Natural-abundance ^{15}N cross-polarization/magic-angle spinning nuclear magnetic resonance study of urea–formaldehyde resins

I-Ssuer Chuang and Gary E. Maciel*
Department of Chemistry, Colorado State University, Fort Collins, CO 80523-0002, USA

(Received 14 September 1993)

High-quality natural-abundance ^{15}N cross-polarization/magic-angle spinning (c.p.-m.a.s.) spectra of urea–formaldehyde (UF) resins were obtained by employing a large-volume (2.5 cm^3) magic-angle spinning (m.a.s.) rotor. ^{15}N c.p.-m.a.s. nuclear magnetic resonance (n.m.r.) spectroscopy can clearly distinguish dimethylene ether linkages from methylol groups for UF resins prepared under neutral or basic conditions, a weak point in ^{13}C c.p.-m.a.s. strategies because of ^{14}N broadening effects, and can detect the existence of tertiary amides and unreacted primary amides in UF resins. ^{15}N c.p.-m.a.s. n.m.r. also establishes the fact that there are methylol aggregates that are spatially separated from some other structural moieties in UF resins and that the domain size of methylol aggregates diminishes with the concentration of methylol groups in UF resins. ^{15}N c.p.-m.a.s. results also indicate that the formation of dimethylene ether linkages is least favourable at pH 9 and most favourable at pH 12 among the three pH values 7, 9 and 12.

(Keywords: urea–formaldehyde resins; ^{15}N c.p.-m.a.s. n.m.r. spectra; spin diffusion)

INTRODUCTION

Urea–formaldehyde (UF) resins[1] have been used in the technological areas of coatings, adhesives, castings, moulding compounds and textile auxiliaries. UF resins are especially important as adhesives for various wood products. The reactions between formaldehyde and urea, or other starting materials that formally 'contain' them, and the structures of the resins formed have been investigated by various methods[1]. Among these methods, liquid-sample ^{13}C n.m.r. studies[2–11] have so far provided the most detailed information on the reactions and structures of UF resins that can be dissolved in suitable solvents. However, the structures of insoluble fractions and the nature of the curing processes of insoluble UF resins, which are very important issues concerning the performance characteristics of UF resins, are out of the range of applicability of liquid-sample spectroscopy.

High-resolution solid-state ^{13}C n.m.r. techniques that utilize cross-polarization (c.p.)[12] with high-power ^{1}H decoupling and magic-angle spinning (m.a.s.)[13] have been shown to be a powerful tool (c.p.-m.a.s.)[14] for elucidating structural details of UF resins[15–18], and for examining the hydrolytic stabilities of various UF resins[19].

Owing to its low natural abundance (0.37%) and low magnetogyric ratio (about 0.4 times that of ^{13}C), ^{15}N is in most cases not suitable for c.p.-m.a.s. studies unless ^{15}N-enriched materials are employed[20–30]. However, there are fragmentary recent reports of examples of natural-abundance ^{15}N c.p.-m.a.s. measurements on some nitrogen-rich samples[23,30–33].

The development of large-volume m.a.s. systems in our laboratory[32,34] has pointed to one avenue for achieving improved signal-to-noise (S/N) ratios in m.a.s. experiments in which sensitivity is a problem, such as natural-abundance ^{15}N experiments. By using large-volume m.a.s. systems, we have been able to investigate routinely natural-abundance UF resins and resins based on 4,4′-methylenebis(phenyl isocyanate) (MDI)[35]. In a previous paper[23], we reported the use of ^{15}N c.p.-m.a.s. techniques to study ^{15}N-enriched UF resin samples prepared with two different extents of curing, and found that ^{15}N c.p.-m.a.s. spectra were overall less useful than ^{13}C c.p.-m.a.s. spectra in providing structural details for the UF resin studied, even though ^{15}N data provided a useful information supplement. In this article, we describe the use of a large-volume m.a.s. rotor system for the natural-abundance ^{15}N c.p.-m.a.s. investigation of a series of systematically synthesized UF resins that were investigated previously by ^{13}C c.p.-m.a.s. methods[16,17]. The ^{15}N c.p.-m.a.s. results are compared with the previously published ^{13}C c.p.-m.a.s. results.

EXPERIMENTAL

Samples

The preparation of solid UF resins from 37% formalin and urea or from a '*N,N*′-dimethylolurea reagent' have been described elsewhere[16,17]. The formalin reagent contains 37% formaldehyde (by weight), 8% methanol (by weight) and 55% water (by weight). The *N,N*′-dimethylolurea reagent contains 92% (by weight) *N,N*′-dimethylolurea ($HOCH_2NHC(O)NHCH_2OH$) and 8% (by weight) monomethylolurea ($NH_2C(O)NHCH_2OH$). The 'equivalent' formaldehyde/urea/water molar ratios

---

*To whom correspondence should be addressed

0032-3861/94/08/1621–08

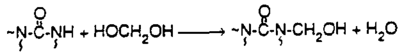
(F/U/W) stated in this paper are based on the $-CH_2O-$ and NC(O)N moieties and the H_2O formally present in the starting reaction mixture of the UF resin preparations. The solid UF resins are denoted in terms of the F/U/W molar ratios in the starting materials and the pH value of the preparative reaction mixture; e.g. 2.00/1.00/25.0(12) designates a solid UF resin prepared from a mixture with a F/U/W molar ratio of 2.00/1.00/25.0 at pH 12.

N.m.r. measurements

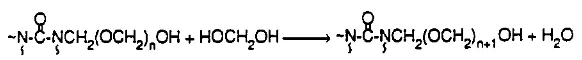
^{15}N c.p.-m.a.s. n.m.r. spectra were obtained at 20.3 MHz on a home-modified wide-bore Nicolet NT-200 spectrometer. Large-volume (2.5 cm^3) m.a.s. spinners of the pencil type from Chemagnetics were used for the sample container. Samples were spun at about 2 kHz at the magic angle. The c.p. contact times and pulse-sequence repetition times are indicated below. The ^1H–^{15}N dipolar-dephasing[36–38] ^{15}N c.p.-m.a.s. technique and ^1H–^1H dipolar dephasing[39] prior to $^1H \rightarrow ^{15}N$ cross-polarization were employed to provide structural information; details are described below. In this article, all ^{15}N chemical shifts are referenced to liquid NH_3 (at 25°C) at 0 ppm.

