\text{-}CH_2\text{-}\ldots$	54.5	54.5–54 .8	53.6
Methylol groups on secondary nitrogen	$HO\text{-}{}^*CH_2\text{-}NH\text{-}CO\text{-}NH\text{-}CH_2O\text{-}\ldots$	65.3	64.5–65.2	64.8
Methylol groups on tertiary nitrogen	$>N\text{-}{}^*CH_2OH$	72.6	71.6–72.8	71.2
Methylene carbons attached to tertiary nitrogen and oxygen atoms	$>N\text{-}{}^*CH_2\text{-}O\text{-}CH_2\text{-}\ldots$ and $>N\text{-}{}^*CH_2\text{-}O\text{-}CH_3$	77	78.7	75.3
Methylene ether carbons	$\text{-}({}^*CH_2\text{-}O\text{-}CH_2\text{-}O)_{\overline{n}}$	88–90	–	88–90.5
Carbonyl carbons:		158–160	159.3–169	158–160
Monosubstituted urea	$H_2N\text{-}{}^*CO\text{-}NH\text{-}CH_2\text{-}\ldots$			
Disubstituted urea	$\ldots\text{-}CH_2\text{-}NH\text{-}{}^*CO\text{-}NH\text{-}CH_2\text{-}\ldots$			
Trisubstituted urea	$>N\text{-}{}^*CO\text{-}NH\text{-}CH_2\text{-}\ldots$			
Tetrasubstituted urea	$>N\text{-}{}^*CO\text{-}N<$			

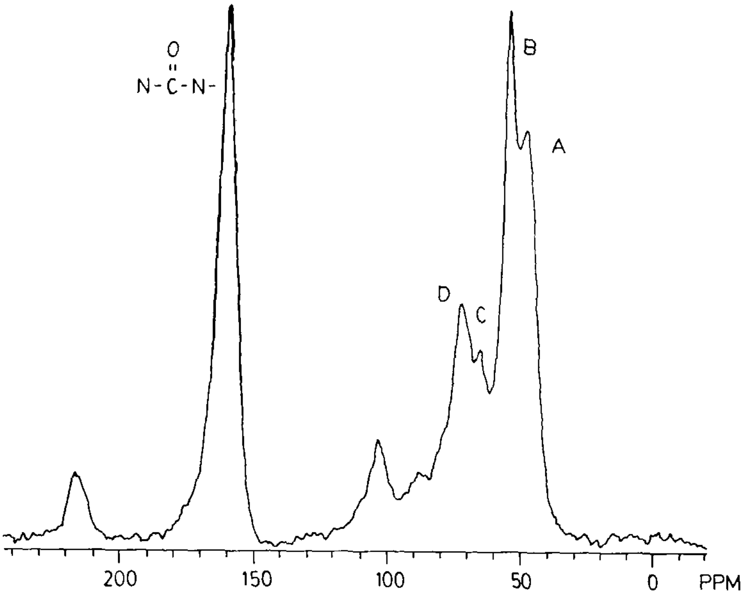


FIG. 3. ^{13}C CP/MAS spectrum of acid-catalyzed UF prepolymer, Resin A, using Kel-F rotor.

