Characterization of urea–formaldehyde and melamine–formaldehyde adducts and resins by ^{15}N n.m.r. spectroscopy

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^{15}N n.m.r. spectra have been recorded for some urea–formaldehyde and some melamine–formaldehyde adducts and resins. For the urea–formaldehyde system, the technique can be used to distinguish between unsubstituted amino groups, secondary and tertiary amino groups carrying methyol substituents, and secondary and tertiary amino groups involved in methylene and methylene ether linkages. For the melamine–formaldehyde system, additional information is available from the aromatic azine nitrogen signals. The information available from ^{15}N n.m.r. spectra supports and augments that from ^{13}C and ^{1}H spectra.

(Keywords: urea; melamine; formaldehyde; adducts; resins; ^{15}N nuclear magnetic resonance)

INTRODUCTION

Many reports have now appeared concerning the use of ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy to characterize urea–formaldehyde and melamine–formaldehyde adducts and resins; both qualitatively and quantitively[1-8]. With the aid of this technique, information may be obtained for example about amine–formaldehyde ratios; the proportions of formaldehyde incorporated as methylol groups; methylene linkages and methylene ether linkages; and extents of branching. Most recently, ^{13}C n.m.r. has been used to examine cured aminoresins[9]. However, to date there have been no reports of the use of ^{15}N n.m.r. to characterize aminoresins, although this technique has been shown to be of use in providing information about the chemical microstructures of polypeptides and polyamides[10]; polyureas[11]; polyurethanes[12]; and a variety of biopolymers[13]. In part, the reluctance to employ the ^{15}N n.m.r. technique more widely has arisen from the low natural abundance (0.4%) and the low magnetogyric ratio of ^{15}N which combine to give this nucleus a low receptivity. However, with the aid of modern Fourier–transform and signal enhancement techniques, it is now possible to obtain well-resolved ^{15}N n.m.r. spectra on samples which contain only natural levels of ^{15}N in a matter of a few hours. In this paper we report the results of the spectral examinations of some urea–formaldehyde and melamine–formaldehyde adducts, and uncured resins using ^{15}N n.m.r.

The chemistry of aminoresin formation

The fundamental chemistry of aminoresin formation has been described elsewhere[14]. Formaldehyde (F), in aqueous solutions, over a range of pHs, and at ambient temperatures, will add to urea (U) and to melamine (2,4,6-triaminotriazine) (M) to give mixtures of methylolureas and methylolmelamines. If these mixtures are made acidic and/or are heated, then condensation takes place with the formation of methylene and methylene ether linkages. As the reaction continues, the product becomes more branched and ultimately will gel and irreversibly cross-link. Aminoresins are still widely employed as moulding materials, adhesives, laminates and surface coatings.

EXPERIMENTAL

Preparation of U–F adducts and resins

Monomethylolurea (**I**), *N,N'*-dimethylolurea (**II**) and methylenediurea (**III**) were prepared by the methods of Ludlam[15] and after separation were found to have purities of 90%, 95% and 75% respectively by ^{1}H n.m.r. *N,N'*-dimethyloloxymethylenediurea (**IV**) was prepared by adding **II** (10 g) to a solution of potassium carbonate (0.33 g) in 33 cm^3 of deionized water. This solution was allowed to stand for three weeks after which time the final white precipitate was filtered off and washed with deionised water and dried in a vacuum oven at room temperature. A crude sample of *N,N,N'*-trimethylolurea (**V**) was prepared by reacting a 1:4 mixture of urea and formaldehyde under conditions similar to those used for the preparation of mono- and *N,N'*-dimethylolureas[16].

Low molecular weight U–F resins were prepared by adding known weights of urea to 44% aqueous formaldehyde (formalin) at pH 9.5 (adjusted with 2N NaOH). The mixtures were heated at 100°C and stirred for various lengths of time. Samples were then cooled in an ice-water bath and freeze-dried.