RESULTS AND DISCUSSION

Urea has four N–H sites available for interaction with formaldehyde, which in turn has two atomic sites available in the carbonyl group for interaction. The following reactions or combinations of reactions are believed to occur to varying extents in the formation of UF resins[1,16]:



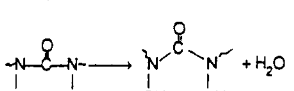
$$\text{-N-}\overset{O}{\overset{\|}{C}}\text{-NH} + HOCH_2OH \longrightarrow \text{-N-}\overset{O}{\overset{\|}{C}}\text{-N-}CH_2OH + H_2O \qquad (1)$$



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

$$\text{-N-}\overset{O}{\overset{\|}{C}}\text{-N}CH_2OH + HN\text{-}\overset{O}{\overset{\|}{C}}\text{-N-} \longrightarrow \text{-N-}\overset{O}{\overset{\|}{C}}\text{-N}CH_2N\text{-}\overset{O}{\overset{\|}{C}}\text{-N-} + H_2O \qquad (3)$$

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



(5)

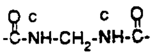
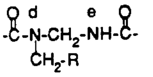
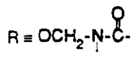
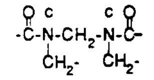
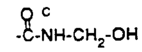
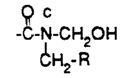
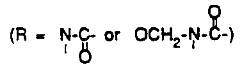
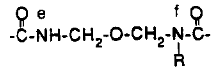
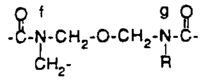
The methylolation reaction (equation (1)) is catalysed by both acids and bases[1], as confirmed by a previous ^{13}C c.p.-m.a.s. study[16]. According to the previous ^{13}C c.p.-m.a.s. study of a series of UF resins[16,17], the formation of methylene linkages (equation (3)) is catalysed only by acid, at least at room temperature, whereas formation of dimethylene ether linkages (equation (4)) is feasible under both low-pH and high-pH conditions. The reaction products formed from urea and formaldehyde can range from very simple ones (formed mainly under basic pH conditions) to very complicated, widely crosslinked products (formed mainly under acidic conditions). The factors[1,16,17] that affect the composition of UF products include the concentrations of the main reagents (formaldehyde and urea sources), pH, temperature and duration of reaction. *Table 1* lists some possible structural fragments that one might expect to appear in UF resins. The numbering system used here is based on what was used in previous articles[16,17].

Crosslinking is a very important structural element in UF resins. Although ^{13}C chemical shifts are sensitive enough to provide some structural information on crosslinking, ^{15}N c.p.-m.a.s. can in principle provide direct evidence of its existence. A nitrogen atom serves as a site for crosslinking (IIB and IIC in *Table 1*) or crosslinking precursor (IIA in *Table 1*) if it has no directly attached hydrogen, but is part of a non-crosslinking moiety. The ^1H–^{15}N dipolar-dephasing c.p.-m.a.s. experiment is a useful means of distinguishing between nitrogen atoms with and without directly attached hydrogen atoms[23,36–38]. *Figure 1* shows the dipolar-dephasing[36–38] ^{15}N c.p.-m.a.s. spectra of UF resin 2.00/1.00/25.0(12) with four different ^1H–^{15}N dipolar-dephasing times. Peak positions at 102 and 90 ppm in *Figure 1a* are assigned to $-C(O)NHCH_2OH$ and $-C(O)NHCH_2OCH_2-$ moieties, respectively; both nitrogen sites have a directly attached proton. Owing to its smaller magnetogyric ratio than that of ^{13}C, the ^{15}N signal of a nitrogen site with a directly attached proton can partially survive a dipolar-dephasing period of up to 50 μs; a 120 μs dipolar-dephasing period is required in order to distinguish clearly a hydrogen-bearing ^{15}N from a non-hydrogen-bearing ^{15}N, as indicated by the surviving behaviour at different dipolar-dephasing times of both peaks in *Figure 1*. *Figure 2* indicates that the 110 and 118 ppm peaks in the ^{15}N c.p.-m.a.s. spectra of UF resin 2.00/1.00/25.0(1) can survive a 120 μs dipolar-dephasing time; therefore, 110 and 118 ppm peaks are assigned to tertiary amides, i.e. crosslinking sites (IIBC, d: 110 ppm) or crosslinking precursor sites (IIA, d: 118 ppm). When a tertiary amide is attached to methylene linkages (II, III) or dimethylene ether linkages (XI), it is a crosslinking site. If a tertiary amide is attached to at least one methylol group (V), it is not a crosslinking site.

Cross-polarization from ^1H to ^{15}N depends on the strength of the ^1H–^{15}N dipolar interaction; the dependence of the cross-polarization rate constant on the inverse sixth power of ^1H–^{15}N internuclear distance[40–45] provides another possible means of distinguishing tertiary amides from primary amides or from secondary amides. The variable-contact-time (VCT) experiment, in which several c.p. contact times are used in a series of ^{15}N c.p.-m.a.s. experiments, is used to determine the cross-polarization rate constant. *Figure 3* shows the ^{15}N c.p.-m.a.s. spectra of UF resin 2.00/1.00/4.96(3) obtained in a variable-contact-time experiment with nine different c.p. contact times ranging from 0.1 to 12 ms. The 110 ppm (IIBC, d) and 118 ppm (IIA, d) peaks in *Figure 3* are assigned to tertiary amides because of the slow build-up of ^{15}N polarization.

Even though the ^1H–^{15}N dipolar-dephasing experiment and variable-contact-time experiment provide direct evidence for the existence of tertiary amides, structural details of these tertiary amides are less obvious in the ^{15}N c.p.-m.a.s. spectra than in the corresponding ^{13}C c.p.-m.a.s. spectra[16,17]. These ^{15}N experiments can provide evidence for the *existence* of tertiary amides, whereas ^{13}C c.p.-m.a.s. spectra can supplement this evidence with better structural details of these tertiary amides. ^{15}N c.p.-m.a.s. spectra (not shown here) of several UF resins prepared under acidic conditions merely confirm the trends observed by ^{13}C c.p.-m.a.s., but without adding structural detail; therefore, chemical shift

Table 1 ^{15}N n.m.r. chemical shifts of some of the most important structural fragments that may exist in the UF resins discussed in this article

Structural fragment[a]	Name of group	Position label	^{15}N chemical shift (ppm)
 $-\overset{\overset{O}{\Vert}}{C}-\overset{c}{N}H-CH_2-\overset{c}{N}H-\overset{\overset{O}{\Vert}}{C}-$	Methylene linkage	Ic	94
 $-\overset{\overset{O}{\Vert}}{C}-\overset{d}{N}(CH_2-R)-CH_2-\overset{e}{N}H-\overset{\overset{O}{\Vert}}{C}-$	Methylene linkage		
A: R ≡ OH	Crosslinking precursor	IIA, d IIA, e	118 94
B:  $R \equiv NH-\overset{\overset{O}{\Vert}}{C}-$	Crosslinking methylene	IIB, d IIB, e	110 94
C:  $R \equiv OCH_2-\underset{\mid}{N}-\overset{\overset{O}{\Vert}}{C}-$	Crosslinking methylene	IIC, d IIC, e	110 94
 $-\overset{\overset{O}{\Vert}}{C}-\overset{c}{N}(CH_2-)-CH_2-\overset{c}{N}(CH_2-)-\overset{\overset{O}{\Vert}}{C}-$	Methylene linkage (crosslinking)	IIIc	110
 $-\overset{\overset{O}{\Vert}}{C}-\overset{c}{N}H-CH_2-OH$	Methylol	IVc	102
 $-\overset{\overset{O}{\Vert}}{C}-\overset{c}{N}(CH_2-R)-CH_2OH$			
A:  $(R = \underset{\mid}{N}-\underset{\underset{O}{\Vert}}{C}- \text{ or } OCH_2-\underset{\mid}{N}-\overset{\overset{O}{\Vert}}{C}-)$	Pendent methylol	VA, c	118
B: R ≡ OH	Geminate methylol	VB, c	118
 $-\overset{\overset{O}{\Vert}}{C}-\overset{e}{N}H-CH_2-O-CH_2-\overset{f}{N}(R)-\overset{\overset{O}{\Vert}}{C}-$ (R ≡ H or -CH$_2$-)	Dimethylene ether linkage	Xe	90
 $-\overset{\overset{O}{\Vert}}{C}-\overset{f}{N}(CH_2-)-CH_2-O-CH_2-\overset{g}{N}(R)-\overset{\overset{O}{\Vert}}{C}-$ (R ≡ H or -CH$_2$-)	Dimethylene ether linkage	XIf	110

[a] Structure indicated by Roman numeral (and, in some cases, upper-case letter, e.g. IIA), position by letter (consistent with earlier papers)[16,17]

details of the ^{15}N c.p.-m.a.s. spectra of UF resins prepared under *acidic* conditions will not be discussed further in this paper.

