A SYNTHETIC AND SPECTROMETRIC STUDY OF THE INITIAL PHASES IN UREA-FORMALDEHYDE RESIN FORMATION

THESIS

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ABSTRACT

In a series of preliminary studies of urea-formaldehyde reactions, the influence of the U:F molar ratio, the temperature and the catalyst were investigated. Subsequently, in a more rigorous evaluation of the influence of four variables on urea-formaldehyde resin formation, *viz.*, U:F molar ratio, pH, temperature and reaction time, a set of twenty reactions were performed using a statistical approach. The results indicate that high resin viscosity is best achieved by using a high U:F molar ratio (1:2) and conducting the reaction at 90 °C.

Several basic components produced in urea-formaldehyde reactions have been synthesised, characterised by NMR spectroscopy, silylated using bis(trimethylsilyl)trifluoroacetamide and analysed by low resolution mass spectrometry. The use of triazones as cross-linking agents has been investigated, and a series of 5-substituted triazones have been prepared and their mass fragmentation patterns explored using a combination of low and high resolution mass spectrometry.

In order to facilitate interpretation of ¹³C NMR data obtained for U-F resins, internal rotation in various urea derivatives was investigated using variable temperature ¹H and ¹³C NMR spectroscopic study. Signal splittings observed below 247 K have been rationalised in terms of various rotameric structures.

1 INTRODUCTION

1.1 HISTORICAL OVERVIEW

Urea was first identified by Rouelle in 1773. Its synthesis by Wöhler, in 1828, marked the beginning of synthetic organic chemistry and it was the first natural product to be synthesized in the laboratory.^{1,87} The reaction between urea and formaldehyde was investigated further by Tollens, who isolated an amorphous insoluble material - an observation which was reported in only one and a half lines.^{5,26} Later, in 1894, Holzer carried out the reaction in the presence of dilute acid and obtained a white precipitate which was considered to be methylenediurea. In the same year Goldschmidt, explored the reaction further under neutral conditions and was able to characterise and isolate the products.¹ The first systematic investigation was undertaken by Hamburger and Einhorn, who were able to isolate important intermediates in the formation of urea-formaldehyde (U-F) resins, *viz.*, monomethylolurea 1 and dimethylolurea 2.^{1,6} Other intermediates were isolated and studied by an Englishman, A.E. Dixon, in 1918.¹

$$HO-CH_2-NH-CO-NH_2$$
 $HO-CH_2-NH-CO-NH-CH_2-OH$
1 2

A series of developments finally resulted in the commercial recognition of the new and important thermosetting plastics, which were called "urea-formaldehyde". Full commercial development was begun in 1920 by Czechoslovakian, Hanns John, who was the first scientist to realise the potential and importance of these resins as surface coatings.^{6,8} He prepared adhesives, and a

number of clear, glass-like polymers and adhesives by heating mixtures of urea and formaldehyde. In 1923, the Austrian chemist, Fritz Pollak, discovered that urea-formaldehyde resins could be used as glass substitutes because they are transparent. It was proposed that this new synthetic material might serve as an organic glass and, in fact, a transparent organic glass called "Pollopas" was launched to be used as a glass substitute.^{5,6} Similar glasses were made in France and England under the trade names, "Prystal" and "Plass", respectively. These plastics were also imported into the United States as "Luxite" and later were manufactured under the name "Aldur".⁵ Although these glasses were tougher, lighter and more transparent to ultraviolet light than ordinary glasses, they did not prove successful. The most serious objection was a lack of weather resistance with a tendency to absorb atmospheric moisture and water. This resulted in loss of lustre and cracking, which seriously reduced their strength.⁵ Attempts to improve the performance of these glasses were made, but without success, and by 1930, defeat was admitted and synthetic glasses disappeared from the scene.

In 1926, a British development team produced moulding powders from urea and thiourea.⁶ The use of thiourea was found to increase the strength and water resistance of the resin. This product was available in a variety of colours and was in favour with British moulders for many years. Its disadvantages were that it was expensive to make, slow to cure and hard upon the moulder because of the presence of sulphur, which caused corrosion in the chromium-planted and stainless steel moulds. Hence the use of thiourea mouldings was short-lived.

At this time, the Toledo scale company was evaluating means of reducing the weight of their butcher's scales. The scale mechanism was placed in a heavy, enamelled iron case, which accounted for a considerable portion of the total mass of the scale. Consumer demand required a decrease in the mass of the scale, which could be best accomplished by resorting to lighter material and, hence, plastics. The only available mouldable plastics were the phenolics, which were brown or black in colour, and consumer tests established that customers would refuse to buy meat from brown or black scales. This psychological factor ruled out the use of phenolic resins and encouraged the development of light coloured plastics.⁷

Urea-formaldehyde products had the advantage of offering wide colour ranges and variations in brilliance and translucency, which were impossible to achieve with phenolic resins because of their dark colour. The first urea-formaldehyde mouldings appeared on the market in 1929 and were very successful; they also provided excellent low cost adhesives for wood products, such as chipboard, and found use as anti-creasing agents for cotton fabrics and as surface coatings.^{2,4}

1.2 THERMOSETTING RESINS

Thermosetting resins are those which change irreversibly, under the influence of heat, from a fusible, soluble material into one which is insoluble and infusible, through the formation of a covalently cross-linked, thermally stable network. Commonly known thermosetting resins are phenol-formaldehyde, urea-formaldehyde and melamine-formaldehyde resins. Other thermosetting resins include epoxy resins, unsaturated polyester resins, urethane foams and the alkyd resins.³

1.2.1 Phenolic resins

Phenol-formaldehyde resins were discovered in 1872 by Baeyer, but were first thoroughly studied by an American, Baekeland.^{9,10,69,70} The nature of the resin was found to be greatly influenced by the catalyst (acid or base) and the molar ratio of phenol to formaldehyde, while heating the reaction mixture for long periods led to the formation of infusible and insoluble cross-linked polymers.³ The initial reactions involve formation of the methylolated products 5, 6 and 7 (Scheme 1).



Under acidic conditions and with a formaldehyde:phenol ratio of less than 1, the phenol methylol derivative 5 condenses with phenol 3 to form the bisphenolic derivative 8; further condensation then occurs to form low molecular weight polymers called "novolacs" 9 (Scheme 2).³ In the

presence of an alkaline catalyst and a formaldehyde:phenol ratio of greater than 1, phenol 3 condenses with the phenoldimethylol derivative 6 to form a methylene-linked product 10 (Scheme 3).



Ether linked products, such as 11, are also formed (Scheme 4), but the subsequent loss of formaldehyde affords soluble and fusible methylene-linked products, such as 10, called "resoles".



SCHEME 4

1.2.1.1. Phenol-formaldehyde applications and properties

1.2.1.1.1 Moulding resins

It has been estimated that about 25 % of the phenolic resins produced are used in compression or transfer mouldings.¹¹ These resins can be prepared by a one- or two-stage process. In the one-

stage process, approximately 1.2 moles of formaldehyde is reduced by heating with one mole of phenol in the presence of an acid or base catalyst. The time taken for complete reaction depends upon the type and amount of catalyst used, while the temperature may be controlled to ensure a uniform product. After the initial reactions have progressed to the desired extent, water is removed under vacuum. The methylol content at this stage is insufficient to ensure resin formation at moulding temperature and, consequently, it is often necessary to add more formaldehyde or to mix the resin with another batch with higher or lower methylol content in order to obtain a suitable, final resin. The resin is then mixed with fillers and mould lubricants on heated rolls at 90-107 °C. Such treatment serves to bring about further condensation of the resin to a viscous, but fusible, state and is continued until the desired degree of plasticity is obtained.¹²

In the two stage process, fusible and soluble resins are first formed by the reaction of phenol and formaldehyde as in the one-stage process, an acid catalyst being used and later neutralised. After removal of water, sufficient formaldehyde to cure the resin is added in the form of hexamethylenetetramine or paraformaldehyde, together with fillers, pigments and lubricants.¹² Commonly used fillers are asbestos, fibrous glass and wood flour. Phenolic moulding resins were found to have outstanding heat resistance, dimensional stability and good dielectric properties in electrical, automotive radio and television appliances.

1.2.1.1.2 Cast resins

Cast resins are generally prepared by the one-stage condensation of phenol and formaldehyde in a molar ratio of 1:1.5-2.5 under alkaline conditions.^{11,12,13} After an adequate reaction time, the pH is adjusted to 5 using lactic acid, and water is removed under vacuum. The resin is then mixed with a colouring agent and cast into lead moulds, which are baked in a steam-heated oven for a long period in order to bring about thermosetting. The moulded resin is produced as sheets, rods and tubes, which are then processed further to give articles such as buttons, brush and door handles, shoe heels, trays, ornaments and some jewellery.¹³

1.2.1.1.3 Laminating phenolic resins

No fundamental difference exists between laminating resin and moulding resin except in the nature of the filler. Moulding resins are generally developed for speed cure whereas laminating resins do not require this characteristic. Paper , linen, canvas, cotton and silk are all used as fillers in laminating resins. The important uses are as gears, in tubing, electrical insulation, rods, decorative finishes, barrels and pails.¹²

1.2.1.1.4 Phenolic resins as adhesives

A number of industrial applications are based on the excellent adhesive properties and bonding strength of phenolic resins. In recent years, wood products have developed greatly and the use of synthetic resins as adhesives has come under investigation. Phenolic resins are highly resistant to water and, hence, have replaced glues like casein and gelatin.¹¹ Adhesive phenolic resins are prepared by reacting 1.1 to 2.0 moles of formaldehyde with 1 mole of phenol in the presence of an alkaline catalyst, water being finally removed to afford the adhesive as a viscous liquid.

1.2.2 Melamine-formaldehyde resins

2,4,6-Triamino-1,3,5-triazine (melamine) 12 was first prepared by Liebig in 1834, but only came to the market in 1939.¹⁴ Melamine is a white crystalline, heterocyclic aromatic compound, the primary amino groups of which react with formaldehyde to give derivatives containing one to six methylol groups, *e.g.* compound 13 (Scheme 5).



SCHEME 5

The methylol hydroxyl groups may react further with unsubstituted melamine amino groups to form methylene-linked derivatives such as 14 (Scheme 6), further reaction of which affords melamine polymers.



SCHEME 6

Ether linkages have also been reported but compounds containing them tend to lose formaldehyde to form methylene-linked polymers.^{15,16,17} Melamine **12** has multiple reactive sites and, hence, melamine resins are likely to form cross-linked polymer forms. These polymers tend to be highly insoluble and, to improve their solubility in organic solvents, modified melamine resins are prepared in the presence of alcohols such as butanol and methanol (Scheme 7). The free hydroxyl groups undergo condensation to form methylene-linked polymer forms. Resins made from melamine, formaldehyde and butanol are used in conjunction with alkyd resins in the preparation

of stoving enamels,^{16,19} and in textile printing-ink formulations. A typical textile melamine resin is prepared using the trimethoxy derivative 16, under alkaline conditions.



SCHEME 7

1.2.2.1 Applications of melamine-formaldehyde resins

The applications of melamine-formaldehyde resins are similar to those of phenolic resins except that melamine resins are light in colour and are therefore important where a lack of colouration is required. Objects moulded from melamine resin have high resistance to dry heat, hot beverages, such as coffee and tea, and are free from all taste and smell¹⁸; their main use is in the manufacture

of decorative tableware.¹⁷ These resins are sometimes modified by the addition of fillers such as cellulose, wood flour and pigment. Their heat resistance has also led to their widespread application in mass-produced articles such as refrigerators, switch boards, motor car bodies, electric irons, furnishings, and bathroom and kitchen ware.¹⁸ Together with U-F resins they are used as adhesives, especially in chipboards, the melamine-formaldehyde resins increasing the water resistance. Melamine resins are also used in cellulosic textiles (as crease-resistant finishes) and heavy-duty electrical parts (using glass fibre or asbestos as the filler).^{17,19} Another interesting use is in the preparation of fluorescent inks. The fluorescent powder is mixed with melamine lacquer and then heated to cure, the thermoset product is then ground to a fine powder and dispersed in printing ink.¹⁷

1.2.3 Unsaturated polyester resins

Unsaturated polyesters are produced by the reaction of diols with an acid anhydride or dibasic acid; for example, ethylene glycol 17 reacts with maleic anhydride 18 to form polymeric esters 19 (Scheme 8).



SCHEME 8

In the formation of unsaturated polyester resins the acid and alcohol are condensed to form the soluble polyester 19, followed by and the addition of a cross-linking agent (e.g. styrene) to affod thermosetting resin 21 (Scheme 9). The resin is obtained by heating the mixture at 200 °C for 4 to 20 hours. Unlike most resins the cross-linking process does not involve loss of water. These types of resins are usually used with fillers such as glass fibre and, in this form, they are used in car bodies and in boats.²⁰



SCHEME 9

1.2.4 Epoxy resins

The preparation of epoxy resins 22 is usually based on the reaction between bisphenol and epichlorohydrin under alkaline conditions. The epoxy group is very reactive chemically, the ring being under strain and hence opening readily. When a mixture of bisphenol and epichlorohydrin is treated with curing agents such as diethylenetriamine; triethylenetetramine or metaphenylenediamine, they cross-linking occurs *via* the epoxy group. The resulting resins are used as adhesives, especially for tough environmental or mechanical conditions, for example, in aircraft. Excellent coatings are made by the inclusion of epoxy resin.^{21,71}



1.2.5 Polyurethanes

Polymers containing urethane groups (-NH-CO-O-) are defined as polyurethanes. Urethanes 25 are formed when an isocyanate 23 reacts with a compound containing a hydroxyl group 24 (Scheme 10). Linear polyurethane polymers 28 are produced by reacting diols 26 with diisocyanates 27 (Scheme 11).

Introduction

R-N=CO + R'-OH → R-NH-CO-OR' 23 24 25 SCHEME 10 $n R(OH)_2 + n R'(N=CO)_2 \longrightarrow H^{-(O-R-O-CO-NHR'-)_{n-N} - CO}$ 26 27 28 SCHEME 11

Polyisocyanates tend to give cross-linked polyurethanes with thermosetting and thermoplastic properties. Polyurethanes are used as lacquers for cloth, paper and leather treatment.²² Polyurethanes can also be prepared from the reaction of hexamethylene diisocyanate and 1,4-butanediol; such polyurethanes may be used as thermoplastic moulding material. These materials resemble nylon 6.6 but have low water absorption and, hence, have better dimensional stability.^{24,30}

1.2.6 Alkyd resins

Alkyd resins are formed by treating polyhydric alcohols (*e.g.* glycerol) with acyl compounds (*e.g.* phthalic anhydride) at high temperature. In most cases, alkyd resins are not used on their own but are modified in different ways, two of which involve the addition of urea or melamine. Alkyd resins modified by urea or melamine are used as surface coatings, in which they serve to improve colour retention and increase hardness. When alkyd resins are modified by the addition of phenolic resins, resistance to water, chemicals and heat is improved. Alkyd resins can also be modified by adding drying oils; these types of alkyd resins yield hard films either by baking or by air drying. The hard films are tough and durable and possess high gloss, excellent adhesion to metallic surfaces, and superior resistance to light, heat and chemicals. The drying oils used are soybean, dehydrated castor, perilla and oiticica oils.^{23,37}

1.3 UREA-FORMALDEHYDE REACTIONS

The reaction between urea and formaldehyde involves two stages. The first stage is the addition of formaldehyde to urea to form methylolated ureas. The second stage is the condensation between methylol and amide groups to form methylene-linked polymers, or between two methylol groups to form ether-linked polymers. As is the case with phenolic resins, the formation of ureaformaldehyde resins is known to be greatly influenced by both acid and base catalysts. Other factors such as the temperature at which the reaction is carried out, the time taken to complete the reaction and the U:F molar ratio, also affect the final structure of the resin.