Preparation of M–F adducts and resins

M–F adduct mixtures (**VI**) were prepared by reacting melamine with formaldehyde in aqueous solutions at pH

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I $H_2N-CO-NHCH_2OH$

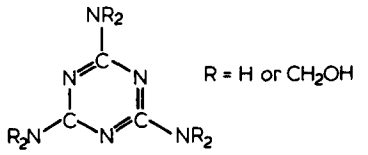
II $HOCH_2NH-CO-NHCH_2OH$

III $H_2N-CO-NH-CH_2-NH-CO-NH_2$

IV $HOCH_2NH-CO-NH-CH_2OCH_2-NH-CO-NHCH_2OH$

V $HOCH_2NH-CO-N(CH_2OH)_2$

VI



9.5. The mixtures were heated with stirring at 70°C for times between 10 min and 4 h until all the melamine had dissolved. After cooling, the resulting white precipitates were filtered off and dried by heating in air at 40°C for 1–2 days. M-F resins were prepared in a manner similar to that used for the adduct mixtures but with heating at 100°C.

^{15}N n.m.r. spectroscopy

^{15}N n.m.r. spectra of adducts, adduct mixtures and resins were recorded on solutions in d_6-DMSO (20% w/v) using a Joel FX100 Fourier transform n.m.r. spectrometer fitted with a multinuclear probe (10.09 MHz for ^{15}N) operating at an ambient temperature of 28°C. Spectra were recorded over a spectral width of 5000 Hz (495 ppm) with a pulse width of 10 μs (corresponding to a nuclear tip angle of 30°). For spectra of reasonable signal-to-noise (S/N) ratio, approximately 20 000 pulses were recorded with an acquisition time of 0.5 s for each accumulation. Resin samples required 48–72 h measurement periods. Coupling of ^{15}N nuclei to neighbouring protons was removed with broadband irradiation. The nuclear Overhauser enhancement was retained to improve the S/N ratio. Spectra were referenced with respect to an external standard consisting of the NH_4^+ ion in a solution of ammonium nitrate (in d_6-DMSO). To aid interpretation, the spectra were phased to produce the maximum number of positive signals producing a straight baseline. The negative magnetogyric ratio of ^{15}N produces true netative peaks except where nuclear Overhauser enhancements (n.O.e.) are particular small. Small n.O.e. values can result in reductions of signal size or even produce resonances of zero intensity.

RESULTS AND DISCUSSION

Spectra of U–F adducts and resins

The ^{15}N spectrum of urea consists of a single peak at 55.6 ppm (*Figure 1a*), while that of monomethylolurea shows two peaks, one at 55.6 ppm and another at 80.4 ppm (*Figure 1b*). The former peak is thus assigned to the unsubstituted primary amino nitrogen and the latter to the methylol-substituted secondary amino nitrogen. A peak at 80.2 ppm is the sole signal in the spectrum of *N,N'*-dimethylolurea (*Figure 1c*) and is attributed to the methylol-substituted secondary amino nitrogen. In the spectrum of the crude *N,N,N'*-trimethylolurea (*Figure 1d*), a signal characteristic of a dimethylol-substituted tertiary amino nitrogen is seen at 101.6 ppm amongst others.