Another important structural element in UF resins, besides crosslinking, is the existence of unreacted urea sites, i.e. primary amide sites. Because the ^{13}C chemical shifts of carbonyl groups in solid UF resins are quite insensitive to their environment[16,17] (relative to the experimental linewidth) and because of the associated difficulty in determining the peak intensity assigned to a specific type of carbonyl group, it is not possible to detect or to determine the quantity of primary amides by ^{13}C c.p.-m.a.s. *Figure 4* shows the ^{15}N c.p.-m.a.s. spectrum of the solid '*N,N'*-dimethylolurea reagent'. In this spectrum the 10% mole fraction of monomethylolurea in this '*N,N'*-dimethylolurea reagent' is responsible for the roughly 5% intensity at 76 ppm in the spectrum; the intensity of this 76 ppm peak can be used as an indicator of the extent of unreacted amides (primary amides) in a UF resin.

Previous ^{13}C c.p.-m.a.s. studies of UF resins prepared under neutral or basic conditions indicated[16,17] that the main constituents of the reaction mixture are methylols (IV) and dimethylene ether linkages (X). Unfortunately, owing to the residual nuclear electric quadrupolar effect[46-51] of ^{14}N on the ^{13}C spectrum through the ^{13}C–^{14}N dipolar interaction, the ^{13}C c.p.-m.a.s. peaks assigned to methylols (IV) at about 65 ppm and a carbonyl group at 160 ppm show splittings, and the higher-frequency component peak of the methylol multiplet overlaps with the 69 ppm peak assigned to dimethylene ether linkages (X). Hence, in previous studies[16,17] we could only speculate on the influence of pH and reagent concentration on the structures of the UF resin prepared under neutral or basic conditions. *Figure 5* shows the ^{15}N c.p.-m.a.s. spectrum of UF resin 2.00/1.00/25.0(12). In this spectrum, the 102 ppm peak assigned to secondary amides attached to methylols (IVc) is well separated from the 90 ppm peak assigned to secondary amides attached to dimethylene ether linkages (Xe) in the ^{15}N c.p.-m.a.s. spectrum; therefore, ^{15}N c.p.-m.a.s. can be used to quantify the methylols (IV) and dimethylene linkages (X) in a UF resin sample. The 78 ppm peak in the spectrum of *Figure 5* indicates the existence of some unreacted primary amide (*vide supra*).

The reaction mixture leading to resin 1.00/1.00/12.5(9)

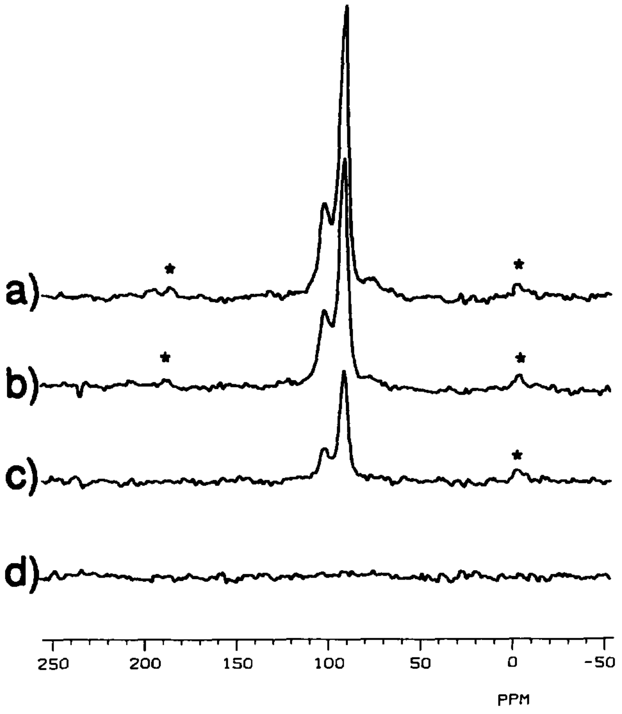


Figure 1 The 20.3 MHz natural-abundance dipolar-dephasing ^{15}N c.p.-m.a.s. n.m.r. spectra of a UF resin prepared with a F/U/W molar ratio of 2.00/1.00/25.0 at pH 12. C.p. contact time = 1 ms; repetition time = 5 s; number of accumulations = 2120. The dipolar-dephasing time is (a) 0 μs, (b) 20 μs, (c) 50 μs, (d) 120 μs. Spinning sidebands are denoted by asterisks

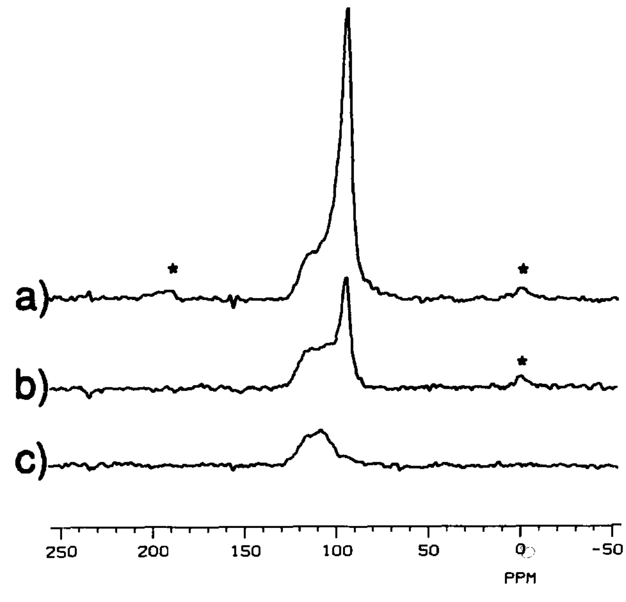


Figure 2 The 20.3 MHz natural-abundance dipolar-dephasing ^{15}N c.p.-m.a.s. n.m.r. spectra of a UF resin prepared with a F/U/W molar ratio of 2.00/1.00/25.0 at pH 1. C.p. contact time = 3 ms; repetition time = 1 s; number of accumulations = 20000. The dipolar-dephasing time is (a) 0 μs, (b) 50 μs, (c) 120 μs. Spinning sidebands are indicated by asterisks

remained a clear solution, even after 12 h at 23°C. The UF resin sample designated 1.00/1.00/12.5(9) was obtained by vacuum drying of the clear solution at pH 9 and $-5°C$. *Figure 6a* indicates that this UF resin has *N,N'*-dimethylolurea (102 ppm)[23] as its major constituent, with some monomethylolurea (102 and 78 ppm)[23] and/or urea (78 ppm)[23] as a minor constituent.