1.3.1 Methylolated ureas

Methylolureas such as monomethylolurea, dimethylolurea and methylenediurea have been identified as the main products of the first stage of the reaction between urea and formaldehyde.

1.3.1.1 Monomethylolurea

As mentioned earlier, the simplest product of the reaction between urea 29 and formaldehyde 4 is monomethylolurea 1. Monomethylolurea 1 is prepared by reactions equimolar amounts of urea and formaldehyde in the presence of an alkaline catalyst, *e.g.* barium hydroxide, potassium hydroxide or sodium hydroxide (Scheme 12).

The work done by de Jong and de Jonge shows that this reaction is reversible in neutral, acidic and basic solutions.²⁵ The forward reaction is bimolecular and the reverse reaction is monomolecular, and both the forward and reverse processes are catalysed by hydrogen ions or hydroxide ions. In dilute, aqueous solutions, formaldehyde 4 is in equilibrium with methylene glycol 30 (Scheme 13). In acidic conditions, assuming that only the non-hydrated formaldehyde 4 will react with urea, the mechanism follows the steps shown in Scheme 13. The addition of acid (HA) increases the electrophilicity of the carbonyl carbon, which is readily attacked by the nucleophilic urea nitrogen; loss of the proton then gives monomethylolurea 1.



The proposed mechanism²⁵ for the formation of monomethylolurea, under basic conditions, is outlined in Scheme 14. The base (B) removes a proton from a urea nitrogen making it more nucleophilic; this is followed by attack of the nucleophile on the formaldehyde carbonyl carbon to give an anion 34, which is protonated to form monomethylolurea 1.



The formation of methylene glycol in aqueous solution, however, has prompted the suggestion that the condensation involves a direct displacement reaction between urea and methylene glycol (Scheme 15).²⁶

1.3.1.2 Dimethylolurea

Under the same conditions required for the formation of monomethylolurea 1, but using a 2 molar excess of formaldehyde 4, monomethylolurea 1 and formaldehyde 4 react to give dimethylolurea 2 (Scheme 16). The rates of both the forward reaction and the reverse reaction were found to be proportional to the hydrogen ion concentration. The mechanism is considered to be similar to that for the formation of monomethylolurea under both acidic and basic conditions.²⁷



1.3.1.3 Methylenediureas

Under acidic conditions and at temperatures of 25-45 °C, the *N*-methylol group in monomethylolurea 1 or dimethylolurea 2 condenses with an amino group to form a methylene bridge between two urea fragments (Scheme 17).

$$-N-CH_2-OH + H-N \xrightarrow{[-H_2O]}$$
 $-N-CH_2-N-$

SCHEME 17

Methylene-linked molecules can also be formed by the reaction of two monomethylolurea molecules to afford the methylol derivative 35 (Scheme 18), while reaction of monomethylolurea 1 with urea 29 gives methylenediurea 36 (Scheme 19).²⁸ The reaction between two dimethylolurea molecules 2 with the release of formaldehyde is known to result in the formation of the dimethylol derivative 37 of methylenediurea (Scheme 20), while reaction of dimethylolurea 29 affords the methylenediurea derivative 35 (Scheme 21).²⁸

2 H₂N-CO-NH-CH₂-OH
1

$$[-H_2O]|_{\downarrow}$$

H₂N-CO-NH-CH₂-NH-CO-NH-CH₂-OH
35

SCHEME 18



HO-CH₂--NH-CO-NH-CH₂--NH-CO-NH-CH₂-OH 37

21

A problem with the last reaction (Scheme 21) is that dimethylolurea 2 dissociates to monomethylolurea 1 and formaldehyde 4 in aqueous solutions. The experiments by de Jong and de Jonge²⁸ have shown that, at pH = 3.6 - 4.5, the dissociation of dimethylolurea 2 is not significant and, hence, it would be proper to conclude that under these experimental conditions the reaction in Scheme 21 is dominant. The dimethylol derivative **37** of methylenediurea is also formed by the reaction of monomethylolurea 1 with dimethylolurea 2 (Scheme 22). The general mechanism for the formation of the methylene-linked urea derivatives is shown in Scheme 23, and involves acid catalysed dehydration to afford a resonance stabilised carbocation **39**. Nucleophilic attack by amino nitrogen, followed by deprotonation then affords the methylene-linked product.²⁸

HO-CH₂-NH-CO-NH₂ + HO-CH₂-NH-CO-NH-CH₂-OH
1 2
SCHEME 22
$$[-H_2O]$$

37

In acidic conditions (pH = 3-5), methylenediurea derivatives can be hydrolysed to urea and monomethylolurea derivatives, while the hydrolysis of dimethylolurea 2 is a reversible process, with the rates of both the forward and reverse reactions being directly proportional to the hydrogen ion concentration. The mechanism proposed by de Jong and de Jonge for the hydrolysis of methylene-linked ureas is outlined in Scheme 24.²⁹



Dimethylenetriurea 41 can be formed by the reaction of methylenediurea 36 and monomethylolurea 1 as shown in Scheme 25. The difficulty in this reaction is that both methylenediurea 36 and monomethylolurea 1 are not stable under the experimental conditions used. Monomethylolurea 1 dissociates to form urea and formaldehyde, while methylenediurea 36 dissociates to form monomethylolurea 1 and urea. There is also a possibility of reaction between two monomethylolurea molecules 1 to form the methylol derivative of methylenediurea.

$$H_{2}N-CO-NH-CH_{2}-OH + H_{2}N-CO-NH-CH_{2}-NH-CO-NH_{2}$$

$$1 \qquad 36$$

$$[-H_{2}O] \downarrow$$

$$H_{2}N-CO-NH-CH_{2}-NH-CO-NH-CH_{2}-NH-CO-NH_{2}$$

$$41$$

SCHEME 25

Experiments by de Jong and de Jonge ³¹ have shown that, at 25° C and in the pH range 3-4, dissociation of monomethylolurea 1 is very small and their experimental results indicated that the reaction between methylenediurea 36 and monomethylolurea 1 predominates.³¹ Other methylene-linked ureas, such as trimethylenetetraurea 42 and pentamethylenehexaurea 43, have been isolated by Kadowaki.²⁶



1.3.1.4 Other products of urea-formaldehyde reactions

It is apparent that the "urea-formaldehyde reaction" is made up of many different components, one of which involves the reaction of urea, formaldehyde and methanol. Methanol is present in aqueous formaldehyde, comprising 5-10 % of the solution. Its presence serves to stabilise the formaldehyde solution so that paraformaldehyde do not precipitate when the solution is stored at room temperature. At high temperatures, trimethylolurea 44 is known to form (Scheme 26)³³; in this product, three of the urea amide hydrogens have been replaced by methylol groups.

HO-CH₂--NH-CO--NH--CH₂--OH + HCHO
2

$$\Delta \downarrow$$
 [-H₂O]
HO--CH₂--N-CO--NH--CH₂--OH
 \dot{C} H₂--OH
44

SCHEME 26

Of course, urea has four reactive hydrogens, but the first three are more readily replaced than the fourth. Under strongly basic conditions and at 60 °C, the fourth hydrogen may be lost with the formation of tetrasubstituted ureas. The treatment of tetramethylolurea **45** with excess methanol, under acidic conditions at room temperature, results in rearrangement and methylation of the hydroxyl groups to form the substituted uron **46** (Scheme 27).³⁴ Other products obtained in urea-formaldehyde reactions include:- the methyl ether **47** of monomethylolurea; dimethylolurea

monomethyl ether 48; dimethylolurea dimethylether 49; monomethylolmethylenediurea 50; monomethylolmethylenediurea methyl ether 51; dimethylolmethylenediurea monomethyl ether 52; dimethylolmethylene diurea 53 and dimethylolmethylenediurea dimethylether 54 (Table 5). These compounds were all synthesised and characterised by Lundlam.³⁵



SCHEME 27

Table 1	l:-	Urea-	form	ıldehy	/de re	eaction	products	synthesized	and	charact	erised	by	Lundlam.	35
---------	-----	-------	------	--------	--------	---------	----------	-------------	-----	---------	--------	----	----------	----

Compound	Structure
47	H ₂ N-CO-NH-CH ₂ -O-CH ₃
48	HO-CH ₂ -NH-CO-NH-CH ₂ -O-CH ₃
49	H ₃ C-O-CH ₂ -NH-CO-NH-CH ₂ -O-CH ₃
50	H ₂ N-CO-NH-CH ₂ -NH-CO-NH-CH ₂ -OH
51	H ₂ N-CO-NH-CH ₂ -NH-CO-NH-CH ₂ -O-CH ₃
52	HO-CH ₂ -NH-CO-NH-CH ₂ -NH-CO-NH-CH ₂ -O-CH ₃
53	HO-CH ₂ -NH-CO-NH-CH ₂ -NH-CO-NH-CH ₂ -OH
54	H ₃ C-O-CH ₂ -NH-CO-NH-CH ₂ -NH-CO-NH-CH ₂ -O-CH ₃

1.3.2 Polymerisation

Urea-formaldehyde polymers are known to result from the reactions of methylolureas. Two types of linear polymers, which have been identified, are methylene-linked and ether-linked polymers. The mechanism for the formation of methylene-linked polymers is assumed to be similar to that for the formation of methylene-linked ureas.²⁶ Although ether-linked polymers have been shown to form, they are not stable, and lose formaldehyde to produce methylene-linked ureas. Hence, it is assumed that the formation of methylene-linked polymers are favoured in urea-formaldehyde resins. Further reaction of the mixture of methylolated ureas leads to the formation of long chains of linear polymers or cyclic systems such as urons and their derivatives 56.^{43,57} Urons 56 are formed by cyclisation of urea derivatives 55, (Scheme 28), while cyclic dimethylene diureas 57 are produced by the reaction of dimethylolurea 2 and urea 29 (Scheme 29).



SCHEME 28

As heating continues, cyclic structures, such as compound 57, react with formaldehyde (methylene glycol 30) to afford methylated dimethylenediureas 58 which polymerise to form large molecules 59, which, because of their size, tend to be highly insoluble. Cross-linked urea-

formaldehyde polymers are formed via the conversion of secondary amide groups to tertiary amides, with the amide nitrogens being the cross-linking points. Since such polymers result from the reaction of methylol groups with amide nitrogens, cross-linked polymers are expected to contain very few or no methylol groups. Although there is clear evidence for formation of the cross-linked polymers, their precise structures are not known. Different researchers have suggested different structures, arising from the different reactions which may lead to their formation. Structure 60 is one of the possible arrangements that have been suggested for crosslinked U-F polymers formed under acidic conditions.



SCHEME 29



Under acidic conditions, monomethylolurea 1 is protonated to form the oxonium ion 61; loss of water affords the iminium 62, condesation of which yields the cyclic triurea 63 (Scheme 30). Subsequent methylolation and condensation gives rise to larger molecules 64, which later form cross-linked urea-formaldehyde resins. ³⁶ Cross-linked polymer resins are infusible and insoluble, properties which are associated with the large size of the molecular structures.³⁸ To improve the solubility of resins in organic solvents, alcohols such as butanol, propanol and methanol may be added to the reaction mixtures.


1.3.3 Alcohol soluble resins

A high concentration of hydroxyl group in U-F polymers corresponds to poor solubility in organic solvents.¹⁶ This solubility problem is normally avoided by the inclusion of alcohols in the urea-formaldehyde reaction mixture, the methylol groups reacting with the alcohols to form ethers (Scheme 31).



Resins generated in the presence of ethanol have been found to be soluble in ethanol, while the inclusion of butanol makes them generally soluble in organic solvents. The nature of the resin depends on the proportions of urea, formaldehyde and the alcohol. Scheme 32 illustrates an idealised reaction in which 1 molar equivalent of urea, 2 molar equivalents of formaldehyde and 1 molar equivalent of butanol are reacted together. In this sequence, urea is treated with formaldehyde, under basic conditions, to afford dimethylolurea 2 which then reacts with butanol in acidic medium to afford the ether 66, which then condenses to the polymer 67. It is known, however, that polymers produced in this way are, in fact, not linear, condensation of amides and methylol groups leads to the formation of cyclic structures.



SCHEME 32

In the presence of unreacted -NH and the CH_2OH groups, the reaction continues with the formation of larger molecules, quenching being effected neutralising the mixture.⁴¹ Butylated resins are mixed with alkyd resins for use in stoving enamels; at 120 °C, hardening is observed, and the products find use in the construction of bodies, bicycles, refrigerators and kitchen equipment.⁴²

1.4 ANALYSIS OF UREA-FORMALDEHYDE RESINS

Several methods have been used to monitor progress and analyse the products of ureaformaldehyde reactions. Sebenik and Osredkar used differential scanning calorimetry to determine the kinetic parameters of the reaction in neutral and acidic medium.⁴⁶ The Kjeldal method for the analysis of nitrogen is commonly used for determining the amount of nitrogen present in the mixture and, hence, the proportion of amide in the resin. Formaldehyde is typically present either as free formaldehyde, or incorporated into the resin in the form of methylol end groups, methylene links, methylated groups (CHOCH₃) and ether-linked moieties (CH₂-O-CH₂). Marath and Woods were able to determine the ratio of free formaldehyde: total formaldehyde, and, hence the formaldehyde bonded to urea using titrimetric methods^{44,45} Chaung and Maciel used ¹⁵N cross-polarization/magic angle spin (c.p.-m.a.s.) NMR spectroscopy of urea-formaldehyde resins to obtain data for the degree of cross-linking and to determine the cross-linking points. This technique enabled them to confirm the presence of tertiary amides, while clearly identifying the unreacted primary amides and permitted a distinction to be drawn between methylol and ether linkages.⁴³

1.5 PROPERTIES AND APPLICATIONS OF UREA-FORMALDEHYDE RESINS

The properties and applications of urea-formaldehyde (U-F) resins are similar to those of melamine and phenolic resins. A major advantage of U-F resins is that they are colourless and transparent and, consequently, particularly useful where colour is important. Melamine resins are also colourless but are very expensive; however, they are more resistant to water than urea resins. Melamine tends to form more cross-linked polymers than urea because the melamine ring has 6 replaceable hydrogen atoms, whereas urea has only 4. Urea-formaldehyde resins have a wide variety of applications, including use as crease-resistant agents, moulding powders, adhesives, laminated products and surface coatings.

1.5.1 Applications of urea-formaldehyde resins to textiles

When the fibre was first invented it had difficulty in competing with the natural fibres, wool and cotton. One of the main disadvantages was its tendency to crease badly, and consequently, resins were examined for use as anti-crease substances. A suitable anti-crease resin must distort the fabric fibres, cover the fabric well and must be retained during washing and urea-formaldehyde resins were found to satisfy these criteria. The anti-creasing resin is prepared by using a urea:formaldehyde ratio of 1:1.6 and an acidic catalyst, such as ammonium dihydrogen phosphate. The mixture is allowed to react at room temperature for 5 hours, by which time the required viscosity is obtained. These reaction conditions give rise to a mixture of soluble, low molecular weight products, such as monomethylolurea 1 and dimethylolurea 2. The fibre is then soaked in the resin solution, mangled, dried and heated to 120 °C for three minutes. In the process, called curing, polymerisation occurs, changing the soluble and low molecular weight resin into an insoluble and high molecular weight resin. Soluble and low molecular weight products, such as monomethylolurea, are expected to enter the fibre where they polymerise during curing and are thus locked inside the fibre. Chemical changes during this process are similar to those occurring during normal polymerisation of urea-formaldehyde resin.⁴⁷

Urea-formaldehyde resins also improve the resilience of rayon, the stability and brilliance of cotton and the handling of many fabrics.⁵¹ These resins do not react with synthetic fibres, but tend to condense at the surface resulting in the stiffness and resilience of the fibre. When the untreated fibre is stretched or deformed by bending, the weak hydrogen bonds are broken and reform at new positions, holding the fibre in a new arrangement. When the resin is applied to the fibre, and polymerised, however, covalent bonds are formed resulting in cross-linking at the surface of the fibre. When the coated, cross-linked fibre is stretched or deformed, the covalent bonds do not break, instead they are stretched or compressed and return to their original position when the strain or deformation is released. Clothing manufactured from such fibres is called "wash-and-wear" because ironing is not necessary. When treated fabric is pressed to induce polymerisation and cross-linking, the resulting crease is maintained throughout wearing and during and after washing.⁵²

1.5.2 Adhesives

1.5.2.1 Properties of adhesives

Good wood adhesives are those that perform well between the glue line and the surface of wood. The study of adhesion properties is complex and can be divided into chemical, mechanical and physical aspects. Adhesion in wood material was reviewed by Marra in 1977.⁴⁸ In his study, he suggested that there were 9 links involved in adhesion and these are illustrated in Figure 1.



FIGURE 1. Marra's nine links in wood adhesion

Link 1 is the intrinsic cohesive strength of the adhesive within itself. Links 2 and 3 represent the cohesion between the bulk glue and the adhesive absorbed on the surface. Links 4 and 5 provide adhesion between the surface of wood and the glue line. Links 6 and 7 represent the adhesive which has been adsorbed on to the surface of the wood, while links 8 and 9 represent the adhesive which has penetrated the surface of wood. The bond performance is determined by how strong the various links are. Sometimes, wood surfaces are not even and, when a glue is applied, the glue line will not have an even thickness. Uneven glue lines produce an intrinsic tension within the bonded layer and, hence, impair the glue performance.⁴⁸

1.5.2.2 Urea-formaldehyde resins as adhesives

Urea-formaldehyde resins have been found to satisfy several criteria considered essential in wood

bonding. They comprise a complex mixture of components with different molecular weights, the properties of which correspond to the requirements of Marra's 9 links. High molecular weight components coalesce to form the bulk of the glue line, while low molecular weight components, such as monomethylolurea 1, penetrate the surface of the wood to provide links 8 and 9 and establish a link between wood and glue by hydrogen bonding to the cellulose. Urea-formaldehyde adhesives are used either in the form of a syrup or a powder. Powder resin, formed by evaporating water from the manufactured resin mixture, is mixed with water, prior to use, to form a solution which cures to produce a three-dimensional water-resistant film upon the addition of acid. This type of resin has been found to be polar and, hence, provides excellent adhesion to polar or hydrophilic surfaces. Urea-formaldehyde resin are used as glues in the plywood used in the manufacture of aircraft structures; boats and in certain military equipment; they are also used as a binding in the production of chipboard.⁴⁹

1.5.3 Urea-formaldehyde resins as surface coatings

As mentioned earlier, organic-soluble U-F resins may be prepared by including alcohols in the reaction mixtures to form ethers. Treatment of urea-formaldehyde resins with excess methanol results in the formation of acetals which can which can be diluted with benzene, xylene or hydrogenated naphthas. By adding a suitable pigment to the diluted resin and applying the resulting lacquer to metal or other surfaces, and then heating, coatings are produced with excellent light stability and good surface hardness. However, these coatings have been found to lack adhesion at the surface of the coated material. To overcome this problem, urea resins for coatings are not used alone, but are mixed with oil, phenolic resin or alkyd resin, normally in the

ratio of 1:1. They are also mixed with other resins such as nitrocellulose, ethyl cellulose and natural resins. Products coated with urea-formaldehyde resins are used in kitchen ware, bathroom materials, hospital equipment and in refrigerators.⁴⁹

1.5.4 Moulding resins

Moulding of urea-formaldehyde resins takes place at high pressure in the temperature range 132-160 °C. Although moulded urea-formaldehyde products are preferred over phenolic products because of their transparency and light colour, they do have a tendency to absorb water. This property is not only related to the presence of carbonyl groups, but also to the presence of free -NH and methylol (-CH₂OH) groups. These groups are hydrophilic and tend to absorb water. To produce good, moulded products, U-F resins must have the minimal number of methylol and -NH groups. Moulded U-F products are highly resistant to alkali and can be used in bathroom equipment; they are also used in electrical appliances such as circuit breakers, switches and wall plates.

1.5.5 Laminating resins

Urea-formaldehyde resins find application in the production of laminated plastics, and may be produced in all colours by selecting suitable pigments. Paper, wood or cloth can be coloured or printed before impregnation with the resin. Decorative laminates based on phenolic and urea resins find use in table tops, and in office wall and door panels. Translucent urea-formaldehyde laminates are also commonly used in illumination, display and decoration, and can be made fluorescent or phosphorescent by including suitable additives.⁵³

1.6 AIMS OF THE PRESENT INVESTIGATION

This research has been aimed at investigating the relationship between the molecular structure and functional properties of urea-formaldehyde resins. More specifically, the objectives have included the following.

- 1. An investigation of the effects of five parameters, *viz.*, pH, temperature, catalyst, U:F molar ratio and the duration of the reaction, on the structure and properties of urea-formaldehyde resins.
- 2. The preparation and characterisation of basic components of urea-formaldehyde resin reactions.
- The formation of triazone-urea-formaldehyde resins by including triazones as cross-linking agents.
- 4. The synthesis, characterisation and detailed mass spectrometric analysis of triazone analogs.
- Dynamic NMR analysis of urea derivatives to explore the influence of temperature on internal rotation and, hence, the complexity of ¹³C NMR structure spectra of urea derivatives in U-F resins.
- An NMR analysis of factory samples of urea-formaldehyde resins in order to correlate molecular structure with physical properties.

DISCUSSION

In the course of this research, urea-formaldehyde resins were synthesized by heating urea and formaldehyde under varius conditions. The final composition and properties of the resin depend on 5 factors, *viz.*, pH, temperature, U:F molar ratio, the duration of the reaction and the type of catalyst used. The effects of varying the U:F molar ratio are discussed in Section 2.1.1 and the the catalyst in Section 2.1.2. Statistical experimental design methods (Chemometrics) were initiated to investigate the influence of four parameters, concurrently, *viz.*, pH, temperature, U:F molar ratio and time of the urea-formaldehyde resin reaction; the results of this study are discussed in Section 2.2. The synthesis of basic resin components is covered in section 2.3, while section 2.4 deals with triazone derivatives, their synthesis, reactions and mass spectroscopic fragmentation characteristics. A dynamic NMR study, to investigate internal rotation in urea-formaldehyde derivatives, is discussed in Section 2.5 and, finally, Section 2.6 deals with the analysis of industrial U:F resins.

2.1 PRELIMINARY STUDIES

2.1.1 The effect of varying the urea:formaldehyde ratio

One of the factors that affects the performance and properties of urea-formaldehyde resins is the U:F molar ratio, and it has been shown that the nature of the resin components depends on the U:F ratio.^{57,58} To observe the effect of this factor, various resins were synthesized using different U:F ratios.

Following the method of Xia, Hse and Tomita⁵⁴, and using the apparatus shown in Figure 2, U:F ratios of 1:1.5, 1:2.0 and 1:3 were examined. Urea and formaldehyde were heated in a flange flask, the formaldehyde fumes being absorbed by a water scrubber. The thermometer was kept in the flange flask to monitor the temperature of the reaction, and the mixture was continuously stirred during the reaction period. In all cases, the pH of the formaldehyde solution was adjusted to pH 5.0 using sodium hydroxide and dilute sulphuric acid. Urea was then added slowly with constant stirring, and the reaction was initiated by heating the solution to 80 °C, a temperature which was maintained throughout the reaction. On extended heating at this temperature, the reaction mixture solidified. The urea:formaldehyde molar ratio (U:F) was varied and the progress of the reaction was monitored, hourly, by measuring the viscosity at 20 °C using a Haake viscometer. The viscosity of the reaction mixture was found to increase exponentially as the heating continued (see Figure 3). This increase in viscosity is undoubtedly due to the formation of long-chain or cross-linked polymers. Polymerisation is, of course, associated with an increase in the average molecular weight which results in high viscosity.⁵⁵ Chiavarine has reported that,

under slightly acidic conditions and at high temperatures, methylene-linked polymers predominate over other polymers.⁵⁶ The experimental results illustrated in Figure 4 show that the viscosity



urea-formaldehyde reaction

FIGURE 2. Apparatus used for urea-formaldehyde reactions in the laboratory.



FIGURE 3. A plot of viscosity against time in the reaction of urea and formaldehyde (U:F=1:3) at 80°C.



FIGURE 4. Comparative plots of viscosity against time for reactions at 80°C using different U:F ratios

increases with an increase in the proportion of urea present in the reaction mixture. The results illustrated in Figures 3 and 4 also show that the duration of heating has a marked effect on the viscosity and, hence, the composition and properties of the resin. Reactions conducted at lower temperatures take longer to reach the required viscosity; under these conditions, different reactions may take place, affording different components and, thus, resins with different properties. In fact, five parameters, viz_{a} , the pH, the reaction temperature, the duration of the reaction, the U:F molar ratio and the nature of the catalyst have all been found to affect the average structure and properties of urea-formaldehyde resins, and resins with particular properties can be produced by varying these parameters. The results of our studies on the influence of these factors will be discussed in the following and subsequent sections.

2.1.2 Effects of the catalyst

Another important factor influencing the course of urea-formaldehyde reactions is the pH, which is determined by the acid or base catalyst used. Previous workers have shown that, at low pH, methylene-linked polymers are favoured and, conversely, as the pH is increased, the proportion of methylene-linked polymers is decreased.^{59,54,60} It is believed that at high pH, ether-linked polymers are formed. Catalysts such as ammonium sulphate and sodium formate have also been used in the synthesis of urea-formaldehyde resins. The influence of these catalysts was examined in several reactions. In the first reaction, the urea-formaldehyde resin was prepared using a U:F molar ratio of 1:2.8 and ammonium sulphate (30 % solution) as catalyst. The initial pH was 3.40, and the reaction mixture was heated at 95 °C for 30 minutes. The resulting resin was found to be very acidic (pH = 1.05), undoubtedly due to the formation of sulphuric acid. To stop the reaction, the pH was to be adjusted to 7.5-8.5 using sodium hydroxide, but the mixture cured before the required pH could be reached. The reaction was repeated with the mixture being heated for only 15 minutes instead of 30 minutes; the pH of the reaction was adjusted to 8.11 to stop the reaction, and the free formaldehyde was found to be 2.6 %.

The ammonium sulphate catalyst gave a highly acidic reaction mixture which reacts fast to form insoluble polymers. A solution containing molar equivalents of sodium formate and ammonium sulphate was then used to adjust the pH of the urea-formaldehyde solution to 3.90. Urea was added and, on heating at 93 °C, the reaction mixture solidified within 5 minutes.

It was apparent that these catalysts were giving highly insoluble resins of very high molecular

weight, which cannot be softened by further heating.⁵⁴ Consequently, subsequent reactions were conducted using combination of sodium hydroxide and sulphuric acid to adjust the initial pH.

2.2 CHEMOMETRICS

Four parameters, viz., the pH, the U:F molar ratio, the temperature and the duration of the reaction are known to affect the chemical structure and composition and, hence, the performance of urea-formaldehyde resins.⁸⁰ A chemometric study was undertaken to establish the effects of these parameters on U:F resins. Chemometrics is a statistical approach to experimental design permitting the effect of each of the experimental parameters to be investigated and, hence, the experimental conditions to be optimised. The experimental design matrix is summarised in Table 2. The viscosities of the reaction mixtures were measured after 6 hours, and the ¹³C NMR spectra were run after 24 hours. Each experiment was carried out using the method of Hse, Xia and Tomita,⁵⁴ the pH being adjusted using sodium hydroxide and formic acid instead of sulphuric acid in order to limit foreign species in the resin. The resulting viscosities (Table 2) are taken to indicate the extent of resinification and are plotted against experiment number in Figure 5. Experiments 5, 13, 18 and 20 clearly emerge as being particularly significant. From these results it is apparent that two factors are critical in determining the final viscosity, viz., the U:F molar ratio and the reaction temperature. For examples, all reactions conducted at 90 °C using a U:F ratio of 1:2 gave viscosities >0.4 m.Pa.s (cf. experiments 5, 13, 18 and 20), but when the U:F ratio was reduced to 1:4 viscosities of $\langle 0.2 \text{ m.Pa.s} \text{ were obtained } (cf. experiments 8-11, 16 and 1)$ 19). The influence of temperature may be seen by comparing experiments 4 and 5, which were conducted using the same U:F ratio (1:2) and initial pH (8.00); in experiment 5 a viscosity of

Expt.	Temperature	U:F ratio	Reaction	Initial	Viscosity
No.	/°C		time/ min.	pН	/m.Pa.s
1	70.0	1:4	75	8.00	0.11
2	80.0	1:3	60	7.00	0.14
3	70.0	1:4	45	6.00	0.10
4	70.0	1:2	75	8.00	0.18
5	90.0	1:2	45	8.00	0.46
6	80.0	1:3	60	7.00	0.13
7	80.0	1:3	60	7.00	0.13
8	90.0	1:4	45	6.00	0.13
9	90.0	1:4	75	8.00	0.13
10	90.0	1:4	75	6.00	0.11
11	90.0	1:4	45	8.00	0.12
12	70.0	1:2	45	6.00	0.18
13	90.0	1:2	75	6.00	0.42
14	70.0	1:2	45	8.00	0.14
15	80.0	1:3	60	7.00	0.14
16	70.0	1:4	75	6.00	0.11
17	70.0	1:2	75	6.00	0.13
18	90.0	1:2	75	8.00	0.48
19	70.0	1:4	45	8.00	0.11
20	90.0	1:2	45	6.00	0.40

Table 2. Experimental design for determining the influence of four parameters in urea-formaldehyde reactions, viz., pH, reaction time, temperature and U:F molar ratio.

0.46 m.Pa.s was measured after only 45 minutes at 90 °C, whereas experiment 4 gave a viscosity of 0.18 m.Pa.s after 75 minutes at 70 °C. In fact, in none of the experiments conducted at 70 °C or 80 °C did the measured viscosity exceed 0.18 m.Pa.s.

Changing the reaction time from 45 to 75 minutes appears to have little effect on the final viscosity. For example, in experiments 3 and 16, the same experimental conditions were used except that the reaction times were 45 minutes for experiment 3 and 75 minutes for experiment 16, resulting in viscosities of 0.10 and 0.11 m.Pa.s respectively; similarly experiments 5 and 18 gave viscosities 0.46 and 0.48 m.Pa.s respectively. No significant viscosity difference was achieved by changing the initial pH. For example, in experiments 1 and 16, initial pH values were 8.00 and 6.00 respectively, but a viscosity of 0.11 m.Pa.s was obtained for both experiments, while experiments 5 (pH 8.00) and 20 (pH 6.00) gave final viscosities of 0.46 and 0.48 m.Pa.s respectively.

The centre point experiments (2, 6, 7 and 15) confirmed the reproducibility of the results, giving viscosities 0.14, 0.13, 0.13 and 0.14 m.Pa.s respectively. For each experiment in Table 2, the progress of the reaction was monitored by measuring the pH at fixed intervals. The pH was found to decrease as the reaction progressed, as shown in Figure 6; this pattern is attributed to the consumption of urea during polymerisation.

The resins resulting from the experiments detailed in Table 2 were further analysed by ¹H and ¹³C NMR spectroscopy. The ¹H NMR spectra of these resins exhibited broad overlapping signals which could not be used to deduce the structure of the resin - an observation in agreement with



Figure 5. Plot of viscosity against experiment number (Table 2).



Figure 6. Plot of pH against time for experiment 5 (Table 2).