The spectrum obtained from the methylenediurea

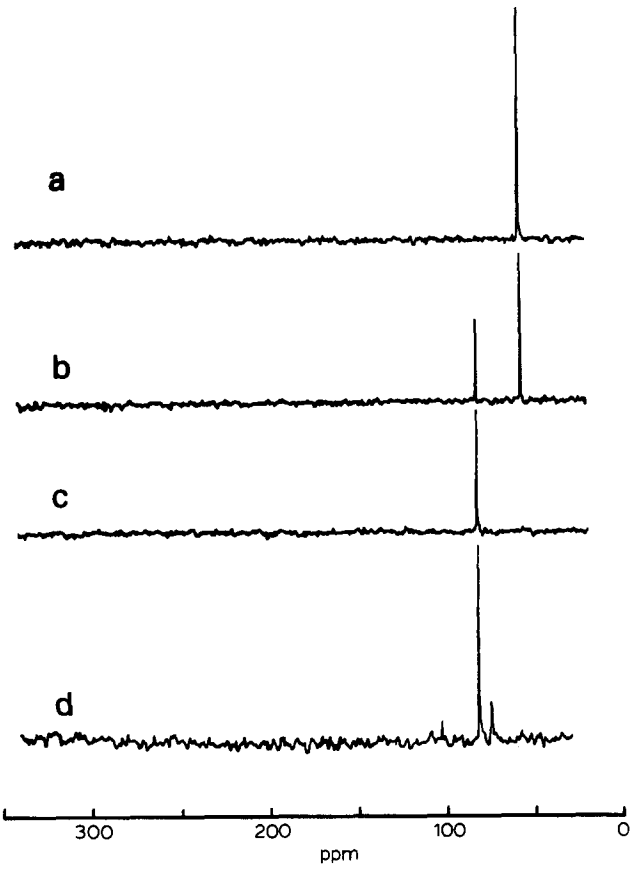


Figure 1 ^{15}N n.m.r. spectra of (a) urea, (b) monomethylolurea, (c) *N,N'*-dimethylolurea and (d) crude *N,N,N'*-trimethylolurea

shows three signals (*Figure 2a*) rather than the expected two. The peak at 54.0 ppm is readily assigned to the unsubstituted primary amino nitrogen while that at 73.2 ppm is assigned to secondary amino nitrogens attached to methylene linkages. The small peak at around 55 ppm probably arises from the primary amino nitrogens of residual urea. In the spectrum of *N,N'*-dimethyloloxymethylenediurea, the most significant peaks are those at around 72 ppm, containing two main components. The larger of these at 72.6 ppm is assigned to secondary amino nitrogens attached to ether linkages in the intended compound, whilst that at 72.1 ppm is assigned to similar nitrogens within higher oligomers. The presence of four peaks at around 80 ppm in *Figure 2b* indicates the presence in this sample also of at least four slightly different types of monomethylol amino groups. It is thought that these correspond to the monomethylol amino groups in various methylolureas and at the chain-ends of oligomers, as well as to those in *N,N'*-dimethylol-oxymethylenediurea. Additional components were shown to be present in the impure *N,N'*-dimethyloloxymethyl-enediurea by ^{13}C n.m.r. spectroscopy.

These assignments may now be used in the interpretation of the ^{15}N n.m.r. spectra of low molecular weight U–F resins. *Figure 3a* shows the ^{15}N n.m.r. spectrum obtained from a U–F resin preparation (1:1 F/U ratio) after 15 min reaction, and *Figure 3b* shows that obtained from the same preparation after 1 h. Three main groups of resonances are visible in both spectra although the relative intensities of the components of these groups differ. The group at around 55 ppm, containing three principal components at 55.3, 54.8 and 54.2 ppm respectively, arise from primary amino nitrogens in urea,

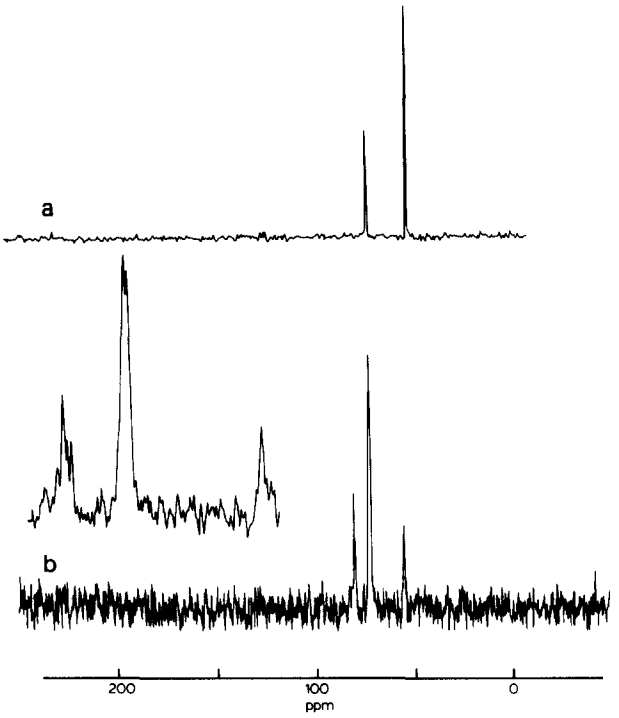


Figure 2 ^{15}N n.m.r. spectra (with expansions) of (a) methylenediurea and (b) *N,N'*-dimethyloloxymethylenediurea