In a different procedure, the reaction mixture with a F/U/W molar ratio of 1.00/1.00/12.5 at pH 9 was neutralized with a 0.1 M aqueous phosphoric acid solution to pH 7 after a 12 h reaction period at 23°C and then vacuum dried at $-5°C$; this solid UF resin is designated 1.00/1.00/12.5(9/7), and its ^{15}N c.p.-m.a.s. spectrum is shown in *Figure 6b*. The main differences between the spectra in *Figures 6a* and *6b* are the smaller relative intensity at 102 ppm and the appearance of peaks at 95 and 90 ppm in *Figure 6b*. During neutralization of the reaction mixture with a F/U/W molar ratio of 1.00/1.00/12.5 from pH 9 to pH 7, some portion of the solution was briefly under acidic conditions; therefore,

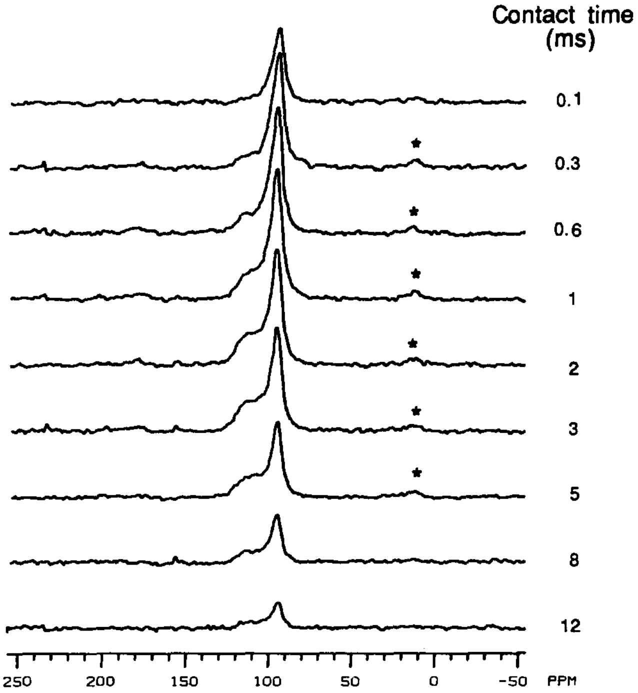


Figure 3 The 20.3 MHz natural-abundance variable-contact-time ^{15}N c.p.-m.a.s. n.m.r. spectra of a UF resin prepared with a F/U/W molar ratio of 2.00/1.00/4.96 at pH 3. C.p. contact times are indicated with spectra. Repetition time = 1 s; number of accumulations = 5000. Spinning sidebands are indicated by asterisks

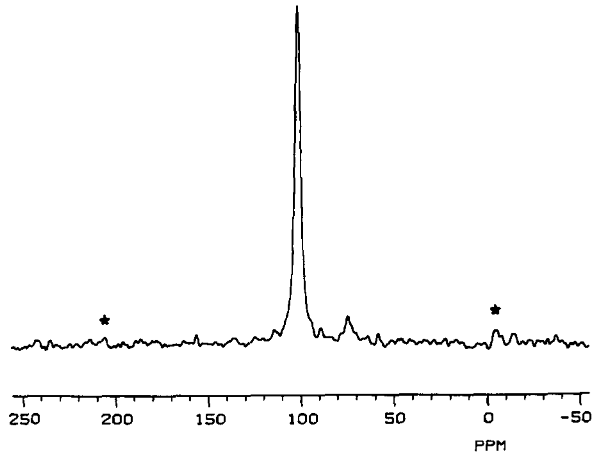


Figure 4 The 20.3 MHz natural-abundance ^{15}N c.p.-m.a.s. n.m.r. spectrum of '*N,N'*-dimethylolurea reagent' (see text). C.p. contact time = 1 ms; repetition time = 30 s; number of accumulations = 1352. Spinning sidebands are indicated by asterisks

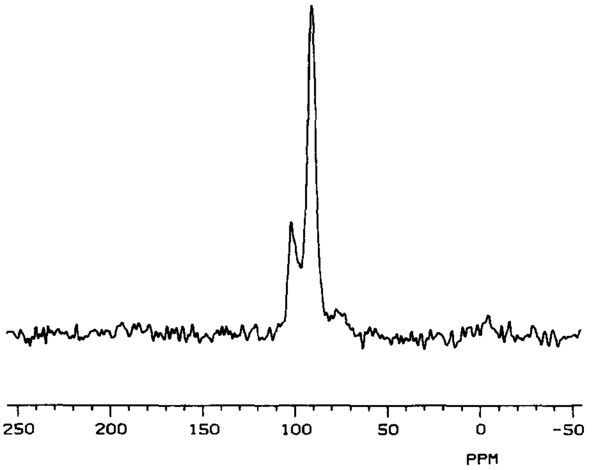


Figure 5 The 20.3 MHz natural-abundance ^{15}N c.p.-m.a.s. n.m.r. spectrum of a UF resin prepared with a F/U/W molar ratio of 2.00/1.00/25.0 at pH 12. C.p. contact time = 1 ms; repetition time = 30 s; number of accumulations = 400

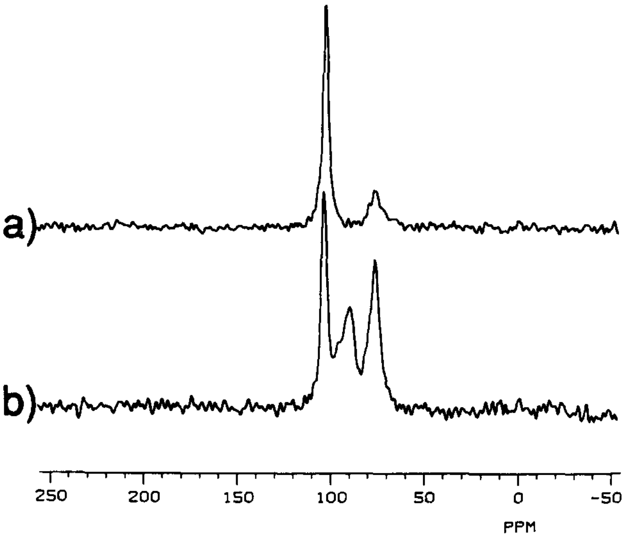


Figure 6 The 20.3 MHz natural-abundance ^{15}N c.p.-m.a.s. n.m.r. spectra of UF resin prepared with a F/U/W molar ratio of 1.00/1.00/12.5 at pH 9. UF resin solids were obtained by: (a) vacuum drying at 10^{-2} Torr and -5°C the clear 1.00/1.00/12.5 solution at pH 9 (1.00/1.00/12.5(9)); (b) vacuum drying at 10^{-2} Torr and -5°C the clear 1.00/1.00/12.5 solution after neutralization to pH 7 (1.00/1.00/12.5(9/7)). C.p. contact time = 1 ms; repetition time = 30 s

formation of methylene linkages (I, as indicated by the 94 ppm peak in the ^{15}N c.p.-m.a.s. spectrum) and dimethylene ether linkages (X, as indicated by the 90 ppm peak in the ^{15}N c.p.-m.a.s. spectrum) apparently occurred in this acidic regime. Furthermore, the formation of dimethylene ether linkages (*vide infra*) is more feasible at pH 7 than at pH 9 during the vacuum drying period. In a previous article[16], we showed that bringing the UF reaction mixture to pH 7 and -5°C did not quench methylolation (equation (1)). The results of *Figure 6* indicate that the neutralization must be executed extremely carefully, if one wishes to avoid the faulty impression that methylene linkages (I) can be formed under neutral or basic conditions.

