

New Melamine Resins. I. Synthesis of Reactive Solvents for Melamine

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ABSTRACT: Some results are presented on the studies of reactive solvents for melamine obtained from acetone and formaldehyde in the presence of potassium bicarbonate or triethylamine as catalysts. The chemical structure of the solvents, as well as their ability to dissolve melamine, have been determined. The mechanism of melamine dissolution in the reactive solvents has been analyzed by using the ¹H-NMR technique.

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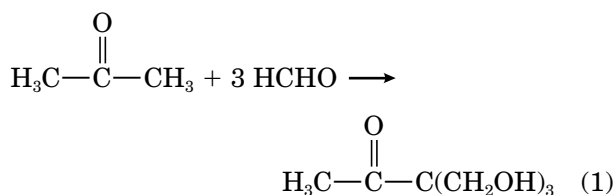
Key words: acetone, formaldehyde, reactive solvent, melamine, dissolution

INTRODUCTION

Melamine is an amide of cyanuric acid capable of addition reactions, particularly with formaldehyde¹ and oxirane,² as well as proton substitution reactions.³ The presence of the *s*-triazine ring in the molecule of melamine provides the resins obtained from it with an improved thermal stability, compared with hydrocarbon resins. The melamine-based resins are also excellent electrical insulators. The main disadvantage of melamine is its poor solubility in water¹ (0.32 g/100 cm³ at 20°C and 5 g at 100°C), dimethylsulfoxide⁴ (6 g/100 cm³ at 30°C), or in glycols or glycerine⁵ (4–11 g/100 g). Melamine dissolves pretty well in formalin at 80°C. Here, the dissolution is accompanied by the chemical reaction leading to formation of hydroxymethyl derivatives and then melamine–formaldehyde resins. An important step in the industrial realization of the latter sequence of reactions is the need for water removal from prepolymer solutions. Because the prepolymers

are very unstable, the operation is not always an easy one.

Methods of avoiding the problems with water removal have been sought after for many years. Because melamine fairly dissolve in polyhydroxy compounds, an acceptable solubility of this substance was expected in hydroxymethyl derivatives of acetone obtained in reactions with formaldehyde:



Indeed, it has been found that the solubility of melamine in the product of this reaction at 140°C is as high as 150 g/100 g (i.e., corresponds to ~ 60 wt %⁵). Melamine does not only dissolve in the solvent, but also reacts yielding a thick liquid hardening when heated (at > 80°C) in the presence of acidic or basic catalysts.

Furthermore, it has been found that other hydroxymethyl derivatives of the aliphatic com-

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Table I Conditions of Synthesis and Mass Balance for the Reaction of Acetone with Formaldehyde

Reactive Solvent	Sample No.	Synthesis Conditions			Mass Balance					
		Catalyst*	Temperature (°C)	Time (h)	Acetone	Formalin	% CH ₂ O in Formalin	Mass of Product (g)		Molar Excess of CH ₂ O in Product
								Calcd. ^a	Found	
1-HMA	1	K ₂ CO ₃	40	26	34.8	100.0	30.1	64.9	52.4	1.0
3-HMA	2	K ₂ CO ₃	40	26	29.0	150.0	28.6	71.9	71.0	2.8
3-HMA	3	TEA	40	26	17.4	103.8	32.4	51.0	44.4	3.0
3-HMA	4	TEA	80	16	17.4	102.2	28.2	46.2	44.3	3.0
4-HMA	5	TEA	40	26	17.4	104.2	35.6	54.5	52.6	3.9
5-HMA	6	K ₂ CO ₃	40	40	23.2	213.2	28.2	83.3	80.0	4.7
5-HMA	7	TEA	40	50	17.4	133.2	36.5	66.0	65.6	5.3
5-HMA	8	TEA	40	26	17.4	133.2	36.5	66.0	61.6	4.9
6-HMA	9	TEA	40	46	17.4	153.0	36.5	73.2	71.1	6.0
8-HMA	10	TEA	40	50	17.4	200.4	36.5	90.5	90.0	8.1
8-HMA	11	TEA	80	4	17.4	215.0	36.3	95.3	82.8	7.3
8-HMA	12	TEA	80	8	17.4	215.0	36.3	95.3	85.2	7.5
8-HMA	13	TEA	80	16	17.4	215.0	36.3	95.3	90.0	8.0
10-HMA	14	TEA	40	52	14.5	20.5	37.8	90.9	90.0	10.2
10-HMA	15	TEA	80	10	14.5	223.5	36.3	95.6	90.2	10.1
11-HMA	16	TEA	40	55	14.5	236.5	37.8	103.6	95.6	10.8
12-HMA	17	TEA	40	120	17.4	314.5	36.3	131.6	123.6	11.8

^a The sum of masses of acetone and formaldehyde were taken as the mass of product. Water and amine were distilled off under 13–20 hPa.

* Catalyst: 2 g of potassium bicarbonate or 1 cm³ of triethylamine (TEA)

pounds containing electronegative groupings activating C—H links at the α position are good solvents of melamine.⁵ A new group of reactive melamine solvents was thus discovered consisting of hydroxymethyl derivatives of some aldehydes, ketones, or nitro compound.