monomethylolurea, dimeric species such as methylenediurea, and endgroups of oligomers. It is noticeable that this group as a whole becomes smaller (relative to the major group) as the reaction time increases; and that the 55.3 ppm component (attributable to urea and monomethylolurea) is the most reduced. Therefore, this group of peaks alone provides evidence of increasing chain extension. The group of peaks at around 80 ppm (containing principal components at 80.3, 79.8 and 79.2 ppm), is attributable to methylol-substituted secondary amino nitrogens in monomethylolurea; *N,N'*-dimethylolurea; dimeric compounds such as *N,N'*-dimethylolmethylenediurea, and methylolated endgroups of oligomers. This group is also reduced in size relative to the main group as the reaction proceeds. Evidence of chain extension is visible in this group too through changes in the relative sizes of the components; in *Figure 3a* the 80.3 ppm component is the largest, whilst in *Figure 3b* it is the component at 79.8 ppm. The major group of resonances at around 72 ppm, which contain principal components at 73.5, 73.0 and 72.4 ppm and which are attributable to secondary amino nitrogens adjacent to methylene and methylene ether linkages, is a direct measure of chain extension and, as expected, this group increases in size relative to the others as the reaction proceeds. In view of the assignments made earlier for methylenediurea and for *N,N'*-dimethyloloxymethylenediurea, it is likely that the lowest field component of this group is an indication of methylene linkages in dimeric compounds such as methylenediurea, whilst the highest field component is an indication of methylene ether linkages in similar dimers. The central component at 73.0 ppm probably arises from secondary amino nitrogens adjacent to methylene linkages within higher oligomers. Both methylene ether and methylene linkages can be seen in this type of resin by ^{13}C n.m.r.[2,17] and as the reaction proceeds, methylene linkages tend to increase in number, at the expense of ether linkages. This growth in relative importance of methylene linkages is reflected in the changes in the relative intensities of the nitrogen signals at around 72 ppm between the spectrum recorded after 15 min reaction and that recorded after 1 h reaction. There is no group of resonances at around 100 ppm (indicating an absence of dimethylol-substituted tertiary nitrogens) nor any peaks at around 93 ppm. Peaks at around 93 ppm would be expected for tertiary nitrogens attached to methylene or methylene ether linkages, since the conversion of a methylol group to a linkage, appears to move the resonance of the attached nitrogen upfield by about 7 ppm. (For secondary nitrogens, the change is from around 80 ppm to around 73 ppm.) A virtual absence of chain branching in low molecular weight resins under the conditions described here (low F/U ratio) has been demonstrated before by ^{13}C n.m.r. spectroscopy[17]. The complete set of ^{15}N assignments for the U–F system is given in *Table 1*.

Spectra of M–F adducts and resins

The ^{15}N spectrum of melamine is shown in *Figure 4a* and that for a mixture of M–F adducts prepared from a 1.5:1 F/M ratio in *Figure 4b*. For melamine, the peak at 60.7 ppm is assigned to the primary amino nitrogens and that at 153.6 ppm to the azine ring nitrogens; the small

