Investigation of the reaction between melamine and unsaturated aldehydes

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The reactions between melamine and acrolein, crotonaldehyde or cinnamaldehyde were studied by 1-D and 2-D ^{1}H and ^{13}C n.m.r. spectroscopy. Regardless of the type of the unsaturated aldehyde used, all spectra of the resins have common characteristic regions, indicating that in the first step of the reaction similar reactive oligomers are formed. The oligomers further react via different mechanisms to form crosslinked products. Of the aldehydes, acrolein is the most reactive, while cinnamaldehyde is the least reactive. The rate of the reactions depends on reaction conditions, on molar ratios and on the type and quantity of the catalysts. Crosslinking of the resins with acids or amines gives insoluble products with a low content of monomers and oligomers.

INTRODUCTION

In previous works we investigated the reaction of unsaturated aldehydes with phenols and urea[1-2]. All these reactions have a similar mechanism: the electrons of the conjugated carbonyl groups and of the double bonds of the unsaturated aldehydes are hybridized and positive centres are formed on positions 2 and 4 of the phenols. The Michael's addition of phenols or amines to the unsaturated aldehydes takes place. The reactivity depends on the type of monomers. Acid catalysts and higher temperatures increase the reaction rate.

In this paper the syntheses of resins from melamine and acrolein, crotonaldehyde or cinnamaldehyde are described. Melamine is poorly soluble in most organic solvents, while the unsaturated aldehydes and resins are poorly soluble in water. For this reason DMSO was used as solvent. The resins were yellow to red coloured high viscous solutions. To determine the mechanism of the reactions one (1-D) and two dimensional (2-D) ^{1}H and ^{13}C n.m.r. spectroscopy was used.

EXPERIMENTAL

Materials

The unsaturated aldehydes used were products of Merck. Melamine was a product of Aldrich. Before use the aldehydes were dried and distilled under low pressure, while melamine was dried only. As catalysts, analytical grade concentrated hydrochloric, phosphoric or formic acids were used.

Syntheses and measurements

The syntheses of resins were performed in glass vessels at the temperature of reflux, which varied according to the aldehyde used. Melamine was first put in DMSO and warmed to improve its solubility. After a while the mixture was cooled to 50°C and the aldehyde and catalyst were added. The temperature was then raised to the reflux. During the reaction melamine dissolved completely. The longest time of reaction was 17 h.

Molar ratios between melamine, aldehydes and catalysts were 1:1:0.0 to 1:3:0.2. The quantity of catalyst depended on the molar ratio between monomers and on the type of the aldehyde. Depending on reaction conditions, the conversion was between 70 and 95.7%. For n.m.r. measurements the resins were synthesized under the same conditions except for using DMSOd$_6$. The detailed conditions for syntheses are given in *Tables 1* and *2*.

The 1-D and 2-D ^{1}H and ^{13}C n.m.r. spectra were recorded on a VXR 300 Varian superconducting magnet. For measurements the following conditions were used: phase sensitive, homonuclear shift correlation (correlated spectroscopy (COSY)), double quantum filtered COSY experiment, heteronuclear C–H correlation 2-D spectra and attached proton test (APT). For all experiments equivalent pulse sequence programs were used. The pulse width was 15 μs (90°) for carbon and 17.3 for proton; the pulse delay was 3 s and the temperature 50°C. For APT τ delay was 7.5 ms. DMSOd$_6$ was used as solvent and TMS as internal standard.

The unreacted aldehydes were determined by gas chromatography and ^{1}H n.m.r. spectroscopy, while the unreacted melamine was determined by potentiometric titration with HCl.

The resins were crosslinked with hexamethylenetetramine or with phosphoric acid at 135°C. The residual monomers and oligomers were extracted with hot water and acetone.

RESULTS AND DISCUSSION

The spectra of the resins depend on the type of the unsaturated aldehyde, on molar ratio, on reaction time and on the type and quantity of the catalyst. Nevertheless all spectra have common characteristic regions, regardless of the type of the unsaturated aldehyde. Therefore we explain the structure of the resins on the basis of the reaction products between acrolein and melamine.