The novel resins obtained by dissolving melamine in the reactive solvents are expected to find applications in manufacturing the same products as those obtained from the traditional melamine–formaldehyde resins, but in more convenient ways. Preparation of a liquid oligomer from mela-

Table II The Highest Amount of Melamine Dissolved in the Reactive Solvents (RS) Obtained with the Amine Catalyst at 40°C

Reactive Solvent	Amount of Melamine Added (g/100 g of RS) ^a	Loss of RS Mass during Melamine Dissolution (wt %)	Melamine Solubility (g/100 g of RS) ^b	% of Melamine (wt %)
3-HMA	10	26.0	13.5	11.9
4-HMA	16	11.2	18.0	15.3
5-HMA	16	12.7	18.3	15.5
6-HMA	28	14.8	32.9	24.7
8-HMA	28	14.6	32.8	24.7
10-HMA	32	8.6	35.0	25.9
11-HMA	28	3.2	28.9	22.4

Melamine introduced stepwise; no water added.

^a Per initial amount of RS.

^b Per final amount of RS.

Table III The Highest Amount of Melamine Dissolved in the Reactive Solvents (RS) Containing Water

Reactive Solvent	Synthesis Temperature (°C)	Water Added (g/100 g of RS)	Melamine Dissolved (g/100 g of RS)	Loss of Mass during Melamine Dissolution (wt %)	Concentration of Melamine (wt %)	
3-HMA	40	20	55	9.1	34.3	
		30	80	7.9	41.1	
		80	60	5.8	35.4	
8-HMA	40	20	90	7.2	43.9	
		30	65	6.2	37.5	
		40	75	5.4	40.7	
		80	80	6.2	42.6	
		30	90	7.7	44.3	
10-HMA	40	20	100	8.6	45.2	
		30	105	5.7	48.5	
		40	135	7.9	53.2	
		80	20	90	4.7	44.9
		30	90	5.4	43.1	
		100	100	6.4	46.5	
		105	105	5.9	47.5	
11-HMA	40	20	110	7.5	49.6	
		30	100	5.3	47.9	
		80	130	7.8	53.9	
12-HMA	40	20	105	6.7	48.0	
		30	105	7.8	48.5	
		20	130	7.9	56.5	
		30	140	5.4	54.8	

mine dissolved in a reactive solvent proceeds sufficiently rapidly to incorporate it into the processes of shaping and hardening. This opens possibilities of the production of parts based on melamine resins by applying reactive injection-molding technique. Furthermore, it becomes feasible to use melamine resins in the synthesis of polyurethane soft and hard foams,⁶ various polymerizing resins, ion exchangers, and many other products.

In this article, we report on our studies of reactive solvents of melamine obtained from acetone and formaldehyde. We concentrate here on the structure of the reactive solvent and the process of melamine dissolution. The possibilities of application of melamine solutions for manufacturing new polymeric materials will be presented in part II of the series.

EXPERIMENTAL

Synthesis of Reactive Solvents

To a round-bottomed flask equipped with a condenser, thermometer, and stirrer, 34.8 g (0.6 mol)

of acetone were introduced with an appropriate amount of 36–40 wt % of formalin (see note 1) and 2 g of potassium bicarbonate dissolved in 3.5 cm³ of water or triethylamine in the quantity sufficient to bring the mixture to pH 11. The reaction was conducted at 40°C (see note 2) for 10–52 h (see note 3). Water and triethylamine were removed under reduced pressure (at 14–21 hPa, not allowing temperature to exceed 50°C). When potassium bicarbonate was used, 1.8 cm³ of concentrated hydrochloric solution were introduced to neutralize the catalyst. Acetone was then added to facilitate potassium chloride precipitation (see note 4). The precipitate was filtered off, and acetone and water were removed under reduced pressure as described previously. Details on individual samples are listed in Table I.

Notes:

1. To obtain a product with a molar ratio of acetone⁷ to formaldehyde 1: n , ($n + 0.67$) moles of formaldehyde per mole of acetone were used ($n = 1, 2, \dots, 12$).

Table IV Estimation of Functional Group Content in Acetone-Formaldehyde Reactive Solvents (RS) (from $^1\text{H-NMR}$ Spectra)

Reactive Solvent	Sample No. as in Table I	Moles of Groups Per Mole of RS				Methylvinyl Ketone (mol/mol RS)
		$-\text{O}-\text{CH}_2-\text{O}-$	$-(\text{CH}_2-\text{O})_x-\text{H}$	$-\text{OH}$	$\text{CH}_3\text{CO}-$	
1-HMA	1	0.03	0.1	0.8	1.0	0.02
3-HMA	2	0.1	0.4	1.9	1.0	Trace
	3	0.1	1.4	2.6	0.5	0.05
	4	0.6	1.3	1.3	0.3	0.03
	5	0.2	1.9	2.8	0.5	0.02
4-HMA	5	0.2	1.9	2.8	0.5	0.02
5-HMA	6	0.2	1.9	2.0	0.5	No
	8	0.2	2.6	3.1	0.8	0.03
	9	0.1	3.7	3.7	0.6	0.03
6-HMA	9	0.1	3.7	3.7	0.6	0.03
8-HMA	10	0.0	5.1	3.7	0.6	No
	11	0.5	6.7	2.9	0.3	0.05
	12	0.4	7.0	2.7	0.3	0.05
	13	0.6	7.5	3.4	0.2	0.02
10-HMA	14	1.5	6.0	3.3	0.7	No
	15	0.6	7.0	4.0	0.5	Trace
11-HMA	16	1.7	5.3	3.8	1.0	No