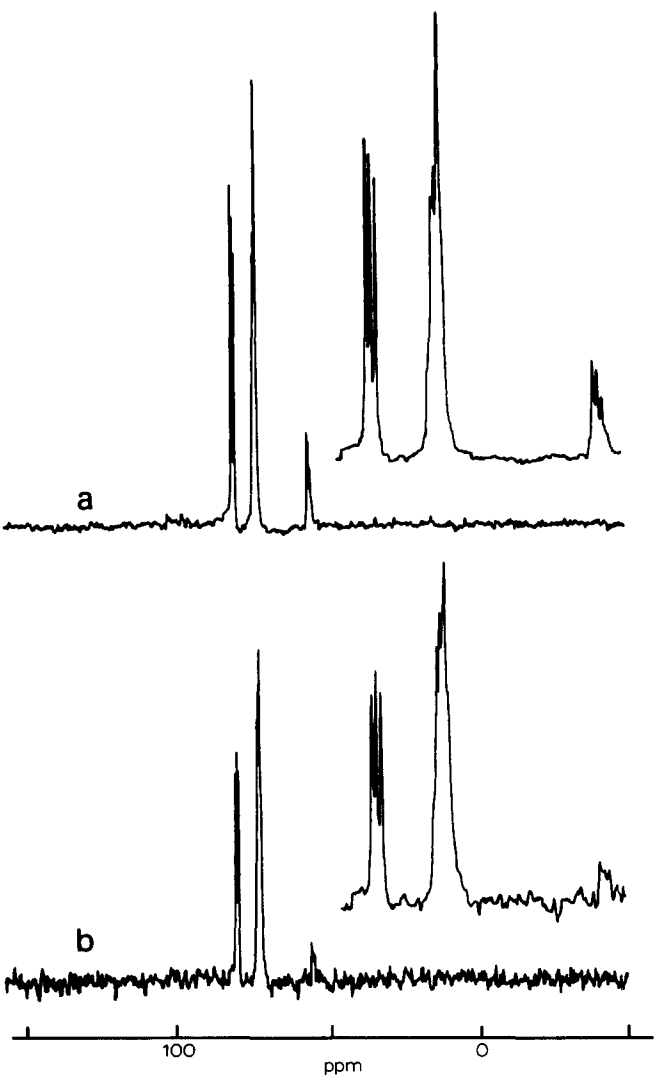


Figure 3 ^{15}N n.m.r. spectra (with expansions) of a U–F resin sample made with a 1:1 F/U ratio (a) after 15 min reaction and (b) after 1 h reaction

Table 1 ^{15}N assignments for the U–F system

Assignment	Compound	Chemical shift* (ppm)
$\underline{N}H_2CO\underline{N}H_2$	Urea	55.6
$\underline{N}H_2CO\underline{N}HCH_2OH$	Monomethylolurea	55.3
$\underline{N}H_2CONH-$	Methylenediurea and chain ends	54.2, 54.8
$HOCH_2\underline{N}HCONH_2$	Monomethylolurea	80.4
$HOCH_2\underline{N}HCO\underline{N}HCH_2OH$	N,N'-dimethylolurea	80.2
$HOCH_2\underline{N}HCO\underline{N}H-$	Chain ends	79.2, 79.8
$(HOCH_2)_2\underline{N}CONHCH_2OH$	Trimethylolurea	101.6
$NH_2CONHCH_2\underline{N}HCONH_2$	Methylenediurea and other dimers	73.2, 73.5
$-\underline{N}HCH_2\underline{N}H-$	Within chains	73.0
$-\underline{N}HCH_2O\underline{C}H_2\underline{N}H-$	Ether linked dimers	72.6
$>\underline{N}-CH_2(-O\underline{C}H_2-)$ or $(-N<)$	Branch points in chains	~93 (predicted)