Table 1 Synthesis data of melamine (M)–acrolein (Ac) (upper) and melamine-crotonaldehyde (Crot) (lower) resins

Synthesis	Molar ratio M:Ac:Cat	Catalyst	Solvent (%)	Solid contents (%)	Reacton time (min)	Reaction temperature (°C)	Unreacted acrolein	Unreacted melamine
1	1:2:0.02	HCOOH	60	34.4	255	50	1.2	7.3
2	1:2:0.02	H_3PO_4	60	34.8	155	50	1.1	8.4
3	1:2	–	60	32.2	225	50	9.3	8.5
4	1:1.5	–	60	37.1	600	50	6.2	10.4
5	1:3	–	60	34.0	290	50	9.6	4.3
	Molar ratio M:Crot:Cat						Unreacted crotonaldehyde (%)	(%)
1	1.1:2:0.2	HCOOH	60	41.1	455	90	3.8	8.3
2	1.1:2:0.1	H_3PO_4	60	45.2	400	90	4.8	9.7
3	1.1:2:0.05	H_3PO_4	60	48.2	370	90	6.9	12.3

Table 2 Synthesis data of melamine (M)–cinnamaldehyde (Cinn) resins

Synthesis	Molar ratio M:Cinn:Cat	Catalyst	Solvent (%)	Solid contents (%)	Reaction time (min)	Reaction temperature (°C)	Unreacted cinnamaldehyde	Unreacted melamine (mol%)
1	1:2:0.02	HCl	60	38.1	530	90	25.0	4.9
2	1:2:0.02	HCOOH	60	39.5	480	90	25.2	4.7
3	1:2:0.04	HCOOH	60	38.1	420	90	20.6	12.7
4	1:2:0.1	HCOOH	60	38.4	420	90	19.3	12.4
5	1:3:0.1	HCOOH	60	31.2	480	90	29.2	10.2
6	1:2:0.2	HCOOH	60	43.6	1020	90	16.6	8.8
7	1:2:0.02	H_3PO_4	60	41.0	480	90	20.8	5.7
8	1:2:0.1	H_3PO_4	60	42.3	760	90	15.1	6.7

The carbon spectra of the acrolein–melamine resins have, at the beginning of the reaction, three characteristic regions: the region between 26–43 ppm, the region between 68–96 ppm and the region between 137–202 ppm[3–5]. The APT spectra show at $\tau = 7.5$ ms that

$-CH_3$ and $-\overset{|}{C}H-$ groups are oriented to the negative side,

with $-CH_2-$ and $-\overset{|}{\underset{|}{C}}-$ groups to the positive side (*Figure*

1). Because there are no negative signals in the region between 10–30 ppm, it can be concluded that all signals in this region belong to $-CH_2-$ groups. In the region between 68–96 ppm all signals are oriented to the negative

side. These signals belong to $-\overset{|}{C}H-$ groups. In the region between 137–202 ppm a small signal at 138 ppm is negatively oriented and belongs to the $=CH-$ group of the unreacted acrolein. The signal at 140 ppm is positively oriented and belongs to the $=CH_2$ group of acrolein.

The signals between 162–167 ppm are positively oriented and belong to the $\overset{\diagdown}{\underset{\diagup}{C}}=N-$ groups of the