- There were also attempts to conduct the reaction with triethylamine catalyst at 80°C .
- Time to completion was estimated in preliminary experiments by controlling the amount of unreacted substrate (formaldehyde) by weight. The reaction time was dependent on the acetone to formaldehyde molar ratio.
- The required amount of acetone was 100 cm^3 for the sample obtained at acetone to

formaldehyde molar ratio of 1 : 1 (1-HMA). This amount increased rapidly with increasing excess of formaldehyde (e.g., $\sim 400\text{ cm}^3$ was required for the sample 2-HMA obtained at acetone : formaldehyde molar ratio of 1 : 2).

The samples of reactive solvents are coded in the text and in tables with the letters HMA (hydroxymethyl-acetone) preceded by a number de-

Table V Content of Unstable Formaldehyde in the Reactive Solvents (RS) as Determined by the Sulfite Method

Reactive Solvent	Sample No. as in Table I	Content of Unstable Formaldehyde	
		Wt %	Mol/Mol of RS
1-HMA	1	8.18	0.24
3-HMA	2	12.0	0.59
	3	30.6	1.51
	4	46.6	2.04
	5	39.3	2.33
4-HMA	5	39.3	2.33
5-HMA	6	29.0	2.01
	8	44.1	3.06
	9	52.4	4.16
6-HMA	9	52.4	4.16
8-HMA	10	55.2	5.48
	13	76.6	7.53
10-HMA	14	51.7	6.17
	15	62.9	7.63
11-HMA	16	45.9	5.90

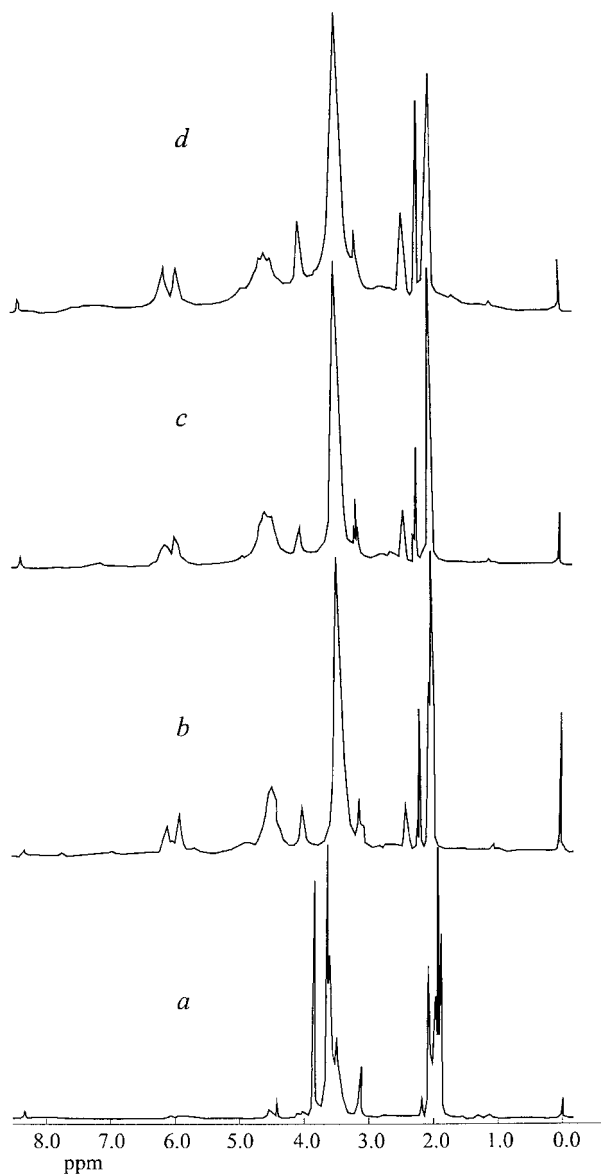


Figure 1 ¹H-NMR spectrum of 1-HMA reactive solvent (a) and those of melamine solutions in the reactive solvent recorded after 3 min (b), 5 min (c), and 7 min (d) from the beginning of dissolution.

noting how many moles of formaldehyde were used per 1 mol of acetone as follows from the mass balance.