It is interesting to see what kinds of distribution of methylene linkages (I) and dimethylene ether linkages (X) are in UF resin 1.00/1.00/12.5(9/7). *Figure 7* shows ^{15}N c.p.-m.a.s. spectra of this resin taken at two different repetition rates, 1 s (*Figure 7a*) and 30 s (*Figure 7b*). These two spectra indicate that protons that contribute via cross-polarization to ^{15}N peaks at 90 ppm (site Xe) and 94 ppm (Ic) have about the same T_1^H value ($\sim$2 s), and protons generating cross-polarized ^{15}N magnetization for peaks at 78 ppm (-C(O)NH$_2$) and 102 ppm (IVc) have about the same T_1 value ($\sim$8 s). Clearly, ^{1}H-^{1}H spin diffusion between these two proton sets with different T_1 values is too slow to yield a uniform T_1.

In order to investigate the basis for this inefficient ^{1}H-^{1}H spin diffusion, a previously reported technique[39] was utilized. In this technique (shown in *Figure 8*), a ^{1}H-^{1}H dipolar-dephasing period (2τ) is introduced prior to $^1H \rightarrow {}^{15}N$ c.p. to eliminate magnetization due to protons that experience strong ^{1}H-^{1}H dipolar interactions; the magnetization of those protons with weak ^{1}H-^{1}H dipolar interactions is still available for c.p. *Figure 9* shows the ^{15}N c.p.-m.a.s. spectrum obtained on UF resin 1.00/1.00/12.5(9/7), using a 40 μs ^{1}H-^{1}H dipolar-dephasing period prior to ^{1}H-^{15}N c.p. Obviously, ^{1}H-^{1}H spin diffusion is sufficiently efficient to dephase almost all the ^{1}H polarization during the 40 μs ^{1}H-^{1}H dipolar-dephasing period. Therefore, ^{1}H-^{1}H spin diffusion is efficient *within* each proton set and the cause of the inefficient ^{1}H-^{1}H spin diffusion *between* two proton sets

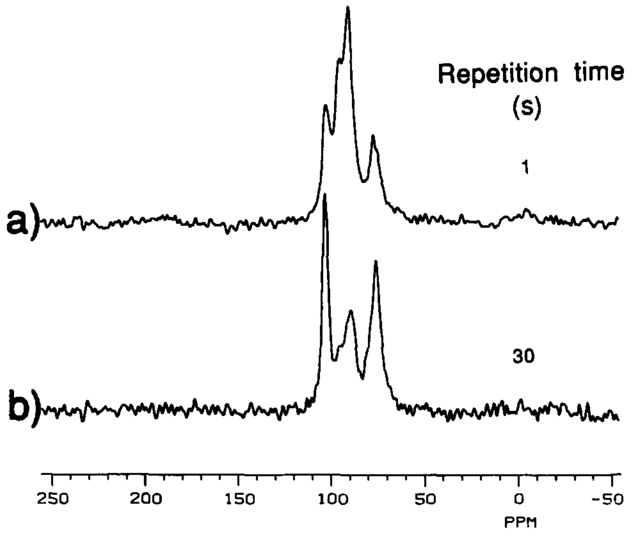


Figure 7 The 20.3 MHz natural-abundance ^{15}N c.p.-m.a.s. n.m.r. spectra of UF resin 1.00/1.00/12.5(9/7) (cf. *Figure 6b*) taken with two different repetition times; (a) 1 s, 83 600 accumulations and (b) 30 s, 2656 accumulations. C.p. contact time = 1 ms

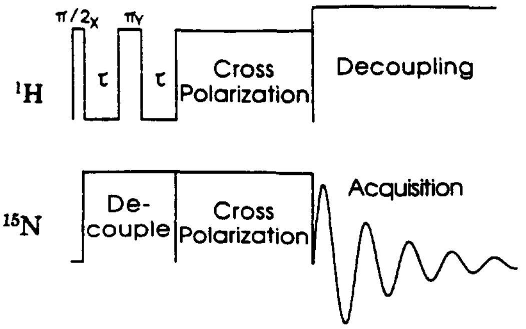


Figure 8 The ^{15}N c.p.-m.a.s. n.m.r. experiment with ^{1}H-^{1}H dipolar dephasing prior to $^1H \rightarrow {}^{15}N$ cross-polarization

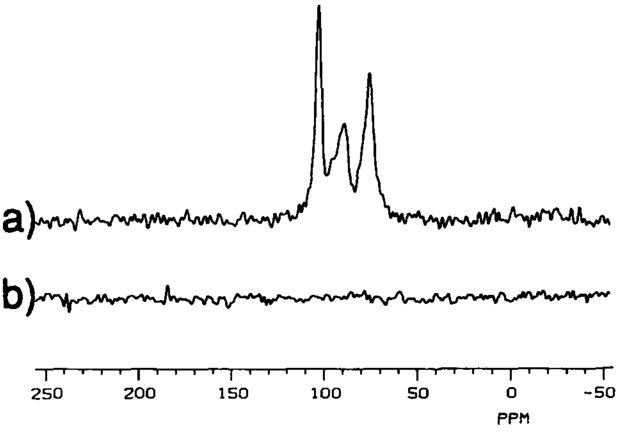


Figure 9 The 20.3 MHz natural-abundance ^{15}N c.p.-m.a.s. n.m.r. spectra of UF resin 1.00/1.00/12.5(9/7): (a) without ^{1}H–^{1}H dipolar dephasing; (b) with a ^{1}H–^{1}H dipolar-dephasing time of 40 μs prior to ^{1}H→^{15}N cross-polarization. C.p. contact time = 1 ms; repetition time = 30 s; number of accumulations = 2656

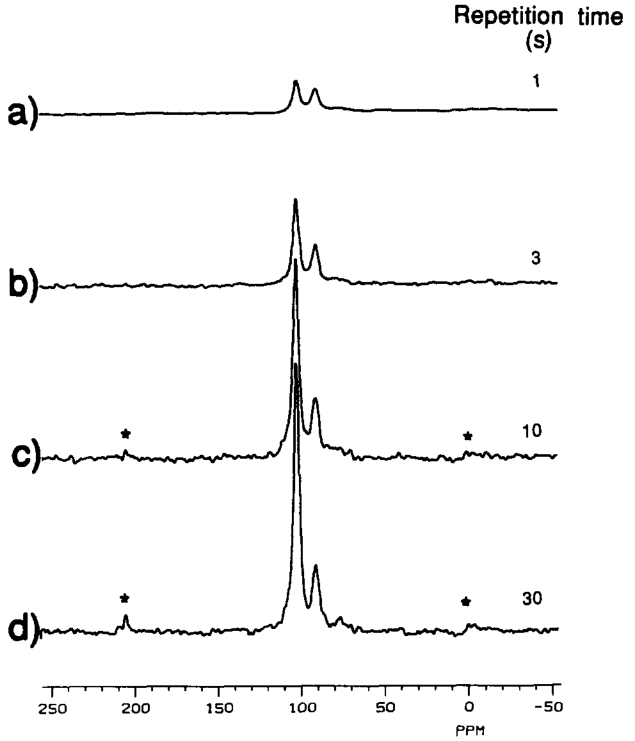


Figure 10 The 20.3 MHz natural-abundance ^{15}N c.p.-m.a.s. n.m.r. spectra of a UF resin prepared with a F/U/W molar ratio of 2.00/1.00/4.96 at pH 7, obtained with four different repetition times: (a) 1 s, 18 600 accumulations; (b) 3 s, 3000 accumulations; (c) 10 s, 1280 accumulations; (d) 30 s, 1280 accumulations. All spectra are scaled to an equivalent number of accumulations (hence, different noise levels). Spinning sidebands are indicated by asterisks

with different T_1 values must be the spatial segregation of methylols (IV) (and/or –C(O)NH$_2$ moieties) from methylene linkages (I) and dimethylene ether linkages (X). From the ^{1}H–^{1}H dipolar-dephasing results described here, we estimate that T_2^H is shorter than 40 μs; with such a small T_2^H value, the ^{1}H–^{1}H spin-diffusion rate should not be affected by m.a.s. at a 2 kHz rate.

According to McBrierty and coworkers[52], the root-mean-square diffusive path length $\langle r^2\rangle^{1/2}$ can be expressed as:

$$\langle r^2\rangle^{1/2}=(6D\tau)^{1/2} \qquad (6)$$

where the spin-diffusion coefficient D for protons is typically 10^{-12} cm^2 s^{-1} and τ is the time over which proton spin diffusion produces a universal relaxation time (e.g. T_1).

The results displayed in *Figure 7* show that the T_1^H values of at least some of the protons responsible for ^{1}H→^{15}N c.p. are 2 s and 8 s. Hence, the τ value for ^{1}H–^{1}H spin diffusion among those protons must be greater than 2 s. With a spin-diffusion rate *between* proton sets with different T_1^H values less than 0.5 s^{-1}, the domain size of methylol aggregates is estimated to be larger than 346 Å.

Figure 10 shows ^{15}N c.p.-m.a.s. spectra of UF resin 2.00/1.00/4.96(7) taken with four different repetition times: 1 s, 3 s, 10 s and 30 s. From these spectra we derived the following rough estimates of T_1^H: 3.5 s for those protons responsible for cross-polarizing ^{15}N nuclei yielding the 90 ppm peak (Xe) and 8 s for those protons responsible for cross-polarizing ^{15}N nuclei of the 102 ppm peak (IVc). Again, spatial segregation of methylols (IV) from dimethylene ether linkages (X) is the cause of this difference in proton T_1 values. Via such differences in T_1^H values, we observed several UF resin samples that display methylol moieties or urea units that are spatially segregated from other components, such as methylene linkages or dimethylene ether linkages. A common spectral feature that is prominent in the ^{15}N c.p.-m.a.s. spectra of all the UF resin samples that display this kind of spatial segregation in T_1^H behavior is strong intensity at 102 ppm, a peak that arises from secondary amides attached to methylols (IV). The cause of this segregation (micro-phase separation) may be the aggregation of methylol-containing resin units, probably because of hydrogen bonding.

Figure 11 presents ^{15}N c.p.-m.a.s. spectra of UF resin 2.00/1.00/25.0(12) obtained with three different repetition times (1 s, 3 s and 5 s). From these spectra, we estimate

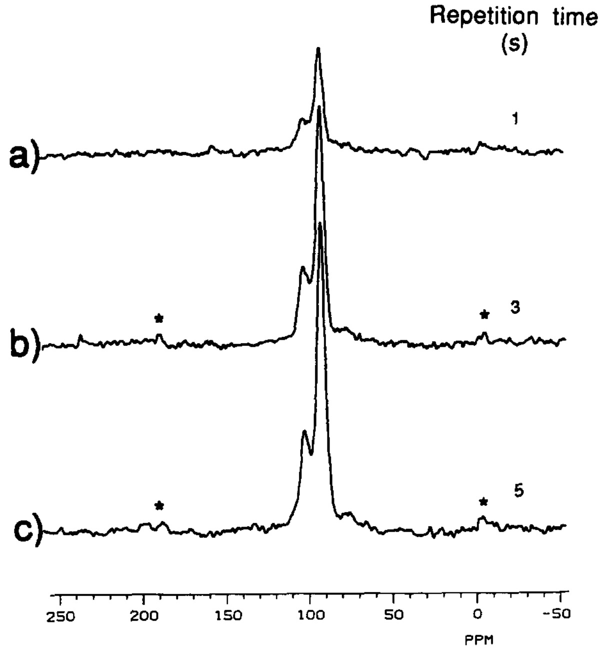


Figure 11 The 20.3 MHz natural-abundance ^{15}N c.p.-m.a.s. n.m.r. spectra of a UF resin prepared with a F/U/W molar ratio of 2.00/1.00/25.0 at pH 12, obtained with three different repetition times: (a) 1 s; (b) 3 s; (c) 5 s. C.p. contact time = 1 ms; number of accumulations = 2120. Spinning sidebands are indicated by asterisks

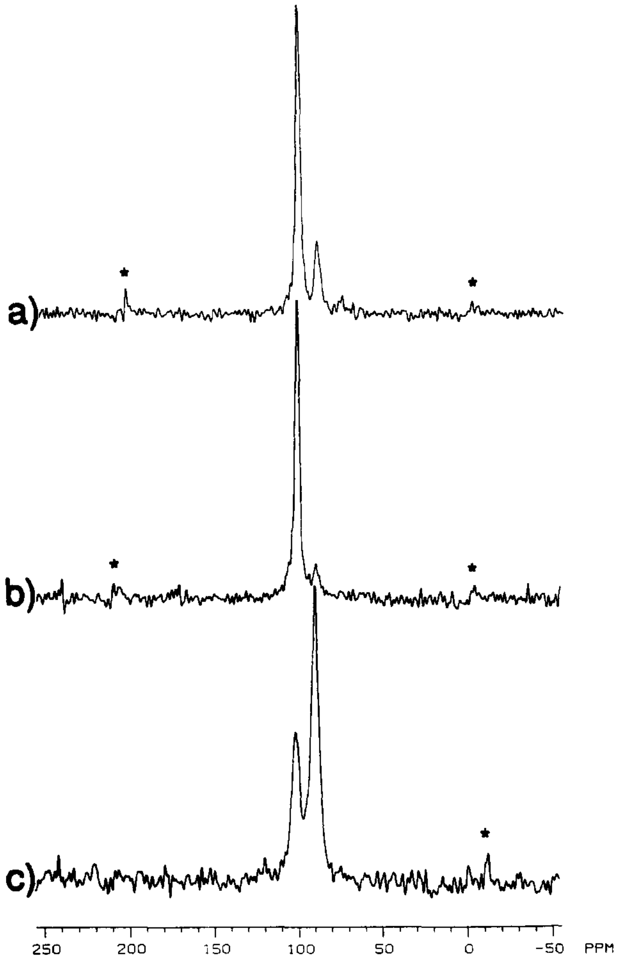


Figure 12 The 20.3 MHz natural-abundance ^{15}N c.p.-m.a.s. n.m.r. spectra of UF resins prepared with a F/U/W molar ratio of 2.00/1.00/4.96 at three different pH values: (a) pH 7; (b) pH 9; (c) pH 12. C.p. contact time = 1 ms; repetition time = 30 s. Spinning sidebands are indicated by asterisks

that T_1^H is 3 s for *all* protons; it can be seen that the *relative* intensities of the 90 ppm (Xe) and 102 ppm (IVc) peaks do not change with repetition times. The domain size of methylol aggregates in UF resin 2/1/25.0(12) is apparently small enough (<245 Å, with a τ value less than 1 s in equation (6)) to have sufficiently effective ^1H–^1H spin diffusion to produce a universal T_1^H value for the entire sample. Thus, when the amount of methylol groups in the resin is smaller, the domain size of methylol aggregates is also smaller. Proton T_1^H values of several UF resins prepared under acidic conditions were measured, and a uniform proton T_1^H *within* each sample was found.

Figure 12 shows ^{15}N c.p.-m.a.s. spectra of UF resin samples 2.00/1.00/4.96(7), 2.00/1.00/4.96(9) and 2.00/1.00/4.96(12) obtained with 30 s repetition times. The proton T_1 value of *N,N'*-dimethylolurea was measured previously[53] via a ^{13}C c.p.-m.a.s. experiment to be 8 s, and it is reasonable to assume that T_1^H values for these UF resins are smaller, because they are generally less rigid and benefit from spin diffusion with protons in relatively mobile segments. Therefore, from the point of view of proton spin–lattice relaxation, we can expect a reliable quantitative relationship between intensities in the ^{15}N c.p.-m.a.s. spectrum obtained with a 30 s repetition time and concentrations in the sample.

Figure 12 indicates that the formation of dimethylene ether linkages (Xe, 90 ppm; Xf (R = H), 90 ppm) is most favourable at pH 12 and least favourable at pH 9, among the three pH values of this study (pH 7, 9, 12). This observation is somewhat different from what was speculated on the basis of previous ^{13}C c.p.-m.a.s. studies[16,17]. In that previous work, it was speculated that the formation of dimethylene ether linkages (X) increases with increasing pH values for these three pH values (7, 9, 12). This discrepancy can probably be attributed to the overlap of peaks arising from dimethylene ether linkages (X) and methylol groups (IV) in the ^{13}C c.p.-m.a.s. spectra[16,17].

Figure 13 presents the ^{15}N c.p.-m.a.s. spectra of UF resins 2.00/1.00/4.96(7) and 2.00/1.00/25.0(7). The conclusion from previous ^{13}C c.p.-m.a.s. studies[16,17] of these resins was that the formation of dimethylene ether linkages (X) increases with reagent dilution under neutral or basic conditions. *Figure 13* and the comparison of *Figures 5* and *12c* confirm that conclusion without question. The reason for this behaviour is presumably that some of the dimethylene ether linkages are formed during the sample-drying (removal of H_2O) period, and the more dilute the solution, the longer it takes to dry, offering more opportunity for the formation of dimethylene ether linkages via equation (4).

CONCLUSIONS

High-quality ^{15}N c.p.-m.a.s. spectra of UF resins can be obtained with ^{15}N in natural abundance if one uses a large-volume m.a.s. rotor. UF resins prepared under acidic conditions contain some crosslinking, and ^{15}N c.p.-m.a.s. spectra can provide direct evidence on the degree of crosslinking or potential crosslinking, and some structural detail by ^1H–^{15}N dipolar-dephasing or

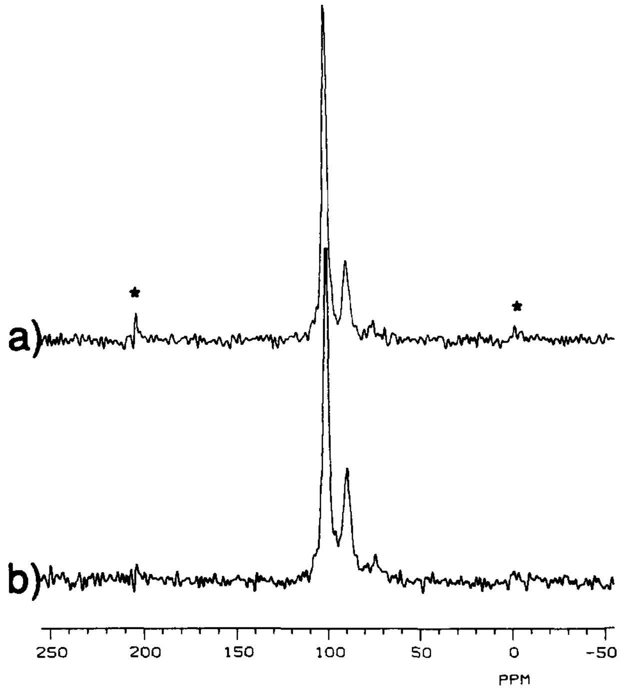


Figure 13 The 20.3 MHz natural-abundance ^{15}N c.p.-m.a.s. n.m.r. spectra of UF resins prepared with (a) F/U/W molar ratio of 2.00/1.00/4.96 and (b) F/U/W molar ratio of 2.00/1.00/25.0 at pH 7. C.p. contact time = 1 ms; repetition time = 30 s. Spinning sidebands are indicated by asterisks

variable-contact-time experiments. However, ^{13}C c.p.-m.a.s. spectra can provide better structural details on these UF resins to supplement the ^{15}N-based information on crosslinking. For UF resins prepared under acidic conditions, ^{15}N c.p.-m.a.s. spectra confirm the occurrence of tertiary amides and confirm the ^{13}C-based relationships between the occurrence of tertiary amides and preparation conditions.

Under neutral or basic conditions, the main constituents of UF resins are *N,N'*-dimethylolurea, monomethylolurea and dimethylene ether linkages. Owing to effects of the ^{14}N nuclear quadrupole interaction on ^{13}C c.p.-m.a.s. spectra, the ^{13}C approach has some limitations in distinguishing among these three types of species. In contrast, ^{15}N c.p.-m.a.s. spectra provide a distinction between methylols and dimethylene ether linkages, while also clearly identifying unreacted primary amides. Because of the clear interpretation possible for ^{15}N c.p.-m.a.s. spectra for UF resins prepared under neutral or basic conditions, we are able to observe aggregation of methylol groups via estimation of ^{1}H–^{1}H spin-diffusion behaviour. The estimated size of methylol aggregates diminishes with a decrease in the methylol concentration in UF resins. The ^{15}N n.m.r. data show that the formation of dimethylene ether linkages is least favourable at pH 9 and most favourable at pH 12, among pH 7, 9 and 12. The formation of dimethylene ether linkages is increased with a decrease in reagent concentrations; presumably some of the dimethylene ether linkages are formed during the final drying period.

ACKNOWLEDGEMENT

We gratefully acknowledge partial support of this research by National Science Foundation Grant No. DMR-8418446.

REFERENCES

1 Meyer, B. 'Urea–Formaldehyde Resins', Addison-Wesley, Reading, MA, 1979

2 de Breet, A. J. J., Dankelman, W., Huysmans, W. G. B. and de Wit, J. *Angew. Makromol. Chem.* 1977, **62**, 7

3 Slonim, I. Y., Alekseyeva, S. G., Urman, Y. G., Arshava, B. M., Aksel'rod, B. Y. and Gurman, I. M. *Polym. Sci. USSR* 1977, **19**, 899

4 Slonim, I. Y., Alekseyeva, S. G., Urman, Y. G., Arshava, B. M., Aksel'rod, B. Y. and Smirnova, L. N. *Polym. Sci. USSR* 1977, **19**, 920

5 Ebdon, J. R. and Heaton, P. E. *Polymer* 1977, **18**, 971

6 Tomita, B. and Hatono, S. *J. Polym. Sci., Polym. Chem. Edn.* 1978, **16**, 2509

7 Slonim, I. Y., Alekseyeva, S. G., Urman, Y. G., Arshava, B. M. and Aksel'rod, B. Y. *Polym. Sci. USSR* 1979, **20**, 1661

8 Slonim, I. Y., Alekseyeva, S. G., Urman, Y. G., Arshava, B. M., Aksel'rod, B. Y., Gurman, I. M. and Smirnova, L. N. *Polym. Sci. USSR* 1979, **20**, 2569

9 Sebenik, A., Osredkar, U., Zigon, M. and Vizovisek, I. *Angew. Makromol. Chem.* 1982, **102**, 81

10 Pasch, H., Dairanieh, I. S. and Al-Tahou, B. *J. Polym. Sci., Polym. Chem. Edn* 1990, **28**, 2049

11 Pasch, H., Hovakeemian, G. and Lahalih, S. *J. Polym. Sci., Polym. Chem. Edn* 1991, **29**, 525

12 Pines, A., Gibby, M. G. and Waugh, J. S. *J. Chem. Phys.* 1973, **59**, 569

13 Andrew, E. R. *Prog. Nucl. Magn. Reson. Spectrosc.* 1972, **8**, Ch. 1

14 Schaefer, J. and Stejskal, E. O. *J. Am. Chem. Soc.* 1976, **98**, 1031

15 Maciel, G. E., Szeverenyi, N. M., Early, T. A. and Myers, G. E. *Macromolecules* 1983, **16**, 598

16 Chuang, I. and Maciel, G. E. *Macromolecules* 1992, **25**, 3204

17 Chuang, I. and Maciel, G. E. *Polymer* in press

18 Jada, S. S. *J. Macromol. Sci.–Chem. (A)* 1990, **27**, 361

19 Chuang, I. and Maciel, G. E. *J. Appl. Polym. Sci.* in press

20 Ripmeester, J. A. *J. Am. Chem. Soc.* 1983, **105**, 2925

21 Maciel, G. E., Haw, J. F., Chuang, I-S., Hawkins, B. L., Early, T. A., McKay, D. Y. and Petrakis, L. *J. Am. Chem. Soc.* 1983, **105**, 5529

22 Haw, J. F., Chuang, I-S., Hawkins, B. L. and Maciel, G. E. *J. Am. Chem. Soc.* 1983, **105**, 7206

23 Chuang, I-S., Hawkins, B. L., Maciel, G. E. and Myers, G. E. *Macromolecules* 1985, **18**, 1482

24 Hatfield, G. R. and Maciel, G. E. *Macromolecules* 1987, **20**, 608

25 Powell, D. G. and Mathias, L. J. *Macromolecules* 1989, **22**, 3812; Powell, D. G. and Mathias, L. J. *J. Am. Chem. Soc.* 1990, **112**, 669; Mathias, L. J., Powell, D. G., Autran, J.-P. and Porter, R. S. *Macromolecules* 1990, **23**, 963

26 Hatfield, G. R., Glans, J. H. and Hammond, W. B. *Macromolecules* 1990, **23**, 1654

27 Lumsden, M. D., Wu, G., Wasylishen, R. E. and Curtis, R. D. *J. Am. Chem. Soc.* 1993, **115**, 2825

28 Opella, S. J., Steward, P. L. and Valentine, K. G. *Q. Rev. Biophys.* 1987, **19**, 7

29 Duff, D. W. and Maciel, G. E. *Macromolecules* 1991, **24**, 387 and 651

30 Witanowski, M., Stefaniak, L. and Webb, G. A. *Annu. Rep. NMR Spectrosc.* 1993, **25**, 1

31 Shoji, A., Ozaki, T., Fujito, T., Deguchi, K. and Ando, I. *Macromolecules* 1987, **20**, 2441

32 Zhang, M. and Maciel, G. E. *Anal. Chem.* 1990, **62**, 633

33 Powell, D. G., Sikes, A. M. and Mathias, L. J. *Polymer* 1991, **32**, 2523; Mathias, L. J., Powell, D. G. and Sikes, A. M. *Polym. Commun.* 1988, **29**, 192; Powell, D. G., Sikes, A. M. and Mathias, L. J. *Macromolecules* 1988, **21**, 1533

34 Zhang, M. and Maciel, G. E. *J. Magn. Reson.* 1989, **85**, 156

35 Chuang, I-S., Maciel, G. E. and Yue, H. unpublished results

36 Opella, S. J. and Frey, M. H. *J. Am. Chem. Soc.* 1979, **101**, 5854

37 Opella, S. J., Frey, M. H. and Cross, T. A. *J. Am. Chem. Soc.* 1979, **101**, 5856

38 Alemany, L. B., Grant, D. M., Alger, T. D. and Pugmire, R. J. *J. Am. Chem. Soc.* 1983, **105**, 6697

39 Chuang, I-S., Kinney, D. R., Bronnimann, C. E., Zeigler, R. C. and Maciel, G. E. *J. Phys. Chem.* 1992, **96**, 4027

40 Zumbulyadis, N. and O'Reilly, J. M. *Macromolecules* 1991, **24**, 5294

41 Mehring, M. 'Principles of High Resolution NMR in Solids', 2nd Edn, Springer-Verlag, New York, 1983

42 Levitt, M. H., Suter, D. and Ernst, R. R. *J. Chem. Phys.* 1986, **84**, 4243

43 Demco, D. E., Tegenfeldt, J. and Waugh, J. S. *Phys. Rev. (B)* 1975, **11**, 4133

44 Klein Douwel, C. H., Maas, W. E. J. R., Veeman, W. S., Buning, G. H. W. and Vankan, J. M. J. *Macromolecules* 1990, **23**, 406

45 Eijkelenboom, A. P. A. M., Maas, W. E. J. R., Veeman, W. S., Buning, G. H. W. and Vankan, J. M. J. *Macromolecules* 1992, **25**, 4511

46 Zumbulyadis, N., Henrichs, P. M. and Young, R. H. *J. Chem. Phys.* 1981, **75**, 1603

47 Naito, A., Ganapathy, S. and McDowell, C. A. *J. Chem. Phys.* 1981, **74**, 5393

48 Hexem, J. G., Frey, M. H. and Opella, S. J. *J. Am. Chem. Soc.* 1981, **103**, 224

49 Harris, R. K., Jonsen, P., Packer, K. J. and Campbell, C. *Magn. Reson. Chem.* 1986, **24**, 977

50 Olivier, A. C., Frydman, L. and Diaz, L. E. *J. Magn. Reson.* 1987, **75**, 50

51 Harris, R. K. and Olivieri, A. C. *Prog. Nucl. Magn. Reson. Spectrosc.* 1992, **24**, 435

52 McBrierty, V. J. *Faraday Disc. Chem. Soc.* 1979, **68**, 78; Albert, B., Jerome, R., Teyssie, P., Symth, G. and McBrierty, V. J. *Macromolecules* 1984, **17**, 2552

53 Maciel, G. E. and Chuang, I. unpublished results