substituted and unsubstituted melamine rings, except for the signal at 165 ppm which belongs to the catalyst HCOOH. The signals at 194 and 201.8 ppm belong to –CHO groups of the substituted and unsubstituted aldehyde. The intensity of signals depends on the reaction time. The intensity of the signals at 26.7, 38.2 and 69.8 ppm first increases, but later decreases with reaction time. In contrast, the intensity of the signals at 25, 30, 36 and 72 ppm increases with the reaction time.
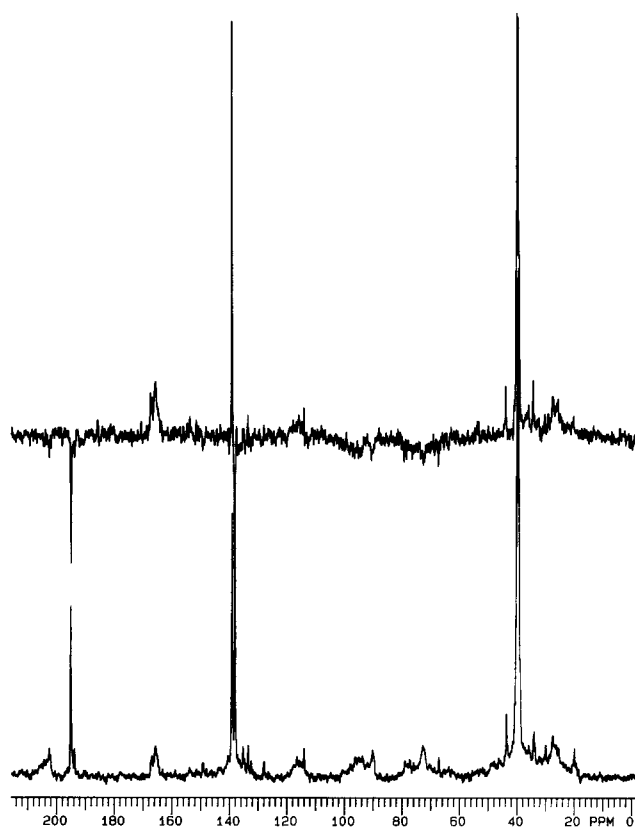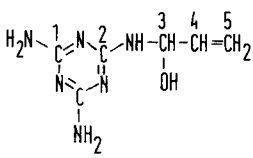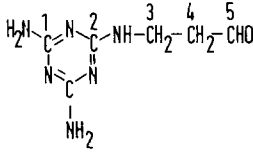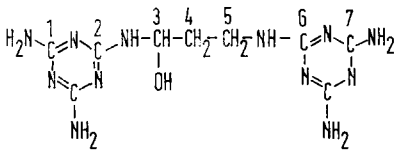

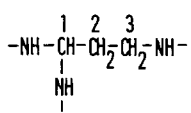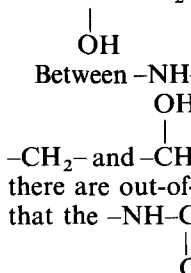200 180 160 140 120 100 80 60 40 20 PPM 0

Figure 1 N.m.r. spectra of the reaction product between melamine and acrolein. ^{13}C n.m.r. spectrum (lower), APT spectrum (upper)

Table 3 Chemical shifts of different products of the reaction between melamine and acrolein in carbon spectra in the strong HCOOH medium

Reactive product		Chemical shifts (ppm)
	1	166.9
	2	165.1
	3	74.1
	4	139.0
	5	114.5
	1	166.9
	2	165.1
	3	42.1
	4	34.1
	5	201.8
	1, 7	166.9
	2, 6	165.1
	3	69.8
	4	26.7
	5	38.2
	1	44.0–50
	2	22–30
	3	30–40

individual signals. In *Table 3* chemical shifts of different products of the reaction between melamine and acrolein are given.

The proton spectra were identified by the hetero 2-D correlation carbon–proton spectra and by the COSY proton–proton correlation spectra. In the 1-D ^{1}H spectra the signals between 1.5–2.5 ppm belong to -CH$_2$- groups of the carbon 3. The signals between 3.8–4.5 ppm belong to -NH-CH$_2$- groups and the signals between 4–5.5 ppm to

$\diagdown$
$\diagup$CHOH groups. The signals between 5.5–7 ppm belong to unbonded or bonded -NH$_2$ or to -NH- groups. Due to coupling with neighbouring atoms all signals are multiplets (*Table 4*). COSY and DQ COSY spectra show connections between groups in the -NH-CH-CH$_2$- CH$_2$-NH- units.