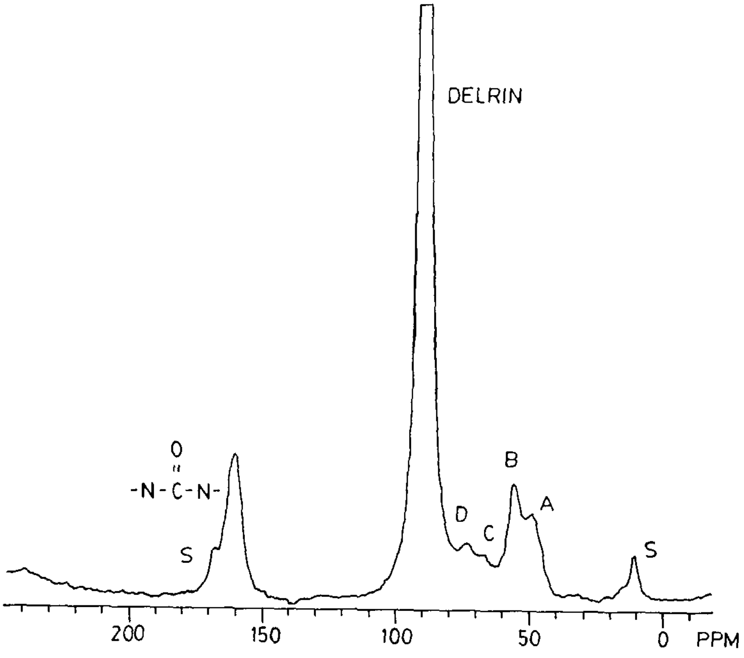


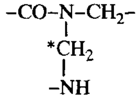
FIG. 4. ^{13}C CP/MAS spectrum of Resin A using Delrin rotor. S = spinning sideband.

because they are distributed in the 158–160 ppm range. The peak assignments for UF resins are listed in Table 2.

(B) Base-Catalyzed Prepolymer (Resin B)

From the solid-state ${}^{13}C$-NMR spectra it appears that the resonances in the solid-state environment are sensitive to pH changes. Figure 5 illustrates the effect of pH change during the condensation reaction between urea and formaldehyde. Figure 5(a) is the spectrum of Resin B (pH 8.0) and Fig. 5(b) is the spectrum of Resin A (pH 3.0). Comparison of these two spectra suggests that the reaction of urea with formaldehyde strongly depends on the pH medium. The complete condensate structure of the resin is different in both prepolymers. The chemical shifts for carbonyl, methylene groups between tertiary, secondary nitrogen atoms, and methylol groups are the same for the solid ${}^{13}C$-NMR spectrum recorded as for resins prepared in higher and lower pH's. The only difference observed was for the methylol group resonance sandwiched between two secondary nitrogens. For acid-catalyzed prepolymer the chemical shift is at 48.3 ppm, and for base-catalyzed prepolymer the chemical shift is at 46.7 ppm. Oxymethylene carbons appear at 88–99 ppm for Resin B.

TABLE 2. Solid-State ${}^{13}C$-NMR Data Analysis of UF Resins

Resonance peak	Carbon fragment type	Chemical shift, ppm	Prepolymer, % carbons[a]	
			Resin A (pH 3.0)	Resin B (pH 8.0)
	Carbonyl	160	41.06	33.22
A	Methylene units in linear chain: $-NH_2-{}^*CH_2-NH-$	48.3[b]	9.61	7.8
B	Methylene units in the branch:  $\begin{array}{l} -CO-N-CH_2- \\ \qquad \vert \\ \qquad {}^*CH_2 \\ \qquad \vert \\ \quad -NH \end{array}$	54.5	38.5	6.9
C	Methylol units on secondary nitrogen atom	65.3	5.33	50.05
D	Methylol units on tertiary nitrogen atom	72.4	2.04	—
E	Methylene ether units on tertiary nitrogen atom	77.2	0.9	—
F	$-(CH_2-O-{}^*CH_2-O-)_n$	88–90	2.33	1.99

[a] Calculated on the basis of total carbons.

[b] 46.7 ppm for Resin B (pH 8.0).

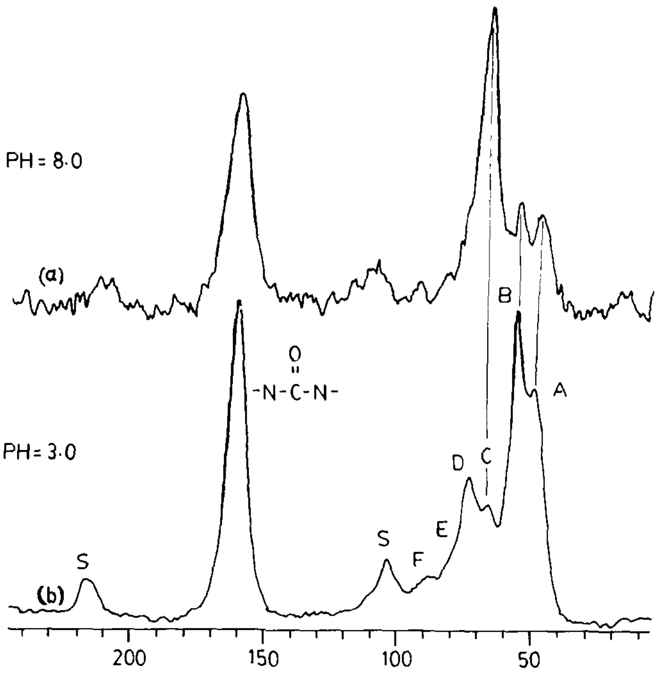


FIG. 5. ^{13}C CP/MAS spectrum of UF prepolymers using Kel-F rotor. (a) Spectrum of Resin B and (b) spectrum of Resin A.