Tomita's work.⁸⁰ The ¹³C NMR spectra, however, were more informative. The resin produced in experiment 5 contains carbonyl carbons due to dimethylolurea and other polymers, as evidenced by signals ca. 159.5 ppm (Figure 7). The carbonyl carbon due to unreacted urea resonates at 161.0 ppm, and the amount of unreacted urea was estimated (from the relative integrals) to be 15%. The proportion of unreacted urea was decreased by heating the reaction mixture for a longer period, as evidenced by the spectrum for experiment 18 (Figure 8), which indicates that, on heating for 75 minutes, the unreacted urea decreased to 10 %. Signals in Figure 7, corresponding to methylene linkages were observed at ca. 47 ppm, and the signal at 55.5 ppm is suspected to be due to methylene linkages at branch points. Methylol carbons attached to secondary and tertiary nitrogens give rise to signals at 65 ppm. Increasing the proportion of formaldehyde clearly reduces the formation of methylene linkages. Consider experiments 5 and 11, in which the same experimental conditions were used except that the U:F molar ratios were 1:4 and 1:2 respectively. The ¹³C NMR spectrum of the resin resulting from experiment 11 (Figure 9), indicates the absence of methylene linkages; the signal at 73.1 ppm is thought to be due to the presence of ether linkages. The ¹³C NMR spectra change little with changing experimental pH, while lowering the reaction temperature resulted in a decrease in methylene linkages and the formation of monomethylolurea 1. Thus, in the spectrum for experiment 5 (Figure 7) small amounts of methylene linkages and monomethylolurea 1 are observed, while the spectrum for experiment 14 (Figure 10) shows signals at 162.2 ppm (due to urea), 160.0 ppm (due to monomethylolurea 1) and at 159.1 ppm (due to dimethylolurea 2 and other polymer forms).



Figure 7. The 100MHz ¹³C NMR spectrum of urea-formaldehyde resin resulting from experiment

5 (Table 2) in DMSO- d_6 .



Figure 8. The 100MHz ¹³C NMR spectrum of urea-formaldehyde resin resulting from experiment

^{18 (}Table 2) DMSO- d_6 .



Figure 9. The 100MHz ¹³C NMR spectrum of urea-formaldehyde resin resulting from experiment





Figure 10. The 100MHz ¹³C NMR spectrum of urea-formaldehyde resin resulting from experiment

14 (Table 2) in DMSO- d_6 .

In summary the chemometric study indicates that the viscosity of the resin and the type of polymer formed depend mainly on the U:F molar ratio and the reaction temperature. The highest viscosities were observed with a U:F molar ratio of 1:2 and a reaction temperature of 90 °C. The initial pH does not appear to exercise a significant effect on the final viscosity or the structure of the resin. Heating the reaction mixture for a longer period reduced the amount of unreacted urea in the resin. Furthermore high viscosity is associated with the formation of methylene linkages and cross-linked polymers in the resin.

2.3 FUNDAMENTAL COMPONENTS PRODUCED IN UREA-FORMALDEHYDE REACTIONS.

2.3.1 Synthesis of monomethylolurea 1, dimethylolurea 2 and methylenediurea 36.

Several components of urea-formaldehyde reactions have been identified. The simplest products are monomethylolurea 1, dimethylolurea 2 and methylenediurea 36, and these were synthesized in the laboratory using Lundlum's method.³⁵ Under basic conditions (using disodium orthophosphate to control the pH), 2 molar equivalents of urea were treated with 1 equivalent of formaldehyde at low temperature (0 °C) to afford monomethylolurea 1 (Scheme 33). An excess of urea was used in order to prevent the formation of dimethylolurea.

$$H_2N-CO-NH_2 + HCHO \xrightarrow{0^\circ C,24 \text{ h}} H_2N-CO-NH-CH_2-OH$$

29 4 1

SCHEME 33

A similar method was employed for the preparation of dimethylolurea 2 but, in this case, excess formaldehyde was used, *i.e.* 2 molar equivalents of formaldehyde and 1 molar equivalent of urea (Scheme 34). Lundlam³⁵ reported that use of this method gave pure dimethylolurea 2. ¹H and ¹³C NMR spectroscopy were used to confirm the formation of monomethylolurea 1 and dimethylolurea 2 in each case. The ¹³C NMR spectrum of monomethylolurea 1 showed the carbonyl carbon to resonate at 158.5 ppm, while the corresponding signal for dimethylolurea 2 appears at 156.9 ppm, the chemical shift difference reflecting the shielding effects of the hydroxy methyl substituents.

Discussion

H₂N-CO-NH₂ + 2 HCHO $\xrightarrow{0^{\circ}C, 24 \text{ h}}$ HO-CH₂-NH-CO-NH-CH₂-OH 29 4 2 SCHEME 34

Methylenediurea 36 was prepared using excess urea in order to prevent the formation of other products. When a 4 molar excess of urea was used, the required product was found to be highly contaminated with dimethylenetriurea.³⁵ However, when 1 molar equivalent of formaldehyde was reacted in acidic medium (using phosphoric acid) with 8 equivalents urea, the desired methylenediurea 36 was obtained in good yield (71.3 %) (Scheme 35). The formation of methylenediurea 36 was confirmed by ¹H and ¹³C NMR analysis.

H₂N-CO-NH₂ + HCHO
$$\stackrel{i)}{ii}$$
 r.t., 24 h
 iii 0°C, 24 h
29 4 36
SCHEME 35

- - -

2.3.2 Silylation of urea and its derivatives 1, 2 and 36.

The mass spectrometric fragmentation patterns of monomethylolurea 1, dimethylolurea 2 and methylenediurea 36 were investigated by low resolution mass spectrometry. However, the mass spectra of these compounds exhibited peaks of higher mass than expected for the molecular ions. The formation of these higher mass species is attributed to the tendency of the urea-formaldehyde compounds to polymerise during analysis. To stabilise the systems, silylated derivatives of urea 29, monomethylolurea 1, dimethylolurea 2 and methylenediurea 36 were prepared using bis(trimethylsilyl)trifluoroacetamide (BSTFA) 83 (e.g. Scheme 84). The method reported by Jan de Wet⁷⁹ was employed, and the silvlated derivatives obtained are detailed in Table 3.

$$\begin{array}{c} O-Si-(CH_{3})_{3} \\ F_{3}C-C=N-Si-(CH_{3})_{3} \\ 29 \\ 83 \\ \end{array}$$

$$\begin{array}{c} i) DMF, EtOAc \\ ii) 40^{\circ}C \\ \downarrow \\ H_{3}C-Si-N-CO-N-Si-CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \\ \end{array}$$

SCHEME 36

Table 3. Silylated products of urea 29, monomethylolurea 1, dimethylolurea 2 and methylenediurea 36

Compound	Silylated product	M ⁺	Structure
urea 29	bis-TMS-U	204	TMS-NHCONH-TMS (84)
monomethylolurea 1	tris-TMS-MMU	306	(TMS) ₂ NCONH-CH ₂ OTMS (85)
dimethylolurea 2	tris-TMS-DMU	336	TMS-OCH ₂ N[TMS]CONHCH ₂ OTMS
			(86)
methylenediurea 36	TMS-MDU	204	TMS-NHCONHCH ₂ NHCONH ₂ (87)

TMS = trimethylsilyl; U = urea; MMU = monomethylolurea; DMU = dimethylolurea; and MDU = methylenediurea.

Jan de Wet⁷⁹ showed that GLC analysis of these silylated derivatives can be used to determine the percentages of urea 29, monomethylolurea 1, dimethylolurea 2 and methylenediurea 36 in U-F resins.

2.4 TRIAZONE-UREA-FORMALDEHYDE RESINS

In the early 80's, urea-formaldehyde resins came under attack because of their tendency to emit formaldehyde.⁶⁸ Several attempts have been made to overcome this problem; these include decreasing the amount of formaldehyde used in the reaction and adding cross-linking agents, such as ammonia and melamine. The high cost of melamine has made its use as a cross-linking agent less attractive. The work done by Pizzi *et al.*⁶⁵ showed that formaldehyde emission can, in fact, be reduced by decreasing the amount of formaldehyde used in the reaction, and urea:formaldehyde ratios as low as 1:0.7 were used successfully. However, low formaldehyde resins are likely to have poor strength as adhesives, low tack, low water tolerance and low reactivity, and thus prove unsuitable for use as adhesives in wood products such as chipboards.

Siimer,^{61,67} observed that the inclusion of ammonia in urea-formaldehyde reactions led to the formation of triazone-urea-formaldehyde resins. Triazone itself has three reactive sites and is likely to increase the formation of cross-linked resins.^{61,67} Cross-linked polymers are known to reduce formaldehyde release and to be cheaper and more resistant to hydrolysis.⁶¹ However, caution must be exercised in the inclusion of triazones in urea-formaldehyde resins for use as adhesives, as too many cross links may result in rigid structures that can fail under stress. In the present study,hexamethylenetetramine was used to generate triazones in urea-formaldehyde resins.

2.4.1 Reaction of urea and formaldehyde in the presence of hexamethylenetetramine

Hexamethylenetetramine, a high melting solid (> 230 °C) which is prepared by reacting ammonia

and formaldehyde,^{66,72} has been used as the cross-linking agent in the formation of cross-linked resins.^{73,74} The work done by Slonin, Arsha and Molatkovas⁶² has shown that triazones can be formed by the inclusion of hexamethylenetetramine in the urea-formaldehyde reaction, and that the resulting resins may be characterised and analysed by ¹³C NMR spectroscopy. In our study hexamethylenetetramine (5% by mass of the urea being used) was mixed with urea and formaldehyde and the reaction mixture was heated at *ca*.95°C for 30 minutes. The¹³ C NMR spectrum of the resulting resin (Figure 11) shows no significant signal between *ca*.156.2 ppm and 155.1 ppm, the region in which Siimer ⁶¹ identified the triazone carbonyl carbons.



FIGURE 11: The 100MHz ¹³C NMR spectrum of the hexamethylenetetramine (5%)-urea-

formaldehyde resin in DMSO- d_6

More hexamethylenetetramine (30 % by mass of urea) was then used. The ¹³C NMR spectrum of the resulting resin (Figure 12) clearly shows the triazone carbonyl carbons at 155.0, 155.8 and 156.0 ppm. Although the spectrum clearly indicates the formation of triazones, not all the hexamethylenetetramine appears to have reacted; the strong characteristic signal at 73.4 ppm suggests the presence of unreacted hexamethylenetetramine.





Triazone-containing urea-formaldehyde resins can also be prepared by using ammonia, urea and formaldehyde under suitable conditions,⁷⁶ and Siimer⁶¹ synthesized various triazone resins by varying the amount of ammonia, formaldehyde and urea. In our study, Siimer's methodology was followed but hexamethylenetetramine was used as a source of ammonia. A urea-formaldehyde-hexamethylenetetramine (1:3:1.5) mixture was heated at 100°C for 16 hours. The¹³ C NMR spectrum of the resulting resin (Figure 13) shows the presence of small amounts of triazones (indicated by the carbonyl carbons at 157.7 and 156.9 ppm); it should be noted that chemical shifts positions may be affected by the type of polymer formed. Inspection of the ¹³C NMR spectrum also reveals the presence of monomethylolurea 1, dimethylolurea 2, methylenediurea 36 and other products of the urea-formaldehyde reaction, while a very intense signal at 73.4 ppm indicates that not all the hexamethylenetetramine had reacted.



FIGURE 13: The 100MHz ¹³C NMR spectrum of the triazone-urea-formaldehyde (1:3:1.5) resin

in DMSO- d_6 .

A series of triazones were synthesised as cross-linking agents in subsequent reactions with formaldehyde.

2.4.2 Synthesis of 5-substituted triazones

Paquin⁷⁶ has shown that 1,2-disubstituted triazones can be prepared from the reaction of aldehyde with ammonia and urea. In the present study, Burke's method⁶⁴ was followed, the 5-substituted triazones being obtained from reactions of primary amines with dimethylolurea 2, as shown in Scheme 37. The 5-substituted triazones 68-73 were obtained in yields ranging from 5 % to 51 % and were all characterised using IR, MS and NMR spectroscopic techniques; compounds 69, 70, 72 and 73 have not been reported previously.



SCHEME 37

The ¹H NMR spectrum of the 5-(2-hydroxyethyl) derivative 68 (Figure 14) shows singlets at *ca*. 4.5 and 6.3 ppm corresponding to the hydroxyl and amide protons respectively. On deuterium exchange (Figure 15), the amide and hydroxyl protons are replaced by deuterium and the 1'- and 2'-methylene groups resonate as clear triplets. The ¹³C NMR spectrum of spectrum of the 5-(2hydroxyethyl) derivative 68 shows the expected signal at *ca*. 154.7 ppm (due to the carbonyl carbon) the methylene carbon signals at 52.0, 59.7 and 61.6 ppm. The triazones 68 - 73 were further characterised by the DEPT, COSY and HETCOR NMR spectra.



in DMSO- d_{6} .



FIGURE 15. The 400 MHz ¹H NMR spectrum of 5(2-hydroxyethyl)triazone derivative 68 in DMSO-d₆

The DEPT spectrum of the 5-*t*-butyl derivative 70 (Figure 16) reveals signals corresponding to the methyl carbons at 28.2 ppm and the methylene carbons at 56.6 ppm, while the COSY spectrum (Figure 17) confirms coupling between the amide protons and the adjacent methylene protons. The HETCOR spectrum (Figure 18) confirms the assignment of the hydrogen-bearing carbons.



FIGURE 17. The COSY spectrum of the 5-t-butyltriazone derivative 70 in DMSO- d_6 .



Using Burke's method,⁶⁴ an attempt was made to synthesize the "parent" triazone 74 (Scheme 38). Equimolar amounts of dimethylolurea 2 and ammonia (25% aqueous solution) were heated together in an autoclave to afford white crystals, shown by NMR and IR spectroscopy to be the expected product 74. The ¹H NMR spectrum of the product in DMSO- d_{6} , revealed singlets at

Discussion

HO-CH₂-NH-CO-NH-CH₂-OH + NH₃ (aq.)
$$\xrightarrow{90 - 100^{\circ}C}$$
 HN NH
2

SCHEME 38

4.55 and 5.43 ppm, corresponding to the methylene and NH protons respectively. The latter were identified by deuterium exchange. The ¹³C NMR spectrum showed the expected carbonyl carbon signal at 159.6 ppm and the methylene carbon signal at 73.7 ppm, while the IR spectrum revealed bands at 3456 and 3314cm⁻¹, due to the amide and amino groups, and a small absorbance in the carbonyl carbon region (*ca*. 1611cm⁻¹). A peak at m/z 141 in the mass spectrum is attributed to subsequent reaction of the expected product 74 (M⁺, m/z 101) during analysis.

Similar attempts to prepare the aniline 76 and the glycine derivative 78 proved unsuccessful. Dimethylolurea 2 was heated under reflux with aniline 75 (Scheme 39). The ¹H NMR spectrum (Figure 19) of the isolated product shows signals in the region corresponding to aromatic protons, but the signal at 4.90 ppm does not integrate for the four, expected methylene protons. Moreover, the IR spectrum shows no NH absorption bands. The product isolated from this reaction has been tentatively identified as the conjugated compound 77.


Glycine 78 and its benzyl ester 80 (prepared by acid catalysed esterification) were each reacted with dimethylolurea 2 (Scheme 40), but without success.



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SCHEME 40
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2.4.3 Mass spectrometric studies of triazone derivatives.

The electron impact (EI) mass spectra of the triazone derivatives (68 - 73) were investigated. The fragmentation pathways were explored using a combination of low resolution and high resolution mass spectrometry. Certain fragmentation patterns are clearly typical of all the triazone derivatives examined, and these are outlined in Scheme 41 and summarised in Table 4.

Discussion



SCHEME 41: Proposed fragmentation pathways for the triazone derivatives 68 - 73; high resolution data (m/z) for specific fragments (Table 4) are followed, in parentheses, by the proposed molecular formula and the calculated molecular mass.