* Relative to NH_4^+ and ±0.1

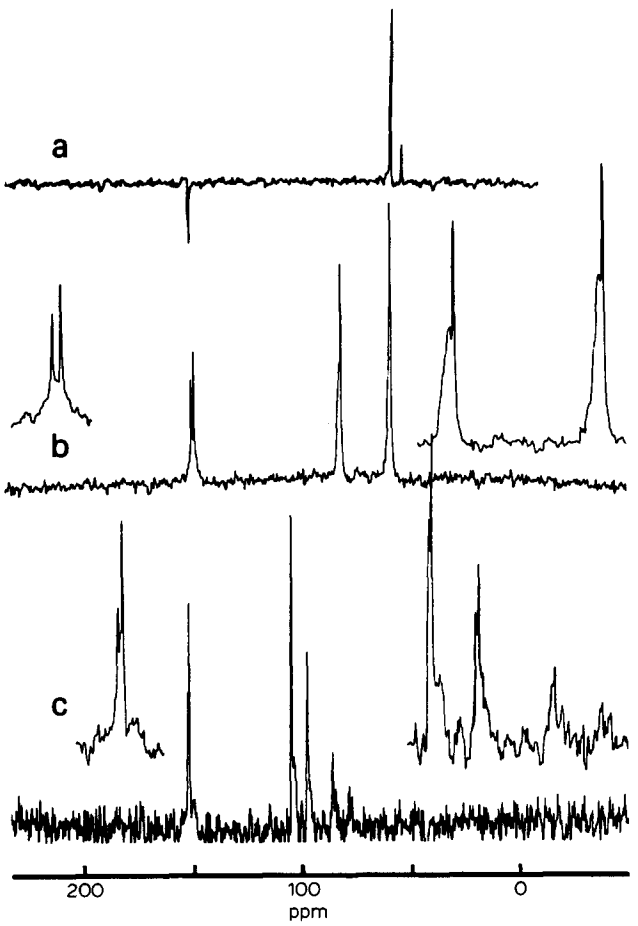


Figure 4 ^{15}N n.m.r. spectra (with expansions) of (a) melamine, (b) an M/F adduct mixture made with F/M=1.5:1 and (c) an M/F adduct mixture made with F/M=10:1

peak at 55.4 ppm arises from a minor urea impurity. In the spectrum of the adduct mixture, an additional group of peaks is seen at around 84 ppm containing a major sharp component at 83.9 ppm. This group together is assigned to methylol-substituted secondary amino nitrogens and it is thought that the major component arises from monomethylolmelamine; the other components must then arise from polymethylol melamines. Within the grouping at around 60 ppm, the major component at 60.8 ppm arises from unreacted melamine whilst the remainder arises from the unsubstituted amino nitrogens in compounds such as mono-, *N,N'*-di- and *N,N,N'*-trimethylolmelamine. The new peak at 152.3 ppm is assigned to azine nitrogens in methylolmelamines. This peak is particularly pronounced in the spectrum of the adduct mixture made with an F/M ratio of 10:1 (*Figure 4c*) where a higher degree of methylolation is expected. Also in *Figure 4c* are new groups of peaks at around 107, 98 and 77 ppm respectively. The first of these is assigned to dimethylol-substituted tertiary amino nitrogens and the others, which are not expected for mixtures of simple adducts, are assigned (by analogy with peak patterns for the U–F system) to tertiary and secondary amino nitrogens adjacent to methylene and methylene ether linkages. The formation of linkages in this adduct mixture was probably mainly a consequence of the high F/M ratio.

Figures 5a and *5b* show the ^{15}N spectra of two M–F resin samples taken from a resin preparation after 15 min and 45 min respectively, in which the initial F/M ratio was 2.3:1. Points to note are (i) the growth in importance of linkages as the reaction proceeds (peaks at around 77 ppm), (ii) changes in the patterns of peaks within the groups at around 60 and 84 ppm indicating changes in patterns of substitution and (iii) the absence of dimethylol substituted tertiary nitrogens and chain branching (absence of peaks at around 107 and 98 ppm respectively). Complete ^{15}N assignments for the M–F system are given in *Table 2*.

Comparisons of the ^{15}N *spectra of* U–F, M–F *and other systems*

As can be seen from the discussion above, in the U–F system, the addition of a single methylol group to an amino group produces a downfield shift in the resonance of the amino nitrogen of about 24 ppm (~56 ppm to ~80 ppm). The addition of a further methylol group produces a downfield shift of a further 22 ppm (~80 ppm to ~102 ppm). Very similar movements are seen within the M–F spectra (~61 ppm to ~84 ppm and ~84 ppm to ~107 ppm respectively). For both systems, the conversion of a methylol group to either a methylene or a methylene ether linkage produces an upfield shift in the resonance of the attached nitrogen of about 7–8 ppm. In the U–F system, and by implication in the M–F system also, nitrogens attached to methylene ether linkages resonate upfield from similar nitrogens attached to methylene linkages by just under 1 ppm. In addition to these marked effects there are also some more minor effects on the positions of nitrogen resonances produced by the natures of the substituents (if there are any) attached to the geminal nitrogen, i.e. the chemical shift of nitrogen A in **VII** below is principally determined by the nature of substituent A, but to a lesser extent also by the nature of substituent B. Simiarly, the chemical shift of nitrogen B is influenced to a slight extent by the nature of substituent A. It is these

Table 2 ^{15}N assignments for the M–F system

Assignment	Compound	Chemical shift* (ppm)
$\underline{N}H_2-$	Melamine	60.7
$\underline{N}H_2-$	Methylolmelamines	~61–63
$HOCH_2\underline{N}H-$	Monomethylolmelamine	83.9
$HOCH_2\underline{N}H-$	Other methylolmelamines	~84–86
$(HOCH_2)_2\underline{N}-$	Polymethylolmelamines	~107
$-\underline{N}HCH_2(-OCH_2-)$ or (–N<)	Linear ether and methylene links	~77
$>\underline{N}CH_2(-OCH_2-)$ or (–N<)	Branched ether and methylene links	~98
$-\underline{C}=N-C=$	Melamine	153.6
$-C=\underline{N}-C=$	Methylolmelamines	152.3

* Relative to NH_4^+ and ±0.1

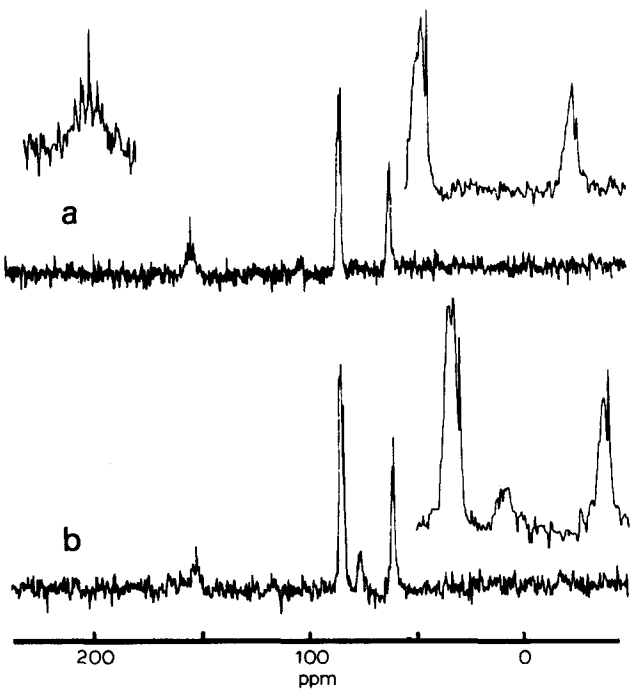


Figure 5 ^{15}N n.m.r. spectra (with expansions) of an M–F resin sample made with a 2.3:1 F/M ratio (a) after 15 min reaction and (b) after 45 min reaction

VII $A-N_AH-CO-N_BH-B$

neighbouring group effects, which are identical in origin (but smaller in size) to those described before for homo- and co-polyureas prepared from diamines and diisocyanates[11], that promise to be particularly useful in elucidating the structures of aminoresins by ^{15}N n.m.r. spectroscopy. Thus, for the U–F system, it is possible to distinguish between methylene linkages near chain ends (nitrogen resonance at about 73.5 ppm) from those within the chain (nitrogen resonance at about 73 ppm). By ^{13}C spectroscopy, it is only possible to distinguish between linear and branched methylene linked sequences; the spectra give no direct information about the lengths of these sequences. For suitable resins, information about the lengths of methylene ether sequences should also be obtainable from ^{15}N spectra. Better resolved spectra will also allow a more complete analysis of M–F resins.

CONCLUSIONS

It has been shown that ^{15}N n.m.r. spectroscopy can be advantageously applied to the analysis of aminoresins. Much of the information available concerning relative proportions of methylol groups, methylene linkages and methylene ether linkages can be obtained more readily from ^{13}C spectra, and to a lesser extent from ^{1}H spectra. However, ^{15}N spectroscopy promises to be particularly useful in determining sequence lengths. We are currently fractionating aminoresins by preparative scale HPLC and characterizing the fractions by very high field ^{15}N and ^{13}C n.m.r. spectroscopy in order to better understand the chemical shift patterns and to develop more modern methods of aminoresin analysis. We shall be reporting on some of this further work shortly.

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