Melamine Dissolution

With Gradual Melamine Introduction

Melamine was introduced in 0.1–0.2 g portions to 5 g of reactive solvent placed in a 25 cm³ beaker. After introducing a portion, the mixture was

heated until homogeneous while stirring with a thermometer. The temperature of homogenization was recorded. The next portion was then introduced without a delay and heated again to dis-

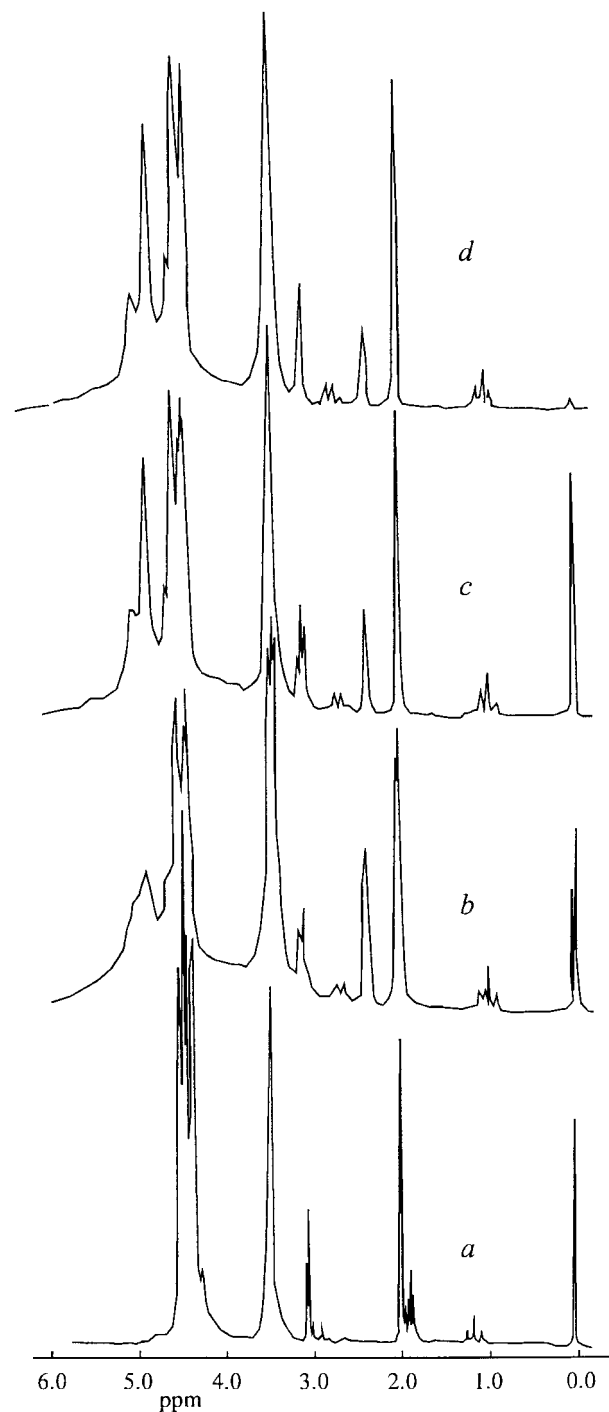


Figure 2 ¹H-NMR spectrum of 10-HMA reactive solvent (a) and those of melamine solutions in the reactive solvent recorded after 3 min (b), 5 min (c), and 7 min (d) from the beginning of dissolution.

solution. This cycle was repeated until a portion of melamine failed to dissolve (solution remained cloudy).

With Melamine Introduced in One Portion (Table II)

The amount of melamine determined as in the previous method was dissolved in 5 g of reactive solvent. While the content of the beaker was vigorously stirred and quickly heated, 0.2 g portions were introduced until the mixture was saturated or gelled.

With 20–30% of Water (Table III)

The amount of melamine determined as in the previous method was dissolved in 5 g of reactive solvent to which 1.0 or 1.5 g of water were added (20 or 30 wt %). Then, further 0.2 g portions of melamine were introduced while increasing temperature until the mixture became cloudy and gelled. Solubility measurements were then repeated by using all of the amount determined. Small portions of melamine were added, if necessary.

The results of solubility measurements are shown in Table III and expressed as the amount of dissolved melamine in 100 g of reactive solvent or as the percentages of melamine in the final solution by weight. Because some volatile compounds present in the reactive solvent (water, formaldehyde) evaporated during dissolution above 100°C, the final mass was smaller than the total mass of introduced components.

Dissolution Chemistry

The chemistry of melamine dissolution was studied in two solvents: 1-HMA and 10-HMA. The solvents contained no water. The time of dissolution was ~ 10 min. Samples for structure investigation were collected after 3, 5, and 7 min from the start of dissolution. ¹H-NMR and infrared (IR) spectra of the collected samples were recorded.

Analytic Methods

The content of bound and free formaldehyde in the reactive solvents were measured by the sulfite method.⁸

The change in composition of the reactive solvents was controlled by keeping them at 105°C for 3 h. The changes in ¹H-NMR spectra of the samples during the thermal treatment were recorded.

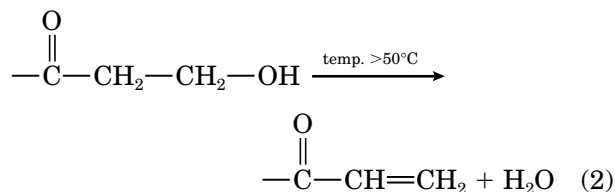
¹H-NMR spectra of the acetone–formaldehyde

reaction products and those of the mixtures of reactive solvents with dissolved melamine were recorded on an 80 MHz BS587A spectrometer (Tesla, Czechoslovakia). The solvent was *d*₆-acetone or *d*₆-dimethylsulfoxide. The samples for IR analysis were prepared in the form of capillary films. Spectra were recorded on a Fourier transform IR PARAGON 1000 spectrometer (Perkin-Elmer Corp., Norwalk, CT).