Discussion

Table 4: Mass fragmentation data (m/z) for selected peaks (see Scheme 41) in the electron impact mass spectra of the triazone derivatives 68 - 73; the % relative abundance being indicated in parentheses in each case.



compound	R'	Ion A	Ion B	Ion C	Ion D	Ion E
68	-(CH ₂) ₂ OH	145ª	144	100	101	115ª
		(3.6)	(23.1)	(2.4)	(13.0)	(64.0)
69	-(CH ₂) ₃ CH ₃	157ª	156	100 ^a	113	127ª
		(27.5)	(45.3)	(8.7)	(31.9)	(20.2)
70	-C(CH ₃) ₃	157ª	156	100	113	127
		11.6	(7.6)	(33.6)	(16.6)	(0.5)
71	-CH ₂ CH ₃	129ª	128	100	85	99
		(30.2)	(100)	(3.0)	(66.4)	(28.6)
72	-CH(CH ₃) ₂	143ª	142	100	99ª	113
		(13.0)	(28.7)	(2.6)	(24.2)	(10.6)
73	-CH ₂ -Ph	191ª	190	100	147	161
		(1.9)	(10.5)	(78.8)	(5.7)	(1.9)

Ion fragmentation types

^aMolecular formula supported by high-resolution mass spectrometric analysis.

Table 4 continued.

compound	R'	Ion F	Ion G	Ion H	Ion I	Ion J
68	-(CH ₂) ₂ OH	114	115	56	85	83
		(100)	(64)	(64.8)	(86.5)	(5.4)
69	-(CH ₂) ₃ CH ₃	114ª	127ª	56ª	85ª	83
		(89.1)	(20.2)	(56.2)	(83.3)	(2.8)
70	-C(CH ₃) ₃	114	127	56	85	83
		(1.5)	(0.5)	(58.2)	(10.9)	(2.4)
71	-CH ₂ CH ₃	114	116	56	85	83ª
		(9.6)	(0.2)	(44.8)	(66.4)	(5.5)
72	-CH(CH ₃) ₂	114	113	56	85	83
		(0.9)	(10.6)	(62.8)	(9.9)	(3.4)
73	-CH ₂ -Ph	114	161	56	85	83
		(0.9)	(1.9)	(12.1)	(9.1)	(5.8)

Ion fragmentation types

^aMolecular formula supported by high-resolution mass spectrometric analysis

.

Ion types A,B, E, D and G retain the substituents R' (\equiv RCH₂), and hence, the *m/z* values are characteristic of the compounds examined (68 - 73). In the remaining ion types, however, the R' substituents have been lost and the fragments exhibit common *m/z* values, irrespective of the compound examined. It is proposed that, in all cases, the molecular ion (M⁺) loses a hydrogen atom to afford the resonance stabilised cations B(or B'), which then undergoes rearrangement to afford cations I and H. The subsequent loss of H₂ from ion I affords the diimino species J. Loss of RCH₂ or formaldehyde from the molecular ion A yields, the common fragments C and the odd electron species E respectively. An iminonium cation F results from the loss of R. from the molecular ion A.

The various fragmentation patterns may be explained in terms of the formation of well-stabilised fragments. Thus, the molecular ion A is likely to lose a methylene proton adjacent to a nitrogen, to afford the resonance stabilised cations B or B' (Scheme 42). The loss of the radical R'· (\equiv RCH₂·) from the molecular ion A accounts for the formation of the even electron species C (Scheme 43).

Discussion



SCHEME 42



Four, important rearrangements involving fragmentation of the heterocyclic ring are apparent. In the first, the loss of a neutral imine, RCH=NH, from ion **B** affords the diazolium cation **I**, which leads to the cation J via elimination of H₂ (Scheme 44). In the second, fission of ion **B** results in the formation of the resonance stabilised aziridine species **H** (Scheme 45).



In the third and fourth rearrangements, fission of ion **B** proceeds with the loss of the neutral molecules, HN=C=O and $HN=CH_2$, resulting in the formation of the cations **D** (Scheme 46) and **G** (Scheme 47) respectively.





In the case of the 5-benzyl derivative 73, additional fragmentations characteristic of the benzyl substituent were investigated and the proposed fragmentations, which are all supported by high resolution data, are shown in Scheme 48.



SCHEME 48. Additional fragmentation patterns proposed for the 5-benzyl derivative 73; high -resolution analyses (m/z) determined for individual ions are followed, in parentheses, by the proposed formula and the corresponding calculated mass. Formation of the resonance-stabilised cations K, I and M (Scheme 49) are all proposed to involve fission of the heterocyclic ring, and the concomitant loss of neutral, four- or five- membered ring systems from ion Q (\equiv ion type B; Scheme 49) and the molecular ion P (\equiv ion type A) respectively.





Benzylic cleavage was also observed in the low resolution mass-spectrum with the formation of the resonance-stabilised cation \mathbf{O} and the aromatic tropylium cation \mathbf{N} , loss of acetylene from the tropylium cation \mathbf{N} then accounting for the carbocation \mathbf{R} . The formation of the odd electron species \mathbf{O} is attributed to the rearrangement outlined in (Scheme 50).



2.4.4 Reactions of triazones with formaldehyde

Selected triazones were reacted with formaldehyde in order to establish the identity of the products which might be formed when such compounds are used in urea-formaldehyde reactions. In the first reaction, "urea-formaldehyde concentrate-85" (comprising 60 % formaldehyde, 25 % urea and water), urea and ethylamine (71 % aqueous solution) were mixed together. After the mixture had been heated at 71°C for 95 minutes, the normal products of urea-formaldehyde reaction products were observed, together with methylolated 5-ethyl triazone derivatives. These components were detected in the ¹³C NMR spectrum (Figure 20). The triazone carbonyl carbons resonating at 155.4, 155.6 and 155.9 ppm are attributed to the 5-ethyltriazone 71 and its mono- and dimethylolated derivatives **88** and **89** respectively (Scheme 51). The excess formaldehyde may also cause methylolation of the urea, and the signals at 158.7, 158.9 and 159.0 ppm are attributed to urea **29** and its mono- and dimethylolated derivatives **1** and **2** respectively (Scheme 51). The ratio of urea-formaldehyde products to the triazone was found to be 1:1, estimated from the relative integrals. Further heating resulted in polymerisation.







The 5(2-hydroxyethyl)triazone 68 was reacted with a 3 molar excess of 40 % formaldehyde to afford a mixture of methylolated triazone derivatives, including 90 and 91 (Scheme 52). The carbonyl carbons at 154.1, 154.5, 54.6, 154.7, 155.6 and 155.7 ppm (Figure 21) are undoubtedly due to the carbonyl carbons of the methylolated triazone systems, suggesting the presence of monomethylolated, dimethylolated and polymeric triazones.

Similarly, treatment of the 5-*t*-butyltriazone 70 with a 3 molar excess of 40 % formaldehyde solution, resulted in the formation of methylolated triazone derivatives. The signal observed at 155.4 ppm in the ¹³C NMR spectrum of the resin is attributed to the unreacted 5-*t*-butyl-triazone, and integration of the carbonyl region indicated more than 90% of the triazone present to be methylolated (assuming comparable relaxation time for the carbonyl carbons).

Discussion



SCHEME 52



5-(2-hydroxyethyl) triazone 68 with a 3 molar excess of formaldehyde, in DMSO- d_6 .

Guanidine has 5 reactive hydrogens and its inclusion in the urea-formaldehyde reaction is expected to result in the formation of cross-linked polymers. Guanidine nitrate is known to react with acetaldehyde and ammonia to give the triazine derivative 95 (Scheme 53),⁷⁶ which contains 4 reactive hydrogens. Cyanoguanidine resins are prepared by reacting cyanoguanidine with formaldehyde under acidic conditions, and these resins are widely used as polymer coagulants.^{77,78} In an attempt to synthesize guanidine-formaldehyde resins, a 4 molar excess of 40 % aqueous formaldehyde was heated together with guanidine acetic acid salt. The product was analysed by ¹³C NMR spectroscopy, and exhibited more signals than expected; further investigation of this resin will require careful separation of all the components.



2.5 VARIABLE TEMPERATURE STUDIES

As mentioned earlier, urea-formaldehyde resins are best analysed by ¹³C NMR spectroscopy. However, amide substituents are known to undergo site exchange which, depending on the temperature may result in an increase in the number of NMR signals. In the ¹H NMR spectrum of $N_{,N}$ -dimethylformamide, the two methyl groups resonate as a time-averaged singlet at room temperature; at low temperature, the two, non-equivalent methyl groups tend to give separate singlets. This phenomenon is associated with the partial double-bond character of the N-C(O) bond in amides, which inhibits internal rotation (Figure 22).⁸¹ Similarly, the amide groups in ureaformaldehyde resins may undergo slow site-exchange resulting in splitting of the signals in both the ¹H and ¹³C NMR spectra. To investigate this behaviour, the ¹H and ¹³C NMR spectra of monomethylolurea 1, dimethylolurea 2, methylenediurea 36, $N_{,N}$ -dimethylolurea 92, $N_{,N}$ dimethylolurea 93, and methylurea 94 were studied at different temperatures in methanol- d_4 . Representative spectra for selected compounds are illustrated in Figures 24, 25 and 26; a full set of spectra appear in the experimental section.



FIGURE 22. Delocalisation in N,N-dimethylformamide inhibiting internal rotation about the N-C(O) bond.

2.5.1 Methylenediurea 36.

At the normal probe temperature (303 K), the ¹H NMR spectrum of methylenediurea **36** shows a singlet at 4.41 ppm due to the methylene protons. At low temperature, the methylene singlet splits into two, discrete signals, one at 4.40 ppm and the other at 4.37 ppm (Figure 24). The partial spectra illustrated in Figure 24 reveal that the two methylene signals do not have the same intensity, indicating that one conformer is more stable than the other. Due to symmetry in the molecule, there are only two non-equivalent rotors, *viz.*, a(=d) and b(=c) (see Figure 23). Site exchange involving the H₂N-C(O) rotors (a=d) gives rise to equivalent rotamers, but rotation about the CH₂NH-C(O) bands (b=c) involves the non-equivalent rotamers **36a** and **36b** (Scheme 54), responsible for the two, methylene signals at low temperature. Rotamer **36a** is expected to





be more stable than 36b due to strong hydrogen bonding between the anionic oxygen and the amide hydrogen. The integral ratio for the two methylene peaks at 196 K (2.27:1) reflects the rotamer ratio (36a:36b) at this temperature. The ¹³C NMR spectrum did not show the expected splitting of the carbonyl and methylene carbons, but broadening of the signals was observed as the temperature was decreased.



SCHEME 54



FIGURE 24. Partial 400 MHz ¹H NMR spectra of methylenediurea 36 in methanol- d_6 at different temperatures.

2.5.2 *N*,*N*'-Dimethylurea (92)

The *N*-methyl signal (a 6 proton singlet at 303 K) in the ¹H NMR spectrum of N,N° -dimethylurea 92 broadens and splits as the temperature is lowered. At 206 K, three discrete methyl signals are apparent (Figure 25). The possible rotamers (92a, 92b, 92c and 92d) are shown in Scheme 55.



SCHEME 55

In rotamer 92a, the *N*-methyl groups are equivalent and, at ≤ 206 K, are proposed to give rise to the singlet at *ca.* 2.65 ppm. Rotamers 92b and 92c are equivalent, each containing a pair of nonequivalent *N*-methyl groups which give rise to the signals at *ca.* 2.63 and 2.69 ppm. While the rotamers 92b and 92c may be stabilised by intramolecular hydrogen bonds, the steric interference between the syn-orientated hydrogen atoms and the methyl groups is expected to reduce their stability. The steric interaction between the two methyl groups in rotamer 92d would be even more severe and, we suggest, effectively inhibits formation of this rotamer. Such steric interaction is absent in rotamer 92a and integration of the signals reveals a predominance of this rotamer [*i.e.* 92a:(92b + 92c)::3:2]. The ¹³C NMR spectrum of *N*,*N*-dimethylurea 92 at 196K, shows two carbonyl signals at ca.162.5 and 162.6 ppm, corresponding to rotamers 92a and 92 b (=92c) (Figure 26). The methyl carbons resonate as doublets at ca.27.0, 27.2 and at 27.8 ppm with respective, relative integrals of 3:1:1. The more stable rotamer 92a is responsible for the signal at ca. 27.0 ppm, while the signals at ca. 27.8 and 27.2 ppm correspond to the non-equivalent Nmethyl groups in rotamers 92b and 92c; the integral ratios confirming the 3:2 predominance of rotamer 92a over rotamers 92b and 92c.



FIGURE 25. Partial 400 MHz ¹H NMR spectra of $N_{,N}$ dimethylurea 92 in methanol- d_4 at

different temperatures.



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2.5.3 *N*-Methylurea (94)

At low temperature 273 K, the methyl proton signal for *N*-methylurea splits into two signals and, at 196 K, the integral ratio was found to be 1:3.5. The more intense, high-field signal, is assigned to the hydrogen-bonded rotamer 94b (Scheme 56), the low-field signal to rotamer 94a, the latter assignment being consistant with anisotropic deshielding by the carbonyl group. The ¹³C NMR spectrum at 196 K shows splitting of the carbonyl carbon signals, with signals at *ca*. 163.1 and 163.6 ppm, the integral ratio being 3:1. At 196 K, the methyl group resonates as a pair of doublets at *ca*. 28.4 and 26.8 ppm. These observations are consistant with the presence of the two rotamers 94a and 94b.



SCHEME 56

2.5.4 N,N-Dimethylurea (93)

At low temperature (196 K), the methyl proton signal broadens but does not split. However, in the ¹³C NMR spectrum at the same temperature, clear splitting of the methyl signal occurs with a pair of doublets being observed at *ca*.36.8 and 36.2 ppm with an integral ratio 1:1. The expected, equivalent rotamers are shown in Scheme 57.



SCHEME 57

2.5.5 Monomethylolurea (1)

At ambient temperature (303 K), the ¹H NMR spectrum of *N*-monomethylolurea shows a methylene singlet at 4.60 ppm, attributed to rotamer **1b**, and a less intense signal at 4.63 ppm, attributed to rotamer **1a** (Scheme 58). Intramolecular hydrogen bonding is expected in both rotamers but, charge stabilisation appears to be more efficient in **1b**, and rotamer is assumed to predominate. At 236.8 K the two singlets split further, the signal at 4.63 ppm splitting into two singlets of equal intensity (at 4.63 and 4.64 ppm), while the signal at *ca*.4.60 ppm splits into an intense signal at 4.60 ppm and a very weak signal at 4.54 ppm. The ¹³C NMR spectrum, however, shows no splitting of either the carbonyl or the methylene carbons, even at 196 K.



SCHEME 58

2.5.6 N,N'-Dimethylolurea (2)

No splitting was observed in either the ¹H or ¹³C NMR spectra of N,N-dimethylolurea at low temperature (196 K). This is attributed to the formation of the strongly hydrogen bonded structure illustrated in Figure 27.



FIGURE 27

In conclusion, the resin sample was run at different temperatures (303 K, 323 K and 353 K) and no change was observed. Rotation may be slowered by polymeric systems and hence, rotational isomerism is not a major factor in urea-formaldehyde resins.

2.6 NMR ANALYSIS OF FACTORY SAMPLES

Eight urea-formaldehyde resin samples from the factory were analysed using both ¹H and ¹³C NMR spectroscopy, in order to establish the functional groups present and, hence, attempt to correlate the molecular structure with the physical properties of the resin. The samples were dissolved in deuterated dimethylsulphoxide (DMSO- d_6) and the ¹H and ¹³C spectra were calibrated using the solvent signals; the viscosities were measured using a Haake viscometer. The samples gave very different viscosity values, ranging from 107.0 to 298.8 m.Pa.s (see Table 5, p. 139); the ¹H and ¹³C NMR spectra, however, proved to be rather similar.



DMSO- d_{6} .

The ¹H NMR spectrum of sample #1 (Figure 28) reveals signals 6.79 ppm, due to NH groups, at 5.76 and 5.65 ppm, due to -NH₂ groups (indicating the presence of urea 29, monomethylolurea 1 and methylenediurea 2), at 5.52 ppm, due to OH, and at ca. 4.5 ppm, due to methylene protons. The strong signal at 3.96 ppm is attributed to the presence of water in the resin mixture. The 13 C NMR spectrum of samples #1 is shown in Figure 29. The signal at 46.2 ppm indicates the presence of methylene linkages, while the signal at 53.0 ppm is attributed to methylene linkages at branch points. The presence of methylol groups attached to the nitrogen is indicated by the signals at 64.2 and 64.3 ppm, while the small signals at 70.5 and at 68.4 ppm indicate the formation of the NHCH₂OCH₂ group. In the carbonyl region, signals due to monomethylolurea 1 (at ca. 159.8 ppm), urea 29 (at ca. 161.4 ppm) and dimethylolurea 2 and other polymer forms (at ca. 158.4 ppm) are apparent. Integration of the signals idicates a relatively high proportion of unreacted urea, suggesting that a low formaldehyde formulation was used for the synthesis of The presence of methylene linkages suggests the presence of methylene-linked the resin. polymers, and cross-linked polymers are indicated by the presence of methylene-linkages at branch points. The ¹H and ¹³C NMR spectra for the resins with high viscosity and the resins with low viscosity exhibited similar patterns. However, integration of the spectra for the high viscosity samples indicated an increase in methylene linkages at branch points, confirming an increase in the cross-linked polymers in these resins. The ¹H and ¹³C NMR signals were assigned using the data reported by de Wet,^{87,79} Tomita⁸⁰ and Ebdon.³³



DMSO- d_{6}

2.7 CONCLUSIONS

During the course of this research, a range of urea-formaldehyde resins have been prepared by heating mixtures of urea and formaldehyde under various conditions. The final composition and the physical properties of the resins have been found to depend on 5 parametes, *viz.*, the catalyst, pH, temperature, U:F molar ratio and the duration of the reaction. A chemometric study of the influence of 4 of these parameters, *viz.*, pH, U:F molar ratio, temperature and time, showed that the final viscosity of the resin is most sensitive to the U:F molar ratio and the results provide patterns for the optimisation of reaction conditions. Basic components in urea-formaldehyde resins have been synthesized and characterised by NMR spectroscopy, while cross-linked triazone-urea-formaldehyde resins, prepared by reactions of hexamethylenetetramine, urea and formaldehyde, have also been analysed by NMR spectroscopy. A series of triazone derivatives , some of which are novel, have been prepared from the reaction of dimethylolurea with primary amines, and the mass fragmentation patterns of these heterocyclic systems were successfully investigated using both the low and high resolution mass spectrometry. Selected triazone derivatives were treated with excess formaldehyde to afford methylolated triazones.

Six selected urea derivatives have been subjected to Dynamic NMR analysis in order to explore the possible effects of internal rotation of the amide groups on the interpretation of the ¹H and ¹³C NMR spectra of the resin samples, and the samples were analysed at temperatures between 303 K and 196 K. Splitting was observed at low temperature (≤ 257.0 K), suggesting that, ureaformaldehyde resins would be best analysed at the normal probe temperature (303 K) or higher. Urea-formaldehyde resin samples obtained from the factory have been also analysed using ¹H and ¹³C NMR spectroscopy in order to correlate the molecular structure and physical properties in urea-formaldehyde resins. These spectra were run at 303 K, but similar spectra was observed in all the samples. The various aims of the investigation have thus been addressed.

Aspects of this project which warrant further research include the following:-

- 1. An extension of the chemometric study to permit optimisation of the experimental conditions for the production of urea-formaldehyde resins having desired properties.
- 2. Methylolation of triazone analogs and the separation and characterisation of the methylolated products.
- 3. An investigation of the use of guanidine in reactions with formaldehyde.

3 EXPERIMENTAL

3.1 GENERAL

400 MHz ¹H and 100 MHz ¹³C NMR spectra were recorded on a Bruker AMX 400 instrument. Chemical shifts are quoted on the δ scale and are referenced using solvent peaks [$\delta_{H} = 7.25$ ppm (CHC1₃) and $\delta_{C} = 77.0$ ppm (CDCl₃); $\delta_{H} = 2.5$ ppm (DMSO) and $\delta_{C} = 39.4$ ppm (DMSO- d_{6}); and $\delta_{H} = 3.30$ ppm (CH₃OH) and $\delta_{C} = 49.05$ ppm (CD₃OD); coupling constants (*J*) are given in Hertz (Hz). Infra-red spectra were recorded on Perkin-Elmer 180 and Perkin Elmer FTIR spectrum 2000 spectrometers using KBr discs or hexachlorobutadiene mulls. Low resolution mass spectra were recorded on a Hewlett Packard 5988A instrument, while high resolution mass spectra were obtained on a Kratos MS80RF double focusing magnetic sector instrument (Cape Technicon Mass Spectrometry Unit). Melting points were determined on a Kofler hot-stage apparatus, and are uncorrected. Reverse-phase chromatography was carried out using C₁₈ silica gel. Solvents and commercially available reagents were purified, when necessary, by standard techniques.⁸² Viscosity was measured at 20 °C using a Haake viscometer, the temperature being maintained by circulating water from a constant temperature bath. The resin was allowed to stand at 20 °C for 15 minutes to equilibrate the temperature before measuring the viscosity.

Gas-chromatography mass spectrometry analyses were conducted on a Hewlett Packard 5980A mass spectrometer, using an OV-17 column (30 m) and 0.5 μ l injections. The following operating conditions were used:

Initial temperature	65 °C for 30 minutes
Rate	10 °C/minute

final temperature 240 °C.

3.1.1 Analytical procedures

Aqueous formaldehyde free solution (75 ml) was placed in a 250 ml conical flask, followed by the addition of *ca*.3 drops of thymol phthalein. The solution was titrated with 1 M hydrochloric acid to achieve a colour change from blue to pale blue. The temperature of the solution was then decreased to 0 $^{\circ}$ C by adding ice. The resin sample (5 g) was then added, and the solution allowed to stand at room temperature for 3 minutes. The resulting solution was titrated using the standardised 1 M hydrochloric acid to a pale blue colour.

The formaldehyde free solution was prepared from 10 g sodium sulphite, 33 ml of 1,4 dioxane and 55.8 ml of deionised water.

3.2 PREPARATION PROCEDURES

3.2.1 Preliminary U-F resin reactions

Urea-formaldehyde resin **A***: using a urea:formaldehyde molar ratio of 1:3.*

Aqueous formaldehyde solution (40 %; 200 ml, 2.90 mol) was placed in a 500 ml flange flask, fitted with a condenser connected to a water scrubber, an overhead stirrer and a pH electrode (as shown by Figure 2, p 42). The pH of the formaldehyde solution was adjusted to 5.0 using dilute sulphuric acid and 10 % sodium hydroxide solution. Urea (58.3 g, 0.97 mol) was then added to the stirred solution in 15 equal parts at 1 minute intervals. After the addition of urea was complete, the mixture was heated at 80 °C in a constant temperature water bath for 60 minutes.

After this period, a sample was removed and the viscosity measured immediately at 20 °C. The reaction was continued by heating the reaction mixture at 80 °C, measuring the viscosity every 60 minutes, until a very viscous resin was obtained. At the end of the reaction, viscosity values were plotted against time as shown by Figures 3 and 4 (pp. 41, 42 respectively).

Urea-formaldehyde resin **B**: using a urea:formaldehyde molar ratio of 1:2.

The same experimental procedure employed for the preparation of U-F resin A (U:F::1:3) was followed, using aqueous formaldehyde (38 %; 350 ml, 4.48 mol). The pH the of formaldehyde solution was adjusted to 5.0 using 10 % sodium hydroxide solution and dilute sulphuric acid before adding urea (134 g, 2.24 mol). The temperature was maintained at 80 °C for 60 minutes before measuring the viscosity of a sample at 20 °C. The reaction was continued by heating the reaction mixture at 80°C, measuring the viscosity every 60 minutes until a very viscous resin resulted. At the end of the reaction, viscosity values were plotted against time as shown in Figure 4.

Urea-formaldehyde resin C: using a urea: formaldehyde molar ratio of 1:1.5.

The same experimental procedure employed for the preparation of U:F resin A (U:F::1:1.5) was followed, using aqueous formaldehyde (38 %; 200 ml, 2.56 mol). The pH of the formaldehyde solution was adjusted to 5.0 using 10 % sodium hydroxide solution and dilute sulphuric acid before adding urea (102.7 g, 1.71 mol). The temperature was maintained at 80 °C for 60 minutes before measuring the viscosity of a sample at 20 °C. The reaction was continued by heating the reaction mixture at 80 °C, measuring the viscosity every 60 minutes until a very viscous resin resulted. At the end of the reaction, viscosity values were plotted against time as shown by

Figure 4.

Urea-formaldehyde reaction using ammonium sulphate.

Aqueous formaldehyde solution (38 %; 50 ml, 0.64 mol) was placed in a 500 ml flange flask fitted with the condenser connected to a water scrubber, a pH electrode and an overhead stirrer as shown in Figure 2 (p.41). Urea (13.7 g, 0.23 mol) was then added with constant stirring to the formaldehyde solution until a clear solution was obtained; the pH of the resulting solution was found be 4.90, which was decreased to 3.40 using a 30 % (m/v) aqueous solution of ammonium sulphate. The resulting mixture was heated at 95-96 °C for 30 minutes, after which time the pH was found to be 1.05. To block the reaction, an attempt was made to raise the pH to 7.5. At pH 2.5, however, the resin solution became too viscous for any further analysis.

The reaction was repeated using the same experimental procedure and quantities, but heating the mixture for 15 minutes. A very low pH of 1.00 was obtained, and the reaction was quenched by adjusting the pH to 8.11. The resulting mixture was found to contain 2.60 % free formaldehyde.

Urea-formaldehyde reaction using sodium formate and ammonium sulphate.

Aqueous formaldehyde solution (40 %; 50 ml, 0.73 mol) was placed in a flange flask, fitted with a condenser connected to a water scrubber, a pH electrode and an overhead stirrer. Urea (15.6 g, 0.26 mol) was added with stirring. The pH of the resulting solution was adjusted to 3.90 using a solution of equimolar in sodium formate and ammonium sulphate. The stirred mixture was heated at 93 °C for 5 minutes, to give a viscous and insoluble resin.

3.2.2 Urea-formaldehyde reactions for the chemometric study

The experiments were designed based on 4 parameters, *viz.*, pH, reaction time, U:F molar ratio and temperature and were carried out in the random sequence as shown in Table 2 (p. 45). All the experiments were conducted in a flange flask fitted with a condenser connected to a water scrubber. The reaction mixture was stirred constantly, and the pH was monitored as the reaction progressed. The viscosity was measured 6 hours after completing the reaction, and the resulting viscosities for each experiment are listed in Table 2. The ¹³C NMR spectra for the resulting resins were recorded 24 hours after completing the reaction.

Experiment 1

Aqueous formaldehyde (40 %; 150 ml, 2.18 mol) was placed in the reaction vessel, and the pH of the solution was adjusted to 8.00 at 22.5 °C using 10 % sodium hydroxide solution and formic acid. Urea (32.7 g, 0.54 mol) was added in 15 equal parts at 1 minute intervals with constant stirring at room temperature. After the addition of urea was complete, the pH of the mixture was 8.12 and the temperature was 19.5 °C. The flask was lowered into a pre-heated, thermostatted oil bath and the mixture was heated at 70 °C for 75 minutes. The pH was measured at 5 minute intervals and at the end of the reaction, the pH was 6.38. The viscosity was found to be 0.11 m.Pa.s.

Experiment 2

The experimental procedure employed in experiment 1 was followed, using formaldehyde (40 %; 150 ml, 2.18 mol). The pH was adjusted to 7.00 at 22.6 °C and urea (43.6 g, 0.73 mol) was added. After the addition of urea was complete, the pH of the mixture was 7.34 and the

temperature was 17.0 °C. The mixture was heated at (80 °C), for 60 minutes. The pH was measured at 5 minute intervals and, at the end of the reaction, the pH was 6.23. The viscosity was found to be 0.14 m.Pa.s.

Experiment 3

The experimental procedure employed in experiment 1 was followed, using formaldehyde (40 %; 150 ml, 2.18 mol). The pH was adjusted to 6.00 at 21.5 °C and urea (32.7 g, 0.54 mol) was added. After the addition of urea was complete, the pH of the mixture was 6.83 and the temperature was 16.5 °C. The mixture was heated at 70° C, for 45 minutes. The pH was measured at 5 minute intervals and, at the end of the reaction, the pH was 6.36. The viscosity was found to be 0.10 m.Pa.s.

Experiment 4

The experimental procedure employed in experiment 1 was followed, using formaldehyde (40 %; 150 ml, 2.18 mol). The pH was adjusted to 8.00 at 23.9 °C and urea (65.5 g, 1.09 mol) was added. After the addition of urea was complete, the pH of the mixture was 8.03 and the temperature was 13.8 °C. The mixture was heated at 70° C, for 75 minutes. The pH was measured at 5 minute intervals and, at the end of the reaction, the pH was 6.38. The viscosity was found to be 0.18 m.Pa.s.

Experiment 5

The experimental procedure employed in experiment 1 was followed, using formaldehyde (40 %; 150 ml, 2.18 mol). The pH was adjusted to 8.00 at 23.3 °C and urea (65.5 g, 1.09 mol) was
added. After the addition of urea was complete, the pH of the mixture was 8.14 and the temperature was 14.3 °C. The mixture was heated at 90 °C, for 45 minutes. The pH was measured at 5 minute intervals and, at the end of the reaction, the pH was 6.10. The viscosity was found to be 0.46 m.Pa.s.

Experiment 6

The experimental procedure employed in experiment 1 was followed, using formaldehyde (40 %; 150 ml, 2.18 mol). The pH was adjusted to 7.00 at 23.2 °C and urea (43.6 g, 0.73 mol) was added. After the addition of urea was complete, the pH of the mixture was 7.45 and the temperature was 15.9 °C. The mixture was heated at 80° C, for 60 minutes. The pH was measured at 5 minute intervals and, at the end of the reaction, the pH was 6.15. The viscosity was found 0.13 m.Pa.s.

Experiment 7

The experimental procedure employed in experiment 1 was followed, using formaldehyde (40 %; 150 ml, 2.18 mol). The pH was adjusted to 7.00 at 21.4 °C and urea (43.6 g, 0.73 mol) was added. After the addition of urea was complete, the pH of the mixture was 7.56 and the temperature was 15.2 °C. The mixture was heated at 80 °C, for 60 minutes. The pH was measured at 5 minute intervals and, at the end of the reaction, the pH was 6.21. The viscosity was found to be 0.13 m.Pa.s.

The experimental procedure employed in experiment 1 was followed, using formaldehyde (40 %; 150 ml, 2.18 mol). The pH was adjusted to 6.00 at 23.2 °C and urea (32.7 g, 0.54 mol) was added. After the addition of urea was complete, the pH of the mixture was 7.03 and the temperature was 17.1 °C. The mixture was heated at 90° C, for 45 minutes. The pH was measured at 5 minute intervals and, at the end of the reaction, the pH was 5.65. The viscosity was found to be 0.13 m.Pa.s.

Experiment 9

The experimental procedure employed in experiment 1 was followed, using formaldehyde (40 %; 150 ml, 2.18 mol). The pH was adjusted to 8.00 at 23.5 °C and urea (32.7 g, 0.54 mol) was added. After the addition of urea was complete, the pH of the mixture was 8.02 and the temperature was 18.0 °C. The mixture was heated at 90° C, for 75 minutes. The pH was measured at 5 minute intervals and, at the end of the reaction, the pH was 5.81. The viscosity was found to be 0.13 m.Pa.s.

Experiment 10

The experimental procedure employed in experiment 1 was followed, using formaldehyde (40 %; 150 ml, 2.18 mol). The pH was adjusted to 6.00 at 18.0 °C and urea (32.7 g, 0.54 mol) was added. After the addition of urea was complete, the pH of the mixture was 7.08 and the temperature was 11.0 °C. The mixture was heated at 90° C, for 75 minutes. The pH was measured at 5 minute intervals and, at the end of the reaction, the pH was 5.73. The viscosity was found to be 0.11 m.Pa.s.

The experimental procedure employed in experiment 1 was followed, using formaldehyde (40 %; 150 ml, 2.18 mol). The pH was adjusted to 8.00 at 16.0 °C and urea (32.7 g, 0.54 mol) was added. After the addition of urea was complete, the pH of the mixture was 8.15 and the temperature was 10.0 °C. The mixture was heated at 90° C for 45 minutes. The pH was measured at 5 minute intervals and, at the end of the reaction, the pH was 6.13. The viscosity was found to be 0.12 m.Pa.s.

Experiment 12

The experimental procedure employed in experiment 1 was followed, using formaldehyde (40 %; 150 ml, 2.18 mol). The pH was adjusted to 6.00 at 24.5 °C and urea (65.5 g, 1.09 mol) was added. After the addition of urea was complete, the pH of the mixture was 7.80 and the temperature was 14.0 °C. The mixture was heated at 70° C for 45 minutes. The pH was measured at 5 minute intervals and, at the end of the reaction, the pH was 6.21. The viscosity was found to be 0.18 m.Pa.s.

Experiment 13

The experimental procedure employed in experiment 1 was followed, using formaldehyde (40 %; 150 ml, 2.18 mol). The pH was adjusted to 6.00 at 18.0 °C and urea (65.5 g, 1.09 mol) was added. After the addition of urea was complete, the pH of the mixture was 7.54 and the temperature was 7.0 °C. The mixture was heated at 90 ° C for 75 minutes. The pH was measured at 5 minute intervals and, at the end of the reaction, the pH was 5.92. The viscosity was found to be 0.42 m.Pa.s.

The experimental procedure employed in experiment 1 was followed, using formaldehyde (40 %; 150 ml, 2.18 mol). The pH was adjusted to 8.00 at 25.8 °C and urea (65.5 g, 1.09 mol) was added. After the addition of urea was complete, the pH of the mixture was 8.20 and the temperature was 14.0 °C. The mixture was heated at 70 °C, for 45 minutes. The pH was measured at 5 minute intervals and, at the end of the reaction, the pH was 6.44. The viscosity was found to be 0.14 m.Pa.s.

Experiment 15

The experimental procedure employed in experiment 1 was followed, using formaldehyde (40 %; 150 ml, 2.18 mol). The pH was adjusted to 7.00 at 23.5 °C and urea (43.6 g, 0.73 mol) was added. After the addition of urea was complete, the pH of the mixture was 7.34 and the temperature was 15.9 °C. The mixture was heated at 80 °C, for 60 minutes. The pH was measured at 5 minute intervals and, at the end of the reaction, the pH was 6.20. The viscosity was found to be 0.14 m.Pa.s.

Experiment 16

The experimental procedure employed in experiment 1 was followed, using formaldehyde (40 %; 150 ml, 2.18 mol). The pH was adjusted to 6.00 at 24.0 °C and urea (32.7 g, 0.54 mol) was added. After the addition of urea was complete, the pH of the mixture was 7.48 and the temperature was 18.0 °C. The mixture was heated at 70° C, for 60 minutes. The pH was measured at 5 minute intervals and, at the end of the reaction, the pH was 6.35. The viscosity was found to be 0.11 m.Pa.s.

The experimental procedure employed in experiment 1 was followed, using formaldehyde (40 %; 150 ml, 2.18 mol). The pH was adjusted to 6.00 at 23.1 °C and urea (65.5 g, 1.09 mol) was added. After the addition of urea was complete, the pH of the mixture was 7.33 and the temperature was 17.0 °C. The mixture was heated at 70 °C, for 75 minutes. The pH was measured at 5 minute intervals and, at the end of the reaction, the pH was 6.25. The viscosity was found to be 0.13 m.Pa.s.

Experiment 18

The experimental procedure employed in experiment 1 was followed, using formaldehyde (40 %; 150 ml, 2.18 mol). The pH was adjusted to 8.00 at 18.0 °C and urea (65.5 g, 1.09 mol) was added. After the addition of urea was complete, the pH of the mixture was 8.22 and the temperature was 7.0 °C. The mixture was heated at 90° C, for 75 minutes. The pH was measured at 5 minute intervals and, at the end of the reaction, the pH was 6.02. The viscosity was found to be 0.48 m.Pa.s.

Experiment 19

The experimental procedure employed in experiment 1 was followed, using formaldehyde (40 %; 150 ml, 2.18 mol). The pH was adjusted to 8.00 at 17.0 °C and urea (32.7 g, 0.54 mol) was added. After the addition of urea was complete, the pH of the mixture was 8.17 and the temperature was 11.0 °C. The mixture was heated at 70 °C, for 45 minutes. The pH was measured at 5 minute intervals and, at the end of the reaction, the pH was 6.62. The viscosity was found to be 0.11 m.Pa.s.

The experimental procedure employed in experiment 1 was followed, using formaldehyde (40 %; 150 ml, 2.18 mol). The pH was adjusted to 6.00 at 18.9 °C and urea (65.5 g, 1.09 mol) was added. After the addition of urea was complete, the pH of the mixture was 7.44 and the temperature was 7.9 °C. The mixture was heated at 90° C, for 45 minutes. The pH was measured at 5 minute intervals and, at the end of the reaction, the pH was 5.84. The viscosity was found to be 0.40 m.Pa.s.

The resulting plots of pH against time for experiments 1-20 are illustrated below (pp. 107-112); followed by the corresponding ¹³C NMR spectra (pp. 113-118).

PLOTS OF pH AGAINST TIME FOR EXPERIMENTS 1 - 20







<u>Experimental</u>





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PARTIAL 100 MHz ¹³C NMR SPECTRA OF UREA-FORMALDEHYDE RESINS OBTAINED IN EXPERIMENTS 1-4, 6-10, 13, 15-17, 19 AND 20 [SPECTRA WERE RUN IN DMSO- d_{o} AND THE CHEMICAL SHIFTS (δ) ARE GIVEN IN ppm. SPECTRA FOR EXPERIMENT 5,11,14 AND 18 APPEAR IN THE DISCUSSION].



Experiment No. 1



Experiment No. 2









<u>Experimental</u>



3.2.3 Preparation of basic urea-formaldehyde components

Monomethylolurea (1).³⁵

Urea (60 g, 1.0 mol) was added to a solution of disodium hydrogen orthophosphate (1 g) in aqueous formaldehyde (40 %; 35 ml, 0.5 mol). The mixture was stirred for 2 hours while maintaining the temperature below 25 °C using constant temperature bath. The reaction mixture was then stored at 0 °C for 24 hours to afford a white solid, which was stirred with ethanol (20 ml) containing 1 % v/v of a 10 % m/v aqueous solution of disodium hydrogen orthophosphate. The crystalline material was filtered off and recrystallised twice from ethanol to afford, as white crystalls, monomethylolurea 1 (22.5 g, 49 %), m.p. 110-111 °C (lit., ³⁵ 111 °C); v_{max} (KBr/cm ⁻¹)3420 (OH)3300, 3310 (NH₂) 1650 (CO). $\delta_{\rm H}$ (400 MHz; DMSO-*d*₆) 4.41 (2H, t, *J* 4.0, CH₂), 5.25 (lH, t, *J* 8.0, OH), 5.65 (2H, s, -NH₂) and 6.60 (1H, t, *J* 8.0, NH); $\delta_{\rm C}$ (100 MHz; DMSO-*d*₆) 63.6 (CH₂) and 158.5 (CO).

Dimethylolurea (2).35

The experimental procedure described for the preparation of monomethylolurea 1 was followed, using disodium orthophosphate (0.3 g), aqueous formaldehyde (40 %; 37.5 g, 0.50 mol) and urea (15 g, 0.25 mol). The crystalline material was filtered off and recrystallised twice from ethanol to afford, as white crystals dimethylolurea 2 (15.7 g, 52.3 %), m.p.129-130 °C (lit.,³⁵ 126-139 °C); v_{max} (KBr /cm⁻¹)3350 (OH) 3300 (NH) and 1650 (CO); δ_{H} (400 MHz; DMSO- d_{6}) 4.46 (4H, t, J4.0 2xCH₂) 5.23 (2H, t, J4.0, OH) and 6.61 (2H, t, J8.0, NH); δ_{C} (100 MHz; DMSO- d_{6}) 63.4 (CH₂) and 156.9 (CO).

Methylenediurea (36).³⁵

A solution of urea (400 g, 6.7 mol), water 300 ml, aqueous formaldehyde (40 %, 21.2 ml, 0.77 mol) and hydrophosphoric acid (1.2 ml) was allowed to stand at room temperature for 24 hours. After this period, the solution was stored at 0 °C for further 24 hours to afford, as white crystals, methylenediurea **36** (73 g, 71.3 %) m.p.200-201 °C (lit., ³⁵ 208 °C); v_{max} (KBr /cm ⁻¹) 3450 and 3340 (NH₂) and 1650 (CO); $\delta_{\rm H}$ (400 MHz; DMSO- d_6) 4.20 (2H, t, *J* 4.0, CH₂), 5.64 (H., br s, NH₂) and 6.49 (2H, br s, NH); $\delta_{\rm C}$ (100 MHz; DMSO- d_6) 158.7 (CO) and 45.5 (CH₂).

3.2.4 Silylation of urea derivatives

Silylation of urea (29).79

Urea (5 mg) was placed in a 10 ml conical flask. The flask was closed and dry N,Ndimethylformamide (200 µl) was added, followed by bis(trimethylsilyl)trifluoroacetamide (BSTFA) (200 µl). The homogeneous mixture was warmed at 40°C for 1 hour, after which dry ethyl acetate (3.6 ml) was added. A sample (0.5 µl) of this solution was injected directly into the GC-MS system, the mass spectrum (see Figures 30 and 31) confirming the formation of bis(trimethylsilyl)urea (84) (M⁺ 204).





FIGURE 30. GLC ion-current trace for silylated urea (84).



FIGURE 31. Mass spectrum of silylated urea (84) (component 1 in Figure 30).

Silylation of monomethylolurea (1).⁷⁹

The experimental procedure employed for the silulation of urea was followed, using monomethylolurea (1) (5 mg), to give tris(trimethylsilyl)monomethylolurea (85). The gas chromatogram and mass spectrum are shown in Figures 33 and 34 (M^+ 306).





FIGURE 32. GLC ion-current trace of the silvlated monomethylolurea.



FIGURE 33. Mass spectrum of the silylated momomethylohurea (85) (component 1 in Figure 32).

Silylation of dimethylolurea (2).79

The experimental procedure employed for the silvlation of urea was employed, using dimethylohurea (2) (5 mg), to give tris(trimethylsilyl)dimethylohurea (86). The gas chromatogram and mass spectrum are illustrated in Figures 35 and 36 (M^+ 336).





FIGURE 34. GLC ion-current trace of the silylated dimethylolurea.





Silylation of methylenediurea (36).⁷⁹

The experimental procedure employed for the silvlation of urea was followed, using methylenediurea (36) (5 mg), to give (trimethylsilyl)methyldiurea (87). The gas chromatogram and the mass spectrum are illustrated in Figure 36 and 37 (M^+ 204).





FIGURE 36. GLC ion-current trace of the silvlated methylenediurea (87).



FIGURE 37. Mass spectrum of the silvlated methylenediurea (87) (component 1 in Figure 36).

3.2.4 Synthesis of triazone-urea-formaldehyde resins.

Triazone-urea-formaldehyde resin A: using 5 % by mass of hexamethylenetetramine relative to urea.

Aqueous formaldehyde (40 %; 29 ml, 0.29 mol) was placed in the reaction vessel. The pH of formaldehyde solution was adjusted to 8.62 using 10 % sodium hydroxide solution and dilute sulphuric acid, and hexamethylenetetramine (0.31 g) was added. Urea (6.22 g, 0.10 mol) was then added with stirring, and the clear solution was heated at 95°C for 30 minutes. After this period, the pH was lowered to 7.6 using acetic acid. Free formaldehyde, as determined by titrimetric analysis, was found to be 2.24 %.

Triazone-urea-formaldehyde resin **B**: using 30 % by mass of hexamethylenetetramine relative to urea.

The experimental procedure employed for the preparation of triazone-urea-formaldehyde resin A was followed using aqueous formaldehyde (40 %; 20 ml, 0.29 mol); the pH of formaldehyde solution was adjusted to 8.83, and hexamethylenetetramine (1.87 g) and urea (6.22 g, 0.10 mol) were then added. After this period, the pH was lowered to 7.6 using acetic acid. Free formaldehyde, as determined by titrimetric analysis, was found to be 1.19 %.

Triazone-urea-formaldehyde resin C: following Siimers method.⁶¹

Aqueous formaldehyde (40 %;10 ml, 0.14 mol) was placed in a reaction vessel. Urea (17.4 g, 0.28 mol) and Hexamethylenetetramine (13.6 g, 0097 mol) were added. The stirred mixture was heated at 100 °C for 16 hours to afford a triazone-urea-formaldehyde resin. Free formaldehyde, as determined by titrimetric analysis, was found to be 0.72%.

3.2.6 Synthesis of triazone analogues

5-(2-hydroxyethyl)hexahydro-1,3,5-triazin-2-one (68).64

2-Aminoethanol (2.5 ml, 0.042 mol) was added, with cooling, to dimethylolurea 2 (5 .0 g, 0.042 mol) in water (7 ml) in a flask fitted reflux apparatus. The resulting solution was heated at 90-100 °C for two hours and then kept at room temperature overnight. The reaction mixture was concentrated under reduced pressure and the solid residue recrystallised twice from ethanol to afford 5-(2-hydroxyethyl)hexahydro-1,3,5-triazin-2-one (68) (2.87 g, 47 %), m.p. 158-159 °C (lit.,⁶⁴ 158 °C) (Found: \mathbf{M}^+ 145.0853. Calc. for C₅H₁₁N₃O₂: *M*, 145.0851); \mathbf{v}_{max} (KBr/cm⁻¹) 3320 (OH), 3220 (NH), 2920, 2860 (CH₂) and 1660 (CO); $\delta_{\rm H}$ (400 MHz; DMSO-*d*₆) 2.65 (2H, t, *J*)

4.0, 1'-CH₂), 3.50 (2H, m,2'-CH₂), 3.99 (4H, s, 2xCH₂), 4.51 (lH, br s, OH) and 6.27 (lH, br s, NH); δ_C(100 MHz; DMSO-*d*₆) 52.05 (1'-CH₂), 59.66 (2'-CH₂), 61.58 (2 x CH₂) and 158. 7 (CO); *m/z* 145 (M⁺, 3.6 %) and 114 (100).

Butylhexahydro-1,3,5-triazin-2-one (69).

The experimental procedure employed for the preparation of 5-(2-hydroxyethyl)hexahydro-1,3,5triazin-2-one (68) was followed, using butylamine (4.11 ml, 0.042 mol), dimethylohurea 2 (5.0 g, 0.042 mol) and water (10 ml). The resulting crystals were recrystallised twice from ethyl acetate to afford *Butylhexahydro-1,3,5-triazin-2-one* (69) (1.52 g, 23 %), m.p. 128-130 °C (Found: M^+ 157.1218. C₇H₁₅N₃O requires: *M*, 157.1215), u_{max} (NaCl plates and hexachlorobutadiene mull /cm⁻¹) 3223.0 (NH), 3060.0, 2865.1, 2934.1 and 2964.4 (CH₂ and CH₃) and 1665.8 (CO); δ_{H} (400 MHz; DMSO-*d*₆) 0.88 (3H, t, *J* 8.0, CH₃), 1.32 (2H, m, CH₂), 1.40 (2H, m, CH₂), 2.55 (2H, t, *J* 8.0, CH₂), 3.97 (4H, s, 2xCH₂) and 6.25 (2H, br s, NH) δ_{c} (100 MHz; DMSO-*d*₆) 13.7 (CH₃), 19.8, 29.5 and 48.8 (3xCH₂), 60.8 (2xCH₂) and 154.6 (CO); *m/z* 157 (M⁺, 27.5 %) and 42 (100).

5-t-Butylhexahydro-1,3,5-triazin-2-one (70).

The experimental procedure employed for the preparation of 5-(2-hydroxyethyl)hexahydro-1,3,5triazin-2-one (68) was followed, using t-butylamine (4.45 ml, 0,042 mol), dimethylolurea 2 (5.0 g, 0.042 mol) and water (10 ml). The resulting product was recrystallised twice from ethanol to afford *5-t-Butylhexahydro-1,3,5-triazin-2-one* (70) (2.72 g, 41 %), m.p. 181-182 °C. (Found: M^+ 157.1209. C₇H₁₅N₃O requires: *M*, 157.1215) v_{max} (KBr/cm⁻¹) 3220 (NH), 3010 (CH₂) and 1690 (CO); δ_{H} (400 MHz; DMSO-*d*₆) 1.12 (9H, s, 3xCH₃), 4.10 (4H., d, *J* 4.0, 2xCH₂) and 6.19 (2H, br s, NH); δ_{C} (100 MHz; DMSO-*d*₆) 28.2 (3xCH₃), 52.9 [(CH₃)₃C)], 56.7 (2xCH₂) and 155.0 (CO); m/z 157 (M⁺, 11.6 %) and 58 (100).

5-Ethylhexahydro-1,3,5-triazin-2-one (71).

The experimental procedure employed for the preparation of 5-(2-hydroxyethyl)hexahydro-1,3,5triazin-2-one (**68**) was followed, using monoethylamine (6.5 ml, 0.08 mol), dimethylolurea **2** (9.5 g, 0.08 mol) and water (10 ml). The resulting crystals were recrystallised twice from ethanol to afford 5-ethylhexahydro-1,3,5-triazin-2-one (**71**) (2.0 g, 19.4 %), m.p.156-158 °C (Found: \mathbf{M}^+ 129.0910. C₅H₁₁N₃O requires: *M*, 129.0902); \mathbf{v}_{max} (KBr/cm⁻¹) 3220 (NH), 3060, 2990 (CH₂) and 1650 (CO); $\delta_{\rm H}$ (400 MHz; DMSO-*d*₆) 1.03 (2H, *J* 8.0, CH₃), 2.61 (2H, q, *J* 8.0, 1'-CH₂) 3.99 (4H, d, *J* 2.8, 2xCH₂) and 6.15 (2H, br s, NH); $\delta_{\rm C}$ (100 MHz; DMSO-*d*₆) 12.9 (CH₃), 43.1 (1'-CH₂), 60.4 (2xCH₂) and 154.8 (CO); *m/z* 129 (M⁺, 30.2%) and 128 (100).

5-Isopropylhexahydro-1,3,5-triazin-2-one (72).

The experimental procedure employed for the preparation of 5-(2-hydroxyethyl)hexahydro-1,3,5triazin-2-one (68) was followed, using isopropylamine (4.32 ml, 0.025 mol) and dimethylolurea 2 (3.0 g, 0.025 mol). The resulting crystals were recrystallised twice from ethanol to afford *5-Isopropylhexahydro-1,3,5-triazin-2-one* (72) (1.85 g, 51 %), m.p.179-180 °C. (Found: **M** 143.1064 C₆H₁₃N₃O requires: *M*, 143.1058); v_{max} (NaCl plates and hexachlorobutadiene mull / cm⁻¹) 3225.8 (NH), 2969.4, 2847.4 (CH₂ and CH₃) and 1673.0 (CO); $\delta_{\rm H}$ (400 MHz; DMSO-*d*₆) 1.05 (6H, d, *J* 6.3, 2xCH₃), 2.93 (1H, m, CH), 4.06 (4H., d, *J* 2.5, 2xCH₂) and 6.18 (2H, br s, NH); $\delta_{\rm C}$ (100 MHz; DMSO-*d*₆) 21.0 (2xCH₃), 45.9 (CH), 58.5 (2CH₂), and 155.0 (CO); *m/z* 143 (M⁺, 13.0%) and 128 (100).

5-Benzylhexahydro-1,3,5-triazin-2-one (73).

The experimental procedure employed for the preparation of 5-(2-hydroxyethyl)hexahydro-1,3,5triazin-2-one (68) was followed, using benzylamine (4.85 ml, 0.042 mol), dimethylolurea 2 (5.0 g, 0.042 mol) and water (10 ml). The resulting crystals were recrystallised twice from ethyl acetate and then purified by reverse-phase chromatography [elution with water, water:MeOH (4:1,3:2, 2:3, 1:4) and MeOH] to afford *5-benzylhexahydro-1,3,5-triazin-2-one* (73) (0.40 g, 5 %), m.p. 190-192 °C. (Found: M^+ 191.1050. $C_{10}H_{13}N_3O$ requires: *M*, 191.1058); v_{max} (NaCl plates and hexachlorobutadiene mull /cm⁻¹) 3061.5 (NH) and 1680.9 (CO); δ_H (400 MHz; DMSO-*d*₆) 3.78 (2H, s, CH₂), 3.99 (4H., d, *J* 1.8, 2xCH₂), 6.35 (2H, br s, NH), 7.28 (1H, m, ArH), 7.32 (2H, br s, ArH) and 7.34 (2H, br s, ArH); δ_C (100 MHz; DMSO-*d*₆) 53.3 (CH₂), 60.5 (2CH₂), 127.1, 128.2, 128.7 and 138.2 (ArC) and 154.6 (CO). *m*/*z* 191 (M⁺, 0.9%) and 91 (100).

ATTEMPTED PREPARATION OF HEXAHYDRO-1,3,5-TRIAZIN-2-ONE (74).

The experimental procedure employed for the preparation of 5-(2-hydroxyethyl)hexahydro-1,3,5triazin-2-one (68) was followed, using 25 % aqueous ammonia solution (10 ml, 0.021 mol) and dimethylolurea 2 (2.5 g, 0.021 mol) and water (5 ml). The resulting clear solution was heated in an autoclave at 100 °C for 2 hours and then kept at room temperature overnight. The reaction mixture was concentrated under reduced pressure. Spectroscopic analysis of the residue (2.2 g) failed toconfirm the formation of compound 74.

ATTEMPTED PREPARATION OF 5-PHENYLHEXAHYDRO-1,3,5-TRIAZIN-2-ONE (76)

The experimental procedure employed for the preparation of 5-(2-hydroxyethyl)hexahydro-1,3,5triazin-2-one (68) was followed, using aniline (7.6 ml, 0.086 mol) and dimethylolurea 2 (10 g, 0.083 mol). The mixture was stirred at room temperature to afford a clear solution. Work-up afforded a white solid which was recrystallised twice from ethanol. Spectroscopic analysis of the product (2.0 g) failed to confirm the formation of compound 76.

ATTEMPTED SYNTHESIS OF 5-(CARBOXYMETHYL)HEXAHYDRO-1,3,5TRIAZON-2-ONE (79).

The experimental procedure employed for the preparation of 5-(2-hydroxyethyl)hexahydro-1,3,5triazin-2-one (68) was followed, using glycine (6.2 g, 0.083 mol), dimethylolurea 2 (10 g, 0.083 mol) and water (30 ml). A white crystalline solid was obtained which was not the expected product.

N-p-Toluenesulphonylglycine benzyl ester.

Glycine (7.0 g, 0.094 mol) was mixed with p-toluenesulphonic acid monohydrate (21.5 g, 0.11 mol) and benzyl alcohol (19.9 ml, 0.19 mol) in dry benzene (150 ml). The reaction mixture was heated under reflux for 10 hours during the which time *ca*. 4 ml of water was collected in the Dean-Stark trap. The homogeneous yellow solution was cooled to room temperature, diethyl ether (100 ml) was added and the precipitated solid was collected by filtration. The solid was rinsed with diethyl ether (3 x 60 ml) to afford *N-p*-toluenesulphonylglycine benzyl ester (20.6 g, 65 %), m.p. 126 °C; $\delta_{\rm H}$ (400 MHz; CDCl₃) 2.23 (3H, s, CH₃) 3.69 and 4.98 (4H, 2 x s, 2 x CH₂) 6.97 - 7.68 (9H, ArH) and 8.05 (2H, br s, NH₂); $\delta_{\rm C}$ (100 MHz; CDCl₃) 21.2 (CH₃), 40.5 and 67.7 (2 x CH₂), 126.0 128.2, 128.4, 128.5, 128.9, 134.6, 140.4 and 141.1 (Ar-C) and 168.0 (CO).

Glycine benzyl ester (80).

A solution of *N-p*-toluenesulphonylglycine benzyl ester (15 g, 0.044 mol) in chloroform was prepared. Triethylamine (7 ml, 0.051 mol) was added. The mixture was then extracted with water (3 x 100 ml). The solution was dried (anhydrous MgSO₄) and the solvent removed under vacuum to afford, as an oil, glycine benzyl ester (5.0 g, 32.1 %); $\delta_{\rm H}$ (400 MHz; CDCl₃) 1.40 (2H, s, CH₂), 3.30 (2H, s, CH₂Ph), 5.04 (2H, s, NH₂) and 7.14 - 7.19 (5H, Ar-H); $\delta_{\rm C}$ (100 MHz; CDCl₃) 43.4 (CH₂) 65.8 (CH₂Ph) 127.0, 127.7, 135.2 (Ar-C) and 174.0 (CO).

ATTEMPTED PREPARATION OF 5-[(BENZYLOXYCARBONYL)METHYL] HEXAHYDRO-1,3,5-TRIAZIN-2-ONE (81).

The experimental procedure employed for the preparation of 5-(2-hydroxyethyl)hexahydro-1,3,5triazin-2-one (68) was followed, using glycine benzyl ester (3.0 g, 0.018 mol), dimethylolurea 2 (2.2 g, 0.018 mol) and water (10 ml). NMR analysis of the residue, obtained after work-up, indicate the absence of the expected product.

3.2.7 Methylolated triazone derivatives

ATTEMPTED PREPARATION OF 1-HYDROXYMETHYL-(88) AND 1,3-BIS-(HYDROXYMETHYL) (89) DERIVATIVES OF 5-ETHYLHEXAHYDRO-1,3,5-TRIAZIN-2-ONE.

Urea-formaldehyde concentrate-85 (100 g) was mixed with urea (4 g), ethylamine (40 ml) was added slowly, keeping the temperature below 60 °C by cooling. The resulting mixture was then heated in a flask fitted with reflux condensor at 71 °C for 80 minutes, after which it was cooled slightly. A mixture of urea-formaldehyde concentrate-85 (54 g) and urea (18.5 g) was then added, and the resulting mixture was heated to 71 °C for 15 minutes. After cooling to 49 °C, the pH was adjusted to 5.0 using dilute sulphuric acid and 10 % sodium hydroxide solution, to afford a mixture indicated by ¹H and ¹³ C NMR spectroscopy to contain starting material and the expected products (88) and (89), separation of which could not be achieved, thus precluding definitive identification.

ATTEMPTED PREPARATION OF 1-HYDROXYMETHYL-(90) AND 1,3-BIS(HYDROXYMETHYL) (91) DERIVATIVES OF 5-(2-HYDROXYETHYL)HEXAHYDRO -1,3,5-TRIAZIN-2-ONE.

5-(2-hydroxyethyl)hexahydro-1,3,5-triazin-2-one (68) (1 g, 7 mmol) was added slowly to formaldehyde (40 %; 1.4 ml, 0.021 mol) with constant stirring. The mixture was heated slowly to 80 °C in a flask fitted with a reflux condenser, during a period of 15 minutes and this temperature was maintained for 1 hour to afford a mixture indicated by ¹H and ¹³ C NMR spectroscopy to contain starting material and the expected products (90) and (91), separation of which could not be achieved, thus precluding definitive identification.

ATTEMPTED PREPARATION OF 1-HYDROXYMETHYL AND 1,3 BIS(HYDROXYMETHYL) DERIVATIVES OF 5-*t*-BUTYLHEXAHYDRO-1,3,5-TRIAZIN-2-ONE.

The experimental procedure employed for the preparation of the methylolated derivative 90 and 91 was followed, using 5-t-butylhexahydro-1,3,5-triazin-2-one (70) (1g,7mmol) and formaldehyde (40 %, 1.31 ml, 0.019 mol). Work-up afforded a mixture indicated by ¹H and ¹³ C NMR spectroscopy to contain starting material and the expected products, separation of which could

not be achieved, thus precluding definitive identification.

ATTEMPTED REACTION OF GUANIDINE ACETIC ACID WITH FORMALDEHYDE. Guanidine acetic acid (10 g, 0.085 mol) was added with constant stirring to formaldehyde (40 %; 23.5 ml, 0.034 mol). The resulting mixture was heated in a flask fitted with a reflux condensor at 90-95 °C for 1 hour to afford a yellow oily product. The ¹H and ¹³C NMR spectroscopy indicated more products than expected and their separation could not be achieved.

3.3 VARIABLE TEMPERATURE STUDIES.

Six urea derivatives, *viz.*, dimethylolurea 2, monomethylolurea 1, methylenediurea 36, *N*-methylurea 94, *N*,*N*'-dimethylurea 92 and *N*,*N*-dimethylurea 93 were analysed by ¹H and ¹³C NMR spectroscopy at different temperatures. The ¹H and ¹³C NMR spectra were recorded on a Bruker AMX400 spectrometer without spinning. Samples were dissolved in methanol- d_4 and the ¹H NMR spectra of the samples were run at (303 K), 287 K, 277.5 K, 267.5 K, 257.5 K, 247.5 K, 236.8 K, 226.8 K 216.5 K, 206 K and 196 K; the ¹³C NMR spectra were recorded at 303K and at 196 K. The resulting spectra are illustrated in the discussion (Figures 24, 25 and 26) and in the following pages (pp.84, 86 and 87)

PARTIAL 400 MHz ¹H AND 100 MHz ¹³C NMR SPECTRA OF UREA DERIVATIVES IN

METHANOL- d_4 AT DIFFERENT TEMPERATURES

1. Monomethylolurea (1)



2. N,N-Dimethylurea 93

a) ¹H NMR spectra

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3. N-Methylurea 94.

a) ¹H NMR spectra




3.4 NMR ANALYSIS OF FACTORY SAMPLES

Eight samples from the factory were analysed by both the ¹H and ¹³ C NMR spectroscopy. Samples were dissolved in DMSO- d_6 , and the peaks were calibrated using the solvent peaks. Partial ¹H and ¹³C NMR spectra for sample # 1 are shown in Figures 28 and 29 (pp.91 and 93 respectively). The viscosity of each sample was measured using the Haake viscometer and the values found are shown in Table 5. Although the viscosities differ significantly, similar spectroscopic data was observed for all the samples (# 1-8).

Sample	Viscosity in m.Pa.s
# 1	142.0
# 2	132.5
# 3	163.1
# 4	107.9
# 5	163.7
# 6	284.6
#7	228.1
# 8	298.8

 Table 5.
 Viscosities of the factory samples.

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