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    OH

Between -NH- and -CH(OH)-CH$_2$- and -CH$_2$-NH-,
    OH
    |
-CH$_2$- and -CH- and between -CH$_2$- and -NH- groups there are out-of-diagonal signals. These signals confirm that the -NH-CH-CH$_2$-CH$_2$-NH- group is the domi-

    |
    OH

nant structure in the first step of the formation of the melamine–acrolein resins.

The carbon and proton spectra for crotonaldehyde and cinnamaldehyde differ from the spectra for acrolein only in intensities of individual signals and in additional signals of -CH$_3$ groups (in the region from 10 to 20 ppm in carbon and 0.6 to 1.2 ppm in proton spectra) when using crotonaldehyde and additional signals for aromatic rings (*Figure 2*) when using cinnamaldehyde.

Table 4 Chemical shifts of different groups appearing in the reaction products between melamine and unsaturated aldehydes in proton spectra

Groups	Chemical shift (ppm)
=CH$_2$	6.3–6.8
-CH$_3$	0.6–1.2
-phenyl	6.8–7.5
-CH=	6.5–6.8
-CHO	9.4–9.6

-NHCH-
    |
    OH
	4.0–5.5

-CH$_2$-NH-	3.8–4.5
-CH$_2$-	1.5–2.5
-NH$_2$	5.7

With the reaction progressing the signals for both
    |
monomers disappear and signals for groups -CHOH,
-CH$_2$NH- and -CH$_2$- are formed. Later the signal for
$\diagdown$ $\diagup$
$\diagup$CHOH disappears and a new signal for -NH-CH$\diagdown$
groups appears in the region between 50–60 ppm with elimination of water. When the molar ratio between melamine and the unsaturated aldehyde was high and when the reaction time was long, small signals between 70–80 ppm appear, which indicate the possibility of formation of the ether bridges. The signals in the region between 161–164 ppm indicate tetra and higher substituted products of melamine.

The scheme of the reaction was predicted on the basis of the carbon and proton spectra (*Figure 3*).

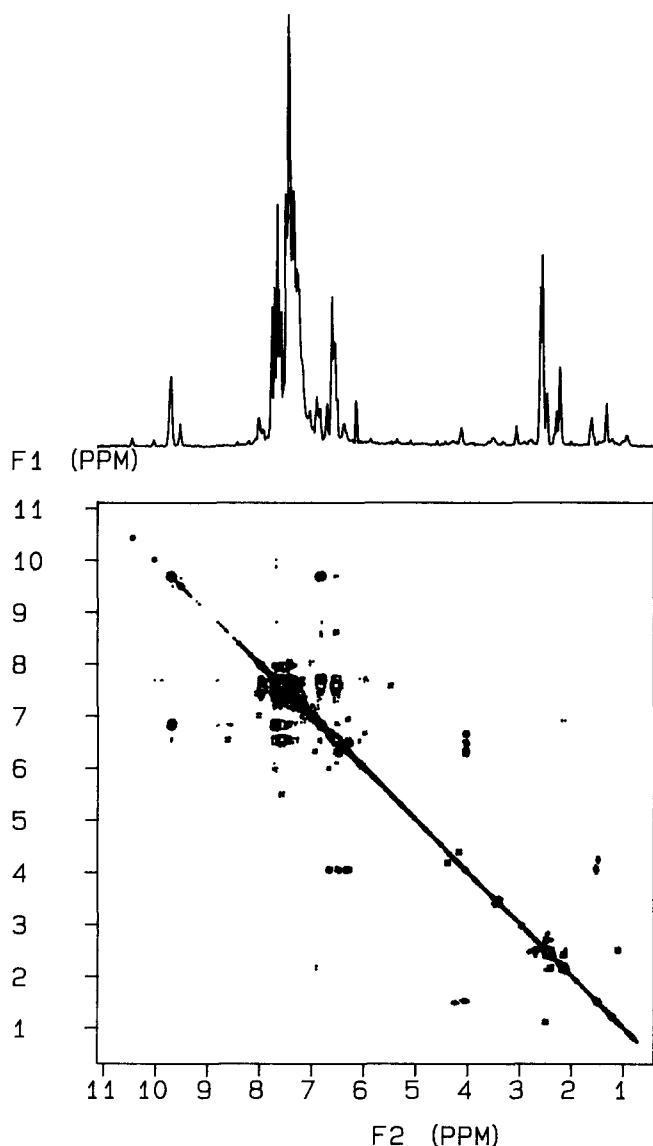The most probable hybrid of acrolein is formed when negative centres are in positions 1 and 3 and positive

Figure 2 COSY H–H spectrum of the reaction products between melamine and cinnamaldehyde

catalyst, while after 17 h 16.6% of unreacted cinnamaldehyde remains even when there is a high concentration of catalysts.

The kinetic parameters were determined from the conversion of aldehydes (*Figure 4*). The kinetic equation
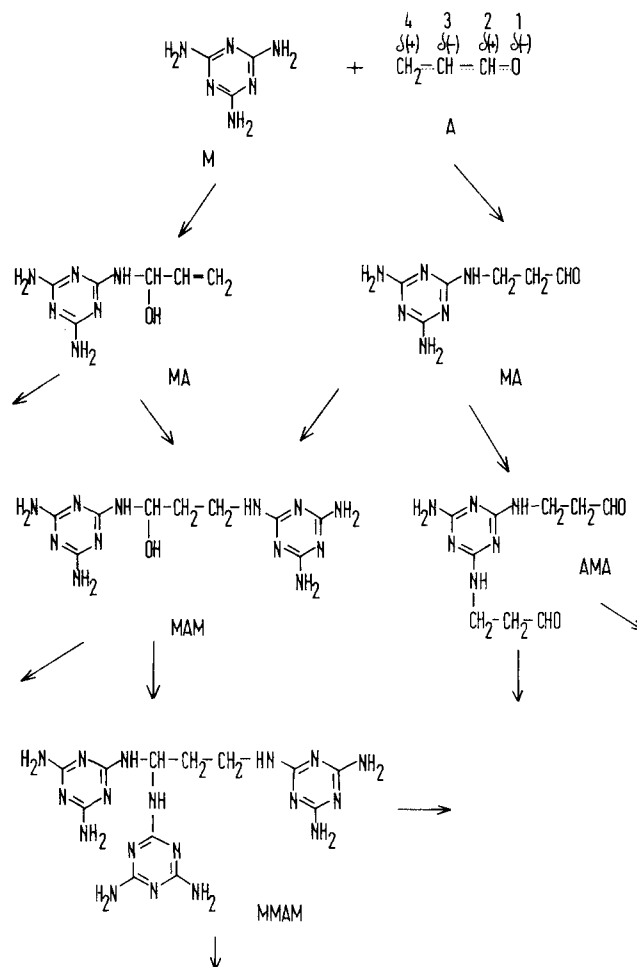

Figure 3 The scheme of the reaction between melamine and acrolein

centres in positions 2 and 4. When the addition of melamine to acrolein takes place, the negative centre on carbon 3 directs the proton of the melamine $-NH_2$ group to carbon 3, while other parts of the molecule are directed to carbon 4. This can be concluded from the APT spectra in which there are no signals of $-CH_3$ groups, which should be formed in the case of addition of melamine proton to carbon 4.

After one hour of reaction the inhomogeneity of the reaction mixture, due to insolubility of melamine, disappeared and the determination of monomers was possible. For the calculation of unreacted cinnamaldehyde the integrals of the signals of the carbonyl group at 9.4 ppm and of the aromatic rings in the proton spectra were used. For calculation of the unreacted crotonaldehyde the ratio of integrals of the carbonyl and methyl groups were used, while unreacted acrolein was determined by gas chromatography. The conversion of monomers during the reaction is given in *Figure 4*. Of the three aldehydes acrolein is the most and cinnamaldehyde the least reactive. Acrolein reacts with melamine completely in 5 h even in molar ratio 1:3 and without
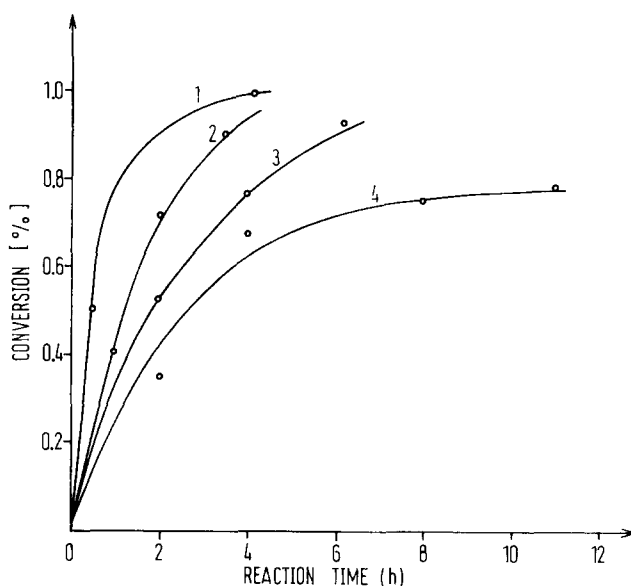

Figure 4 Conversion of aldehydes in the reaction between melamine and unsaturated aldehydes. Acrolein, acid medium (1); acrolein, neutral medium (2); crotonaldehyde, acid medium (3); cinnamaldehyde, acid medium (4)

Table 5 The rate constants for the formation of the melamine–unsaturated aldehydes resins

Type of the resins	Molar ratio	Rate constant $(l\,mol^{-1}s^{-1})$
Melamine:acrolein:H_3PO_4	1:2:0.02	7.9×10^{-4}
Melamine:acrolein: –	1:2: –	1.5×10^{-4}
Melamine:crotonaldehyde: H_3PO_4	1.1:2:0.05	1.1×10^{-4}
Melamine:cinnamaldehyde: H_3PO_4	1:2:0.02	1.0×10^{-4}

for the decreasing concentration of unreacted aldehydes is the following

$$\frac{d|A|}{dt} = k_0 |A|\,|M|$$

where $|A|$ is the concentration of the aldehyde and $|M|$ the concentration of melamine. The rate constants were calculated on the basis of the concentration of both monomers and of the time derivative of experimental values for concentrations. The rate constants for the formation of the resins are given in *Table 5*.

All resins are only partly soluble in acetone, pyridine and DMF but completely soluble in DMSO, formic and acetic acid[6]. After heating the resins for 3 h to 135°C they cure to hard, partly soluble and unmelting products. Curing with hexamethylenetetramine gives a completely insoluble product with a low content of extracted monomers and oligomers.

CONCLUSION

The syntheses of resins from melamine and unsaturated aldehydes in acid media take place in DMSO solution extensively at reflux temperature of the aldehyde. In the first step of the reaction reactive oligomers are formed which further react via different mechanisms to crosslinked macromolecules. The resins are red coloured and highly viscous solutions. Acrolein is the most, while cinnamaldehyde the least reactive aldehyde. The content of unreacted monomers depends on reaction conditions, on molar ratios and on the type and quantity of the catalysts. After heating for 3 h at 135°C the resins cure to partly insoluble compounds. Crosslinking with acids or amines gives insoluble products with low content of monomers and oligomers. Using the combination of proton and carbon n.m.r. spectroscopy it was possible to identify individual oligomers, to set up tentative reaction schemes and to follow the unreacted aldehydes as a function of reaction time.

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