RESULTS AND DISCUSSION

Preparation of Reactive Solvents

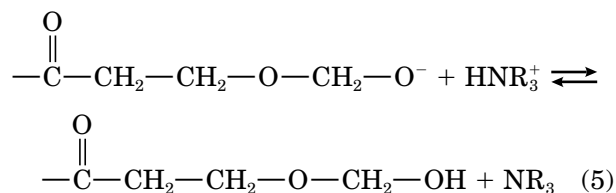
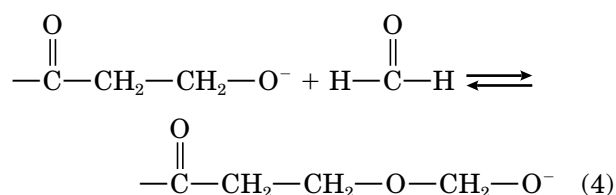
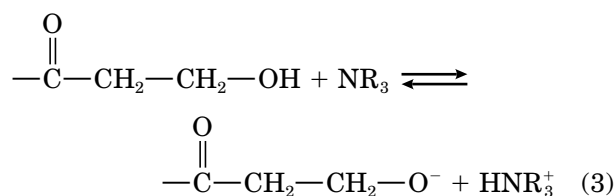
The reactive solvents for melamine were obtained in the aldol condensation of acetone with formaldehyde, in the presence of potassium bicarbonate. Depending on the initial molar ratio of reagents, products of different substitution degrees of hydrogen atoms in acetone molecule were obtained. The actual acetone : formaldehyde molar ratio in the product was determined from the mass balance made for each reaction after water removal (and triethylamine, which later replaced potassium bicarbonate as catalyst; *cf.* Table I). It was found that the temperature of the reaction conducted in the presence of potassium bicarbonate should not exceed 40°C. Water removal should also be conducted at mild conditions (at below 50°C) under reduced pressure (13–20 hPa). At temperatures higher than 50°C, the resulting aldols dehydrate to unsaturated ketones ineffective as melamine solvents:



In ¹H-NMR spectra of the products heated to ≤ 50°C, signals appeared from protons of —CH= and CH₂= groups at 6.1 and 5.9 ppm, respectively.

A disadvantage of using potassium bicarbonate as a catalyst was the need to remove the product of its neutralization with hydrochloric acid : potassium chloride. It was removed by precipitation with acetone from the dehydrated product. This method of catalyst removal was effective for the products containing at most 2 mol of formaldehyde per mole of acetone (ace-

tone : formaldehyde = 1 : \leq 2). For the products containing more formaldehyde, the precipitation method became inefficient because more and more acetone was required. Furthermore, as shown in ref. 5, the products obtained in the presence of potassium bicarbonate or hydroxide required a high temperature (up to 140°C) to dissolve melamine. This was the reason why triethylamine was eventually used as the catalyst. It was easy to remove by distilling it off along with water. The amount of triethylamine was chosen to provide the same basicity as that in the potassium bicarbonate solution (i.e., pH 11). The presence of triethylamine was found to alter the course of reaction compared with that of potassium bicarbonate. Formation of hemiacetal groups in the product seemed favored in expense of direct reaction between acetone and formaldehyde. A clear signal at 4.04 ppm from the protons in the $-\text{O}-\text{CH}_2-\text{O}-$ grouping⁷ was found in the spectra of products obtained in the presence of triethylamine. The intensity of the same signal in the products obtained with potassium bicarbonate catalyst was very small. The reason is the ability of triethylamine to subtract protons from hydroxy groups with formation of alcoholate anions⁹ that easily react with the next formaldehyde molecule:



Later, the presence of hemiacetal groups in the reaction products turned out to be advantageous, because it improved melamine dissolution.

The main sought-for quality of the reactive solvents was their ability to dissolve high amounts of melamine. This ability improved with the number of moles of formaldehyde reacted with acetone. The best were the products 8-HMA and 10-HMA with an acetone : formaldehyde ratio of 1 : 8 and 1 : 10, respectively (*cf.* Table II). With a still higher amount of formaldehyde in the product, no increase in melamine solubility was observed. It was also noticed that, from the reactive solvents obtained with an acetone : formaldehyde ratio of 1 : \geq 8, a white precipitate appeared sometime after water removal. The precipitate vanished again upon heating the solvent with melamine. The melamine solutions in these solvents remained clear.

The addition of 20% water to the reactive solvents increased the solubility of melamine by 2.2–2.3 times. The addition of 30% water further increased this number to 2.8. The amounts of water higher than 30% only slightly improved melamine solubility (*cf.* Table III). During melamine dissolution, which took place at \sim 105°C, water evaporated and its final content was reduced to several percents.

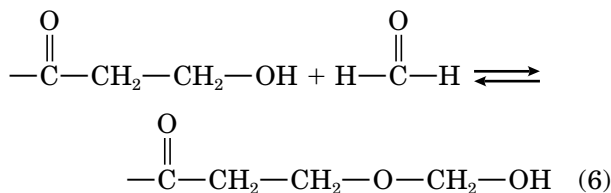
To summarize results of the study on the preparation of reactive solvents, one may state that the highest solubility of melamine had reactive solvents 8-HMA and 10-HMA. The solubility was 75–80 g or 81–98 g/100 g of solvent, respectively, and depended on the amount of water (up to 30% of the latter) introduced into the system. The percentage of melamine in the solutions ranged from \sim 43–50 wt %.

Even higher solubility of melamine was expected from solvents prepared at the temperature of formaldehyde addition to acetone as high as 80°C (just below the triethylamine boiling point). The second methyl group of acetone should have then reacted, too, and increased the number of hydroxy groups in the molecule to favor melamine solubility. Two products with acetone : formaldehyde ratios of 1 : 8 and 1 : 10 were prepared at 80°C. The reaction time reduced from \sim 50 h (at 40°C) to $<$ 10 h (*cf.* Table I). The products were found to dissolve higher amount of melamine than their analogues obtained at 40°C. The structure of these solvents was studied by ¹H-NMR to find the reason for the solubility difference.

Structure of Reactive Solvents

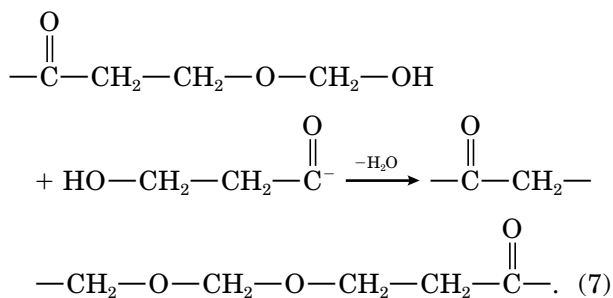
The analysis of the course of reaction between acetone and formaldehyde by ¹H-NMR (Table IV)

revealed that, in 1-HMA, the main component (i.e., 4-hydroxy-butan-2-on) was accompanied by small amounts of side and subsequent products so that the surface areas under peaks were at the ratio $S_{\text{CH}_3} : S_{\text{CH}_2} : S_{\text{OH}} = 3 : 3.6 : 0.7$, whereas for 4-hydroxybutan-2-on, it should be $S_{\text{CH}_3} : S_{\text{CH}_2} : S_{\text{OH}} = 3 : 4 : 1$. Small signals at 4.65 ppm and 4.50 ppm were also observed. The first came from methylene protons of hemiacetal groups formed in the reaction



This conclusion was confirmed by the increase of the signal intensity after the product was treated with gaseous formaldehyde at 40°C. On the other hand, the intensity of this signal decreased when the sample was heated to 90°C. The hemiacetal groups are known to decompose rapidly at this temperature.

The signal at 4.50 ppm came from protons of $\text{—O—CH}_2\text{—O—}$ bridges formed during linear condensation of hemiacetal groups with hydroxymethyl groups of the product:



This conclusion seems to be justified by:

- The presence of the same signal in $^1\text{H-NMR}$ spectra of dimethoxymethane and diethoxymethane¹⁰
- A higher signal intensity in the spectra of acetone derivatives containing more formaldehyde
- An increase of its intensity in the products heated at 105°C [i.e., at the temperature at which the bridge formation (dehydration) is fast].

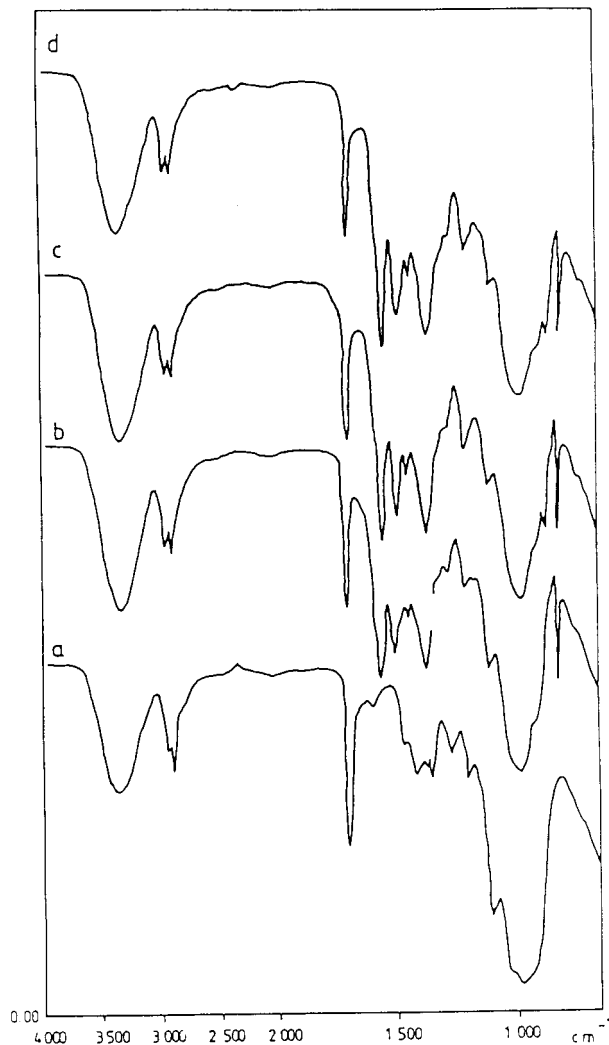


Figure 3 IR spectrum of 10-HMA reactive solvent (a) and those of melamine solutions in the reactive solvent recorded after 3 min (b), 5 min (c), and 7 min (d) from the beginning of dissolution.

The presence of < 1 mol of hydroxy groups per mole of product in 1-HMA can be explained in terms of:

- A “waste” of some formaldehyde in hemiacetal formation
- Condensation of some hydroxy groups as confirmed by the presence of a signal at 4.5 ppm
- Dehydration of the aldol product to an unsaturated ketone.

The presence of methylvinyl ketone, which is the product of aldol dehydration, is confirmed by the signals of vinyl group protons at 5.9–6.4 ppm,

as well as those from methyl protons of methylvinyl ketone at 2.2 ppm.¹⁰ The surface area ratio of these signals is $S_{\text{CH}_3} : S_{\text{CH}_2=\text{CH}} = 1 : 1$, as it should be. The product of reaction between acetone and formaldehyde (for 1-HMA) conducted at temperature higher than 40°C or heated at 100°C for several minutes contains an increased amount of methylvinyl ketone (increased intensity of signals at 5.8–6.4 and the signal at 2.2 ppm).

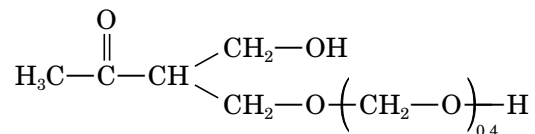
Formation of unsaturated ketones is suppressed when an excess of formaldehyde is used with respect to acetone. The reasons are: (1) a smaller number of protons at position β with respect to the hydroxy group that can form a water molecule, and (2) the presence of more and more hemiacetal groupings that hinder subtraction of β protons (a higher intensity of signals at 4.60 ppm).

A shift toward low field of the signal from hydroxy protons has been observed. This is usually attributed to intermolecular hydrogen bonding that is facilitated by the presence of hydroxy groups.

With some accuracy, one may assume that the surface area per one proton in the ¹H-NMR spectra of the successive products of acetone–formaldehyde condensation is:

$$S_{\text{H}} = (S_{\text{CH}_3} + S_{\text{CH}} + S_{\text{OCH}_2\text{O}} + S_{\text{OH}})/(6 + 2n)$$

where S is the surface area under signals from protons of respective groups, and n is the number of moles of formaldehyde that reacted with 1 mol of acetone. By comparing the values of S_{H} , the average amount of certain functional groups has been estimated in the products of reaction (Table IV). From the results, one may conclude that the product of, say, 1 mol of acetone with 3 mol of formaldehyde (3-HMA) has the structure



that contains exactly one methyl group. Thus, addition of the first formaldehyde molecule activates the methylene group formed, and the subsequent reaction takes place with the remaining proton of that group.

The spectra of products obtained in the presence of triethylamine contained signals from the same functional groups as those in the products

prepared with a potassium bicarbonate catalyst. The only difference was the presence of a higher amount of protons from $-\text{O}-\text{CH}_2-\text{O}-$ groups in the range of 4.4–4.6 ppm. The reason for that explains reactions (3)–(5).

In the products 3-HMA through 6-HMA, one can still find some amount of methylvinyl ketone, although its concentration becomes smaller the more formaldehyde has been used. In 8-HMA or products with more formaldehyde, methylvinyl ketone has not been detected in ¹H-NMR spectra, anymore.

Even in the products obtained at a high formaldehyde : acetone ratio, one can clearly observe the presence of unreacted methyl groups of acetone. Thus, despite reagent molar ratio, as well as the type of catalyst used, mostly one methyl group of acetone has reacted. In 1 mol of 3-HMA through 8-HMA, as much as 0.5–0.8 mol of methyl groups have been found. Formaldehyde was bound in the product in the form of polyoxymethylene groups, rather than just hydroxymethyl groups. For example, 10-HMA contains ~ 0.8 mol of unreacted methyl groups, 3 mol of hydroxy groups, and 6 mol of $-\text{O}-\text{CH}_2-\text{O}-$ bridges.

The presence of polyoxymethylene groups in the products has been confirmed by the total formaldehyde analysis made by using the sulfite method (Table V) combined with ¹H-NMR spectra. The highest fraction of hydroxymethyl groups in the products with the excess of formaldehyde with respect to acetone equal or exceeding 6 was only 3.7–3.8, which confirms the poor reactivity of the “second” methyl group of acetone.

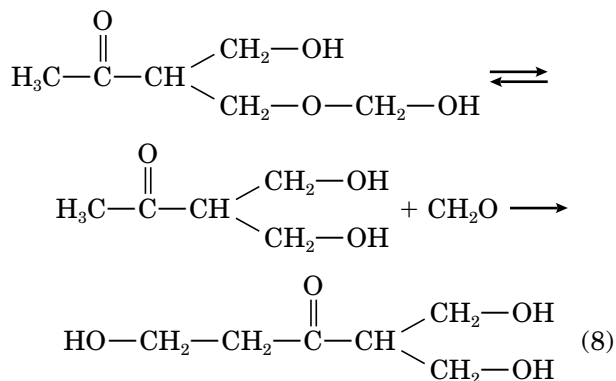
According to the literature,¹⁰ protons of $-\text{O}-\text{CH}_2-\text{O}-$ groups in five- or six-membered rings have chemical shifts of 4.85–4.9 ppm. Although small, signals at ~ 4.8 ppm have been found in the reactive solvents prepared in this work. This is not a conclusive presumption on the presence of ring structure. The signals in question may also be a result of the presence of $-\text{[CH}_2-\text{O]}_n-$ chains. Protons in these chains may have chemical shifts dependent on the value of n . A good consistency between direct formaldehyde determination (Table V, column 4) and ¹H-NMR spectra (Table IV, column 4) seems to confirm the conclusions on the structure of reactive solvents.

In ¹H-NMR spectra of the reactive solvents obtained at 80°C, the signal at 2.1 ppm was considerably smaller than the same signal in the solvents obtained at 40°C. This suggests that, at the elevated temperature, the “second” methyl groups of

acetone enter the reaction easier than at 40°C. Another point supporting this conclusion is a decrease of signal intensity at 3.5–3.6 ppm. The number of hydroxy groups per molecule, however, does not increase, as one might have expected. It is, on average, about three groups per molecule. This suggests that, at elevated temperature, the condensation of formaldehyde proceeds to a higher degree of polymerization than at 40°C.

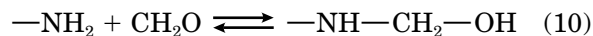
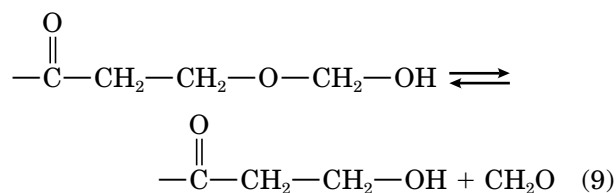
Dissolution Process

The analysis of spectra of reactive solvents that were heated at 105°C for 3 h has revealed the kind of processes one may expect to take place during melamine dissolution. Exposition of the solvents to elevated temperature led to a reduction in the intensity of the signals at 4.80, 4.70, 4.65, and 4.40 ppm. This indicated that a decomposition of $-\text{O}-\text{CH}_2-\text{O}-$ occurred in which both polyoxymethylene chains and hemiacetal groups took place. From the point of view of melamine dissolution, this was a favorable feature because formaldehyde thus liberated could directly react with melamine amino groups yielding its hydroxymethyl derivatives that further reacted with the solvent. On the other hand, the intensity of the signal at 4.5 ppm has been found to increase during heating. This increase indicated that the reaction of hemiacetal groups with hydroxy groups took place according to eq. (7). This reaction was not a desirable one for melamine dissolution, because it reduced the amount of functional groups capable of reaction with melamine. By comparing the ratio of signal areas $S_{\text{CH}_3} : S_{\text{CH}_2}$ in 1-HMA (1 : 2.2) with that after thermal treatment (1 : 3.7), one may conclude that the fraction of acetyl grouping $\text{CH}_3\text{CO}-$ decreases upon heating. This means that at high temperature formaldehyde released from hemiacetal groups condense with the acetyl one to the successive substitution products

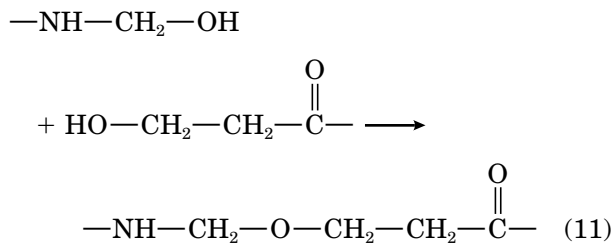


The melamine dissolution experiments were made in anhydrous 1-HMA and 10-HMA. To examine the dissolution process, the spectra of melamine and its hydroxymethyl derivatives were recorded beside those of the solutions. The spectrum of melamine is very simple; it contains just one signal at 6.6–6.5 ppm from all six protons of the amino groups.¹² In the spectra of the hydroxymethyl derivatives of melamine, there are signals from protons in $-\text{NHCH}_2\text{OH}$, $-\text{NH}_2$, $-\text{CHOH}$, $-\text{N}(\text{CH}_2\text{OH})_2$, and $-\text{NHCH}_2\text{OH}$ at 7.4, 6.5, 5.4, 5.1, and 4.8 ppm, respectively. For melamine dissolved in reactive solvents, one observes the following changes in its spectrum:

1. For systems in which melamine dissolution took 3 min, no signal at 6.5 ppm (primary amino groups) was present (Figs. 1 and 2). This means that all amino groups of melamine immediately react with the solvent.
2. The reaction converts the primary groups into secondary ones, as indicated by the presence of the signal at ~ 7.4 ppm (Fig. 1). The secondary groups react further when the system is heated. At the same time, a signal at 4.8 ppm (hydroxymethyl groups, $-\text{NHCH}_2\text{OH}$) appears, as well as a signal at 8.3 ppm that comes from the aldehyde proton of free formaldehyde present in solution. This suggests that melamine dissolution is accompanied by formation of its hydroxymethyl derivatives:



3. The increase in intensity of the signal at 4.0 ppm in the spectra recorded at the start of heating indicates that water has been formed in the system. It was a product of condensation of newly formed melamine hydroxymethyl groups with hydroxy groups of the solvent:



Upon further heating, water evaporated from the solution and the intensity of the signal decreased again. