of sodium poly(L-glutamate) in 90 vol % ethylene glycol. In order to fit this plot to equations (1) and (2), a value of n as small as unity has to be selected. The solid curve in this Figure is a theoretical curve with $n = 1$ obtained by assigning appropriate values to the two parameters, $2\pi(g_1 - g)/\bar{n}\rho\lambda$ and $zeL/2kT$. The agreement between theory and experiment is fairly good. However, such a small value of n is unrealistic. We must take into account the counterion–counterion repulsion to get rid of this difficulty.

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Characterization of urea–formaldehyde adducts and resins by ^{13}C-n.m.r. spectroscopy

Introduction

Despite the continuing development of new polymeric materials, well-established thermosetting resins such as urea–formaldehyde, melamine–formaldehyde and phenol–formaldehyde resins continue to enjoy widespread use as moulding compounds, surface coatings, adhesives and in laminates. Phenol–formaldehyde resins have been extensively studied, but urea–formaldehyde and melamine–formaldehyde systems have been less well characterized although the classical work of de Jong and de Jonge[1] has helped to elucidate the nature of the reactions that occur in the early stages of resin formation. Urea–formaldehyde adducts and resins have also been characterized by infrared spectroscopy[2,3], chromatographic techniques[4–6] and more recently, by proton magentic resonance[7–9].

This paper describes some preliminary results of a study of some urea–formaldehyde adducts and resins using ^{13}C-n.m.r. spectroscopy and represents, as far as we are aware, the first reported application of this technique to the urea–formaldehyde system.

Chemistry of urea-formaldehyde resin formation

The chemistry of urea–formaldehyde resin formation has been discussed in some detail by Vale and Taylor[10]. The formation of low molecular weight resins is believed to occur via the prior formation of methylolureas followed by condensation of these to give short linear and branched chains containing ether and methylene linkages. The more important reactions are indicated below:

$$NH_2CONH_2 + HCHO \rightarrow NH_2CONHCH_2OH$$

monomethylolurea

$$NH_2CONHCH_2OH + HCHO \rightarrow HOCH_2NHCONHCH_2OH$$

N,N'-dimethylolurea

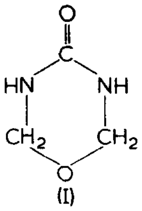
$$\sim\!\sim NH_2 + HOCH_2NH\!\sim\!\sim \rightarrow \sim\!\sim NHCH_2NH\!\sim\!\sim$$

methylene linkage

$$\sim\!\sim NHCH_2OH + HOCH_2NH\!\sim\!\sim \rightarrow \sim\!\sim NHCH_2OCH_2NH\!\sim\!\sim$$

ether linkage

Other products which have been identified in urea–formaldehyde systems include *N,N*-dimethylolurea [$NH_2CON(CH_2OH)_2$], trimethylolurea [$HOCH_2NHCON(CH_2OH)_2$] and uron (I) and its derivatives:


(I)

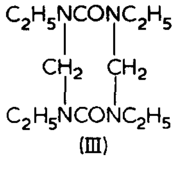
Experimental

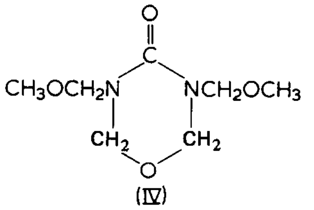
Materials. Aqueous formaldehyde solutions (formalin) were freshly prepared (and thus contained no methanol) by heating paraformaldehyde in a stream of nitrogen and passing this gas stream into distilled water (or D_2O) at ~25°C. The formaldehyde contents of the resulting solutions (normally 30 % w/w) were determined by iodometry[11]. 'Analar' grade urea was used without further purification.

Preparation of model compounds. The following model compounds were prepared as apparently pure crystalline compounds by literature methods: monomethylolurea[12], *N,N'*-dimethylolurea[12], methylene diurea[12], dimethyloloxymethylene diurea (II)[13], the monomethylether of monomethylolurea[14], the dimethylether of dimethylolurea[14], tetraethyldimethylene diureid (III)[14], uron[15] and the dimethylether of dimethyloluron (IV)[14]:

$$HOCH_2NHCONHCH_2OCH_2NHCONHCH_2OH$$

(II)


(III)



(IV)

The purity of these compounds was established by the usual methods (m.p., i.r. spectra, p.m.r. spectra etc.)

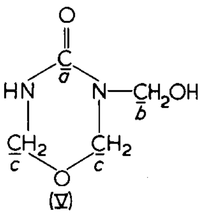
A crude sample of trimethylolurea was prepared following essentially the method proposed by Tomita and Hirose[8] from a 4:1 mixture of formaldehyde and urea at pH 11 (heated for 10 min at 80°C).

Preparation of low molecular weight resins. Low molecular weight urea–formaldehyde resins were prepared by heating aqueous solutions of formaldehyde (F) and urea (U) (molar ratio F:U = 2–2.5, total solids content 60 %w/w) under reflux for up to 5 h at neutral or slightly basic pH (in the presence of the appropriate buffer). In some experiments, samples were withdrawn at intervals from the resin flask and allowed to cool. In the early withdrawals a solid separated on cooling. These solids were filtered off and retained. The residual liquids from these samples were retained for analysis also. The final resin was freeze-dried. When it was desired to record n.m.r. spectra on a resin in D_2O without the need for freeze-drying, the initial resin preparation was carried out using a solution of formaldehyde in D_2O.

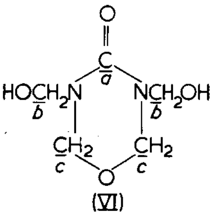
^{13}C spectra. ^{13}C-n.m.r. spectra were recorded using a Varian CFT-20 spectrometer at ambient temperature on 10–20 %w/v solutions of the model compounds and resins in a d_6-DMSO/DMSO solvent mixture and also in D_2O with 1% added DMSO as an internal reference. The spectra were the result of 10–50K accumulations with a pulse width of 3 μsec (corresponding to a tip angle of 13°). All chemical shifts are quoted with respect to tetramethylsilane (TMS) at 0 ppm. Coupling of the carbon nuclei with the neighbouring protons was removed by the usual 'white-noise' decoupling procedure.

Results and Discussions

The ^{13}C-n.m.r. spectrum (D_2O solvent) of a typical commercial liquid urea–formaldehyde resin prepared in water is shown in *Figure 1*. Peaks in two main areas are visible. The peaks between 40 and 85 ppm arise from methylene carbons in a variety of chemical environments and those between 155 and 165 ppm arise from carbonyl carbons. These peaks can be assigned only after consideration of the spectra of the model compounds, a number of which are shown in *Figure 2*. The spectra of the model compounds were recorded using D_2O as solvent with the exception of those of dimethyloloxymethylenediurea and tetraethyldimethylenediureid. These compounds were found not to be soluble in D_2O hence their spectra were recorded in d_6-DMSO/DMSO only. However, the chemical shift changes expected for a change of solvent from DMSO to D_2O can be obtained by considering the spectra of the model compounds that are soluble in both solvents. The chemical shifts of the more important distinguishable carbon atoms in the model compounds are listed in *Table 1*. The carbonyl resonance of uron in D_2O was also calculated from the shift measured in d_6-DMSO/DMSO; no carbonyl peak was visible when the spectrum of uron was recorded in D_2O. The spectrum of the crude sample of trimethylolurea is clearly complicated by the presence of additional components. In view of the high ratio of formaldehyde to urea (4:1) and the high pH of 11 used in the preparation of the trimethylolurea, it is believed that some of these additional components are methylol substituted urons having the structures indicated below (V and VI). Also indicated are the chemical shifts of the constituent carbon atoms in these structures:



(V)



(VI)

a, ~156 ppm; b, 69·1 ppm; c, ~79–80 ppm

Considering the assignments shown in *Table 1*, it can now be seen that the spectrum of the resin (*Figure 1*) reveals that it contains monomethylolurea (C = O at 162.4 ppm), methylol groups attached to secondary and to tertiary nitrogen (CH_2 at 65.5 and 72.3 ppm), linear ether linkages (CH_2 at 70.0 ppm) and methylene groups in linear portions of chain (CH_2 at 47.7 ppm). There is also some free formaldehyde (CH_2 at 83.5 ppm).

However, there is one significant resonance in the resin still unaccounted for, namely that at 54.3 ppm. We believe that this resonance arises from methylene linkages at branch points in the chains (VII) i.e. adjacent to a tertiary nitrogen atom.

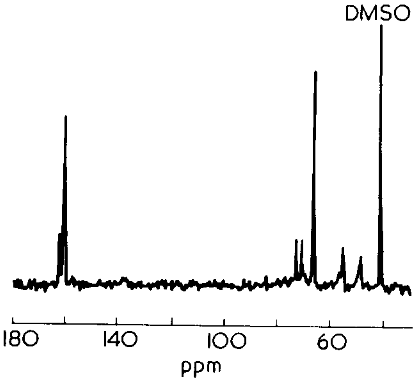


Figure 1 ^{13}C-n.m.r. spectrum of a commercial liquid urea–formaldehyde resin in D_2O

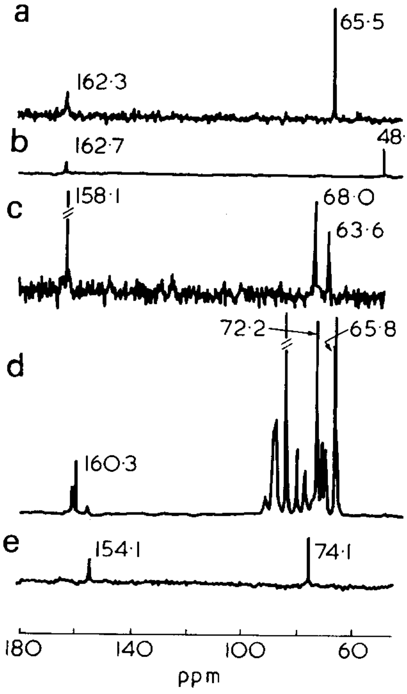
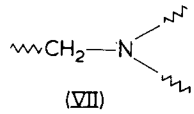


Figure 2 ^{13}C-n.m.r. spectra of some urea–formaldehyde model compounds in D_2O (except where indicated). (a) Monomethylolurea; (b) methylene diurea; (c) dimethyloloxymethylenediurea*; (d) crude trimethylolurea; (e) uron*. * Spectrum in d_6-DMSO/DMSO



(VII)

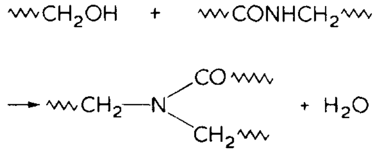
The reason for believing this to be so is that this resonance appears 6.5 ppm to lower field than that of the methylene linkage in a linear portion of chain $\text{-(-NHCH}_2\text{NH-)-}$. This difference in

Table 1 Peak assignments obtained from the ^{13}C-n.m.r. spectra of the model compounds (all chemical shifts are quoted relative to TMS at 0 ppm and apply to D_2O solvent)

Carbon environment	Model compound	Peak position (ppm)
$\mathrm{NH_2\underline{C}ONH_2}$	Urea	164.0
$\mathrm{NH_2\underline{C}ONHCH_2OH}$	Monomethylolurea	162.3
$\sim\mathrm{NHCONH\underline{C}H_2OH}$	Monomethylolurea and dimethylolurea	65.5
$\sim\mathrm{NH\underline{C}ONH}\sim$	Dimethylolurea	160.9
$\mathrm{HO\underline{C}H_2NHCON} <$	Crude trimethylolurea	65.8
$\sim\mathrm{NHCON(\underline{C}H_2OH)_2}$	Crude trimethylolurea	72.2
$\sim\mathrm{NH\underline{C}H_2O\underline{C}H_2NH}\sim$	Dimethyloloxymethylene diurea	70.0* (68.0)
$\sim\mathrm{NH\underline{C}H_2NH}\sim$	Methylene diurea	48.0
$> \mathrm{N\underline{C}H_2N} <$	Tetraethyldimethylenediureid	58.9* (57.0)
$-\mathrm{NH\underline{C}H_2O\underline{C}H_2NH}-$(cyclic)	Uron	75.6
$-\mathrm{NH\underline{C}ONH}-$(cyclic)	Uron	157.8* (154.1)
$> \mathrm{N\underline{C}ON} <$ (cyclic)	Dimethylether of dimethyloluron	156.4
$> \mathrm{N\underline{C}H_2O\underline{C}H_2N} <$ (cyclic)	Dimethylether of dimethyloluron	79.7
$\mathrm{HO\underline{C}H_2OH}$	Formalin	83.5
$\mathrm{HO\underline{C}H_2O\underline{C}H_2OH}$	Formalin	87.4
$\sim\mathrm{CH_2O\underline{C}H_2OCH_2}\sim$	Formalin	90

* Calculated from chemical shifts measured in d_6-DMSO/DMSO (given in parentheses)

chemical shift corresponds closely with that (6.6 ppm) between the methylene carbons in methylol groups attached to secondary nitrogen (65.5 ppm) and those in methylol groups attached to tertiary nitrogen (72.1 ppm). There is also a difference of 6.5 ppm between the methylene carbon resonances in *N,N*-diethylurea (43.1 ppm) and *N,N'*-diethylurea (36.6 ppm). Moreover, the resonance position for a methylene group between *two* tertiary nitrogen atoms is expected, from the spectrum of tetraethyldimethylenediureid, to occur at about 57.8 ppm in D_2O, i.e. to lower field than the resonance of the methylene linkage in a linear portion of chain. Methylene groups at branch points would arise from the reactions of a terminal methylol group on one chain (or adduct) with a secondary nitrogen on another as indicated below:



$$\sim\mathrm{CH_2OH} + \sim\mathrm{CONHCH_2}\sim \;\longrightarrow\; \sim\mathrm{CH_2{-}N}\begin{matrix}\nearrow \mathrm{CO}\sim\\ \searrow \mathrm{CH_2}\sim\end{matrix} + \mathrm{H_2O}$$

This would be expected to be an important reaction also during the cross-linking of urea–formaldehyde resins under acid conditions. Ether linkages at branch points, should they arise, would be expected by analogy with the methylene linkages to give rise to methylene resonances at 76.5 ppm (70.0 + 6.5 ppm). In fact a small peak at 76.5 ppm is visible in the spectrum of the resin shown in *Figure 1*.

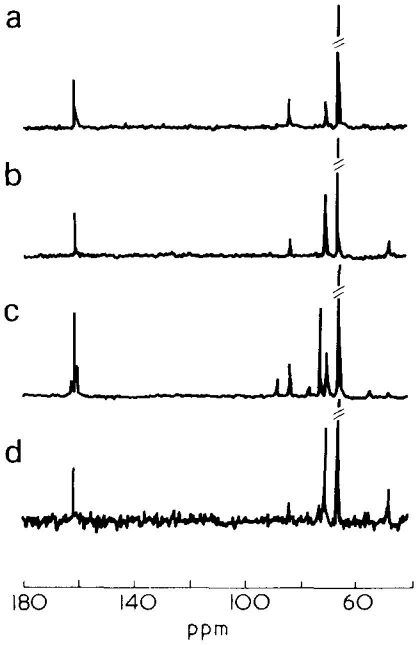


Figure 3 ^{13}C-n.m.r. spectra in D_2O of samples withdrawn from a resin preparation. F:U = 2.5:1, 100°C, pH 7.0 (KH_2PO_4/Na_2HPO_4 buffer). (a) Solid obtained after 5 min; (b) solid obtained after 15 min; (c) liquid fraction after 15 min; (d) final (solid) resin after 45 min.

Figure 3 shows the ^{13}C spectra of various samples withdrawn from a laboratory resin preparation carried out in D_2O (F:U = 2.5:1, pH = 7.0). It can be seen that (*Figure 3c*) the liquid fraction in the sample withdrawn after 15 min at 100°C contains a significant quantity of monomethylolurea and probably also di- and trimethylolureas (C=O peaks at 162.4 and 160.4 ppm and methylol methylene resonances at 65.5 and 72.2 ppm). The solids which separate from the early samples and the final resin appear to be essentially linear polymers containing methylene and methylene ether linkages (47.7 and 70.0 ppm respectively) and with terminal methylol groups (65.5 ppm), although there is some evidence of slight branching (peaks at 54.5, 72.4 and 76.6 ppm) in the final resin obtained after 45 min reflux (*Figure 3d*). All the samples appear to contain some free formaldehyde (methylene peaks at 83.5 ppm).

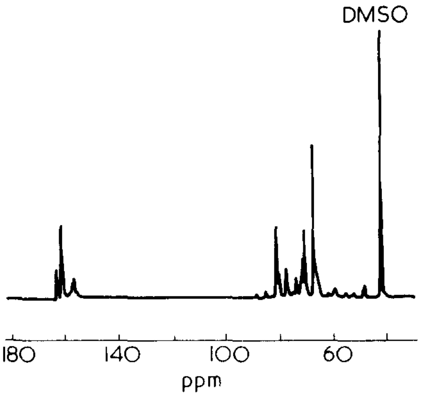


Figure 4 ^{13}C-n.m.r. spectrum in D_2O of resin prepared from 2:1 formaldehyde: urea mixture at pH 10 ($NaHCO_3$/Na_2CO_3 buffer), reaction time 4½ h at 100°C

That the final composition of a urea–formaldehyde resin is critically dependent upon the urea–formaldehyde ratio and the pH during preparation is indicated by *Figure 4*. This depicts the ^{13}C spectrum of a resin prepared from a 2:1 formaldehyde:urea mixture at pH 10 with a reaction time of 4½ h. The spectrum indicates that this resin contains significant quantities of monomethylolurea (C=O at 162.1 ppm) and urons (C=O between 155 and 156 ppm and CH_2 at 79.5 and 69.1 ppm).

Conclusions

It is clear from these preliminary studies that ^{13}C-n.m.r. spectroscopy can be useful in providing information about the chemical constitution of urea–formaldehyde adducts and resins which is not available from either classical chemical analyses or from proton magnetic resonance studies. In particular, ^{13}C-n.m.r. can provide details of the relative amounts of methylol groups attached to secondary and tertiary nitrogen and also the relative amounts of linear methylene linkages and methylene groups at branch points.

At present, ^{13}C-n.m.r. spectroscopy is being used to provide information about the kinetics of urea–formaldehyde condensation under a variety of conditions of reactant concentration, pH and temperature.

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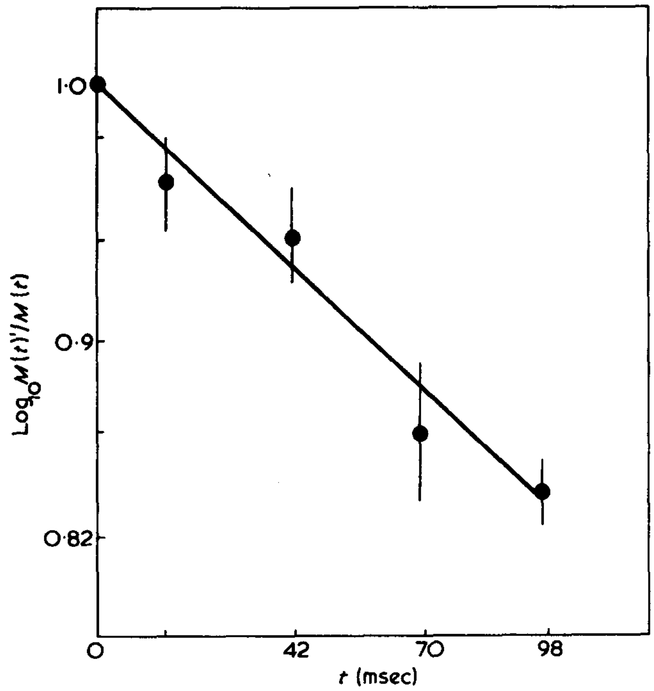
ERRATUM

'Diffusion and nuclear magnetic relaxation in concentrated polystyrene solutions' by T. Cosgrove and R. F. Warren, *Polymer* 1977, **18**, 255–258. Page 256, *Figure 2* should be:



The horizontal scale in the original figure was ambiguous, although the points were correctly positioned with respect to the scale. The horizontal coordinates are 14, 42, 70 and 98 msec. When replotted the graph is still linear within the experimental error and does not alter in any way the scientific discussion of the paper.