In each case the spectrum was deconvoluted using Nicolet software. In Fig. 6 the top spectrum is the experimental sideband-suppressed spectrum for Resin A, the bottom plot shows the separated Gaussian contributions obtained by deconvolution, and the middle plot is the calculated (simulated) spectrum obtained by combining the Gaussian contributions of the lower plot. There is an excellent fit between the experimental and calculated spectra. The peak assignments are shown in Table 2.

DISCUSSION

The solid-state NMR quantitative spectra of resins, see Fig. 5, are relatively simple and have fewer resonance peaks than solution NMR spectra [20]. Unlike in solution NMR, the resonance peaks present in the methylene region (0–100 ppm)—which is an essential part in UF resin identification—are broad and overlapped. Another obvious difference between solid and solution NMR spectra of uncured UF resin is

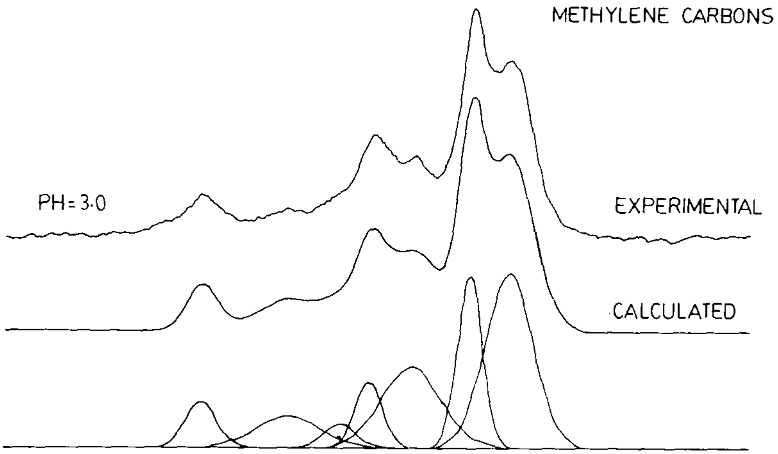
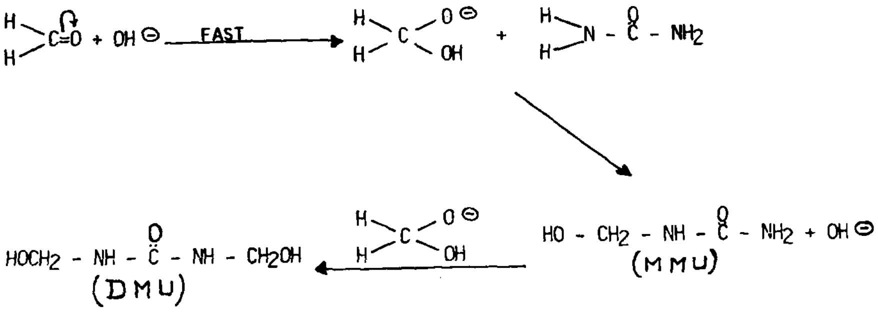


FIG. 6. Deconvolution of the ^{13}C CP/MAS spectra of Resin A. Top: Experimental UF resin spectrum. Middle: Simulated based on deconvoluted spectrum. Bottom: Deconvoluted spectrum.

the lack of resonance peaks characteristic of methanol, methoxy, and cyclic ethers. This means that the solid-state NMR technique utilizing the freeze-dry method for sample preparation may not be suitable to identify and analyze the low concentrated by-products and other low molecular weight condensates present in uncured resin. However, the technique has been shown to be sensitive enough to detect changes in the structure of uncured UF resins due to pH changes. For example, Peak C has the highest intensity in the entire spectrum of Resin B, and in the Resin A spectrum it has lowest intensity. Quantitative analysis showed 50.05% methylol units in Resin B compared to 5.53% in Resin A (see Table 2). This indicates that in the base-catalyzed system, electrophilic and nucleophilic behavior of formaldehyde and urea, respectively, play an important role. Assuming such behavior from the starting materials, one would expect the formation of monomethylolurea (MMU) as an initial condensation product. Subsequent condensation between formaldehyde and MMU would yield dimethylolurea (DMU), $HOH_2C\text{-}NH\text{-}CO\text{-}NH\text{-}CH_2OH$, which has two methylols on its chain terminal. The very large percentage of such methylol content in Resin B also suggests that the probable rate of DMU formation is very high in the early stages of step-growth polymerization. A plausible mechanistic route is shown in Scheme 1.

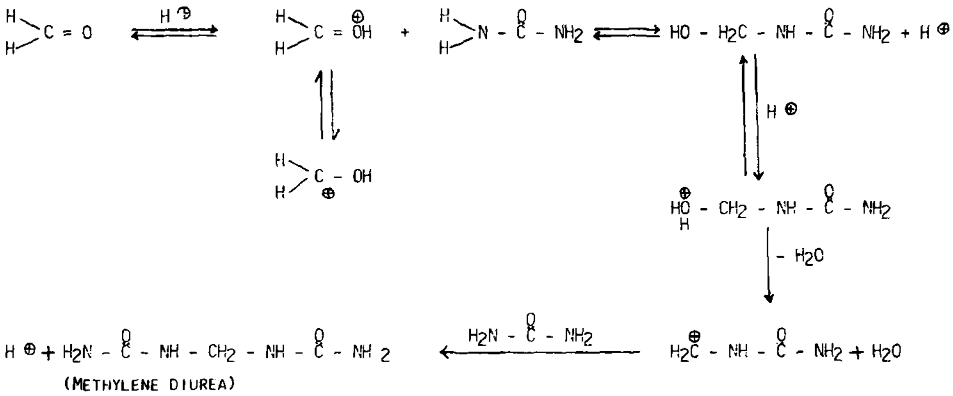


SCHEME 1. Base-catalyzed UF condensation.

The low percent of methylol units bonded to the Amide II nitrogen in the acid-catalyzed system indicates a different reaction mechanism. In acidic condition it is most likely that protonation occurs on the oxygen atom of formaldehyde. The next step is probably the addition of protonated formaldehyde to urea to form a monomethylol urea (MMU), $H_2N-CO-NH-CH_2OH$. Further step-growth condensation may proceed by further protonation of MMU, forming a carbonium ion by the elimination of water. MMU with a reactive carbonium ion may further react with available urea to give methylenediurea (MDU), $H_2N-CO-NH-CH_2-NH-CO-NH_2$. MDU has no methylol units in its structure and is terminated by primary amides. The mechanism is outlined in Scheme 2. Thus, under acidic condition, the $\geq N5CH_2-N\leq$ structure is highly favored, as the results indicate. These observations are consistent with recently published results [1].

Rate of Polymer Branching

pH also has some influence on the rate of polymer branching and the proportion of methylene units present between secondary and tertiary amides. Resin B has 6.9% methylene units between Amide II and/or Amide III, and Resin A has 38.5% (see Table 2). More methylene bridging in the acid-catalyzed system is also seen by solution NMR [10, 20]. It is highly probable that the rate of bridging or branching is dependent on the electron density on the $-CH_2$ group attached to a secondary amide (Amide II). An increase in electron density will enhance the reactivity of a secondary amine with formaldehyde. As our experimental results indicate, Resin A has a



SCHEME 2. Acid-catalyzed UF condensation.

favorable structure to facilitate such polymer branching. Nonetheless, more experimental work needs to be done to confirm these conclusions.

A small percentage of linear methylene units of the type NH_2–CH_2–NH– was found in both resins. This suggests that pH has no influence in forming higher molecular weight intermediates during resin synthesis.

The literature indicates that alkaline pH enhances the possibility of ether formation [21]. Based on our experimental results, it is hard to say whether such an ether linkage is formed by the condensation of two methylols or because of residual paraformaldehyde contamination from the starting material.

In conclusion, the solid-state ^{13}C-NMR technique is sensitive for detecting changes in the structure of uncured UF resins arising from a pH change during synthesis. Kel-F rotors were found to be very useful in obtaining a complete spectrum of UF resin. In the acid-catalyzed system the rate of branching is higher and the proportion of methylol units is lower compared to the base-catalyzed system. These experimental results agree with our previous results obtained by FTIR on the same resins. Carbon-13 solid-state NMR can be used effectively in quantitative interpretation of the structural units present in uncured resins. For comparison, the CP/MAS spectra of "cured" UF Resins A and B are shown in Figs. 7 and 8, respectively. Further research is underway to correlate these results with cured resins.

ACKNOWLEDGMENTS

The author wishes to thank Ashok Cholli for recording the solid-state ^{13}C-NMR spectra of the model compounds and UF resins.

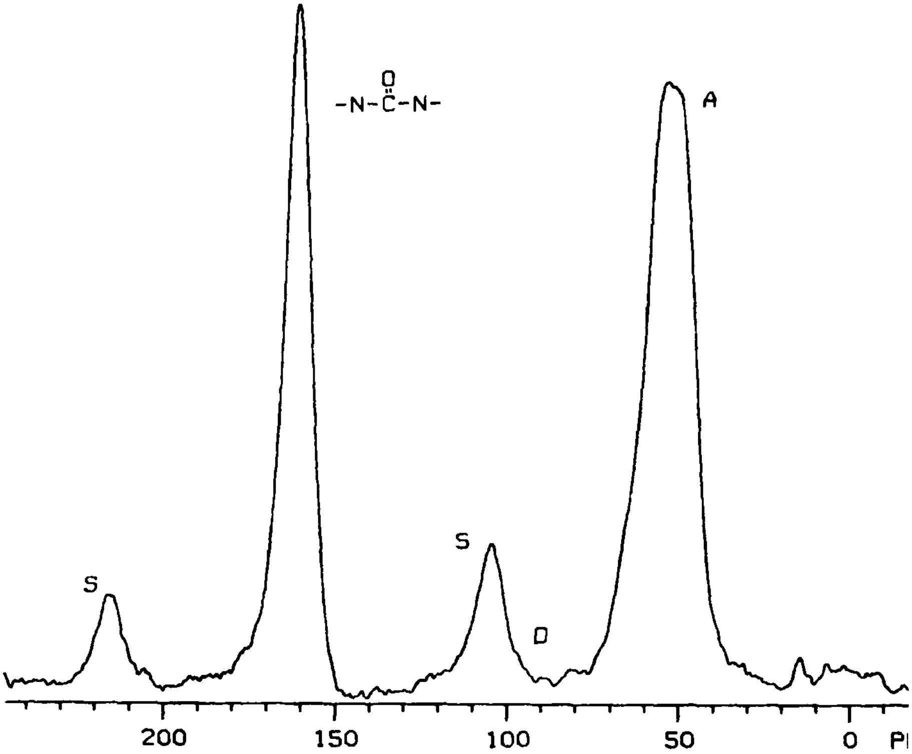


FIG. 7. ^{13}C CP/MAS spectrum of cured urea-formaldehyde Resin A using Kel-F rotor.

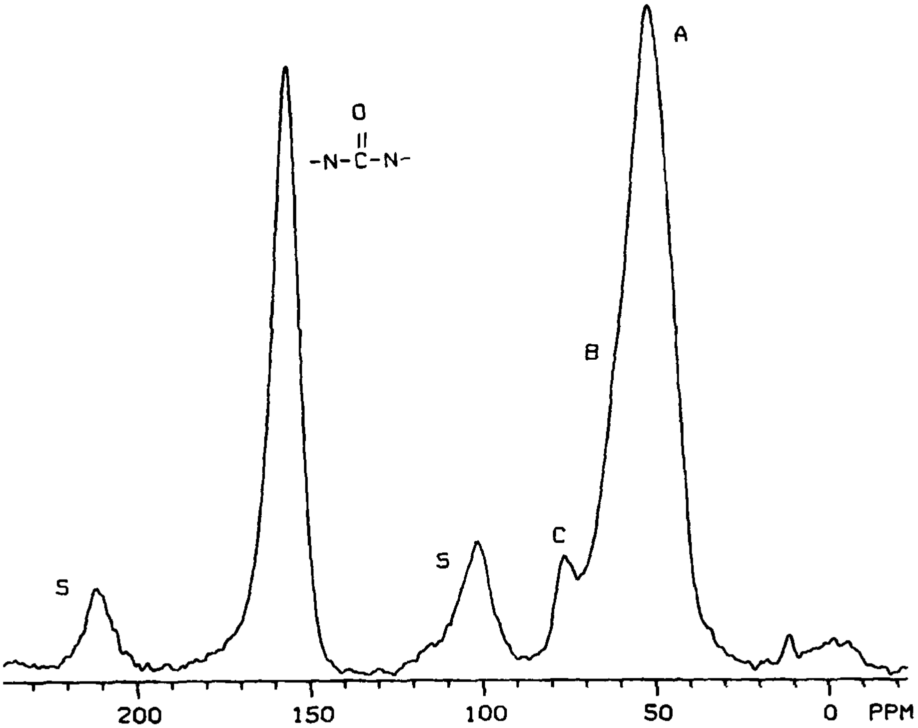


FIG. 8. ^{13}C CP/MAS spectrum of cured urea-formaldehyde Resin B using Kel-F rotor.

REFERENCES

[1] S. Jada, *J. Appl. Polym. Sci., 35,* 1573 (1988).

[2] J. R. Ebdon, P. E. Heaton, T. N. Huckerby, W. T. S. O'Rourke, and J. Parkin, *Polymer, 25*(6), 821 (1984).

[3] G. E. Myers, *Macromolecules, 18*(17), 1482 (1985).

[4] B. Meyer and R. Nunlist, *Polym. Prepr., 22*(1), 130 (1981).

[5] R. Tayler, R. J. Pragnell, J. V. McLaren, and C. E. Snape, *Talata, 29*(6), 489 (1982).

[6] B. Tomita and H. Ono, *J. Polym. Sci., Polym., Chem. Ed., 17,* 3205 (1979).

[7] A. J. J. deBreet, W. Dankelman, W. G. B. Huysmans, and J. DeWit, *Angew. Makromol. Chem., 62*(1), 7 (1977).

[8] I. Ya. Slonim, V. N. Gorbunov, S. G. Alekseeva, and Ya. G. Urman, *Vysokomol. Soedin., Ser. B, 24,* 528 (1982), and earlier papers by the first author.
[9] H. Schindlbauer and J. Schuster, *Kunststoffe, 73*(6), 325 (1983).
[10] R. M. Rammon, W. E. Johns, J. Magnuson, and K. A. Dunker, *J. Adhes. 19*(2), 115 (1986).
[11] I. Ya. Slonim, B. M. Arshave, and Ya. G. Urman, *Sovrem. Metody YaMR EPR Khim. Tverd. Tela,* p. 55 (1985).
[12] G. E. Maciel, N. M. Szeveenyi, T. A. Early, and G. E. Myers, *Macromolecules, 16*(4), 598 (1983).
[13] C. G. Hill, A. M. Hedren, G. E. Myers, and J. A. Koutsky, *J. Appl. Polym. Sci., 29*(9), 2749 (1984).
[14] E. O. Stejskal and J. Schaeffer, *J. Magn. Reson., 18,* 560 (1975).
[15] A. Naito, S. Ganapathy, and C. A. McDowell, *J. Chem. Phys., 74,* 5393 (1981).
[16] S. J. Opella, M. H. Frey, and T. A. Cross, *J. Am. Chem. Soc., 101,* 5856 (1979).
[17] C. L. Groombridge, R. K. Harris, K. J. Packer, B. J. Say, and S. F. Tanner, *J. Chem. Soc., Chem. Commun., 4,* 174 (1980).
[18] M. H. Frey and J. Opella, *Ibid., 11,* 474 (1980).
[19] W. S. Veeman, E. M. Menger, W. M. Ritchey, and E. deBoer, *Macromolecules, 12,* 924 (1979).
[20] S. Jada, Unpublished Results.
[21] B. Meyer, in *Urea-Formaldehyde Resins,* Addison-Wesley, Reading, Massachusetts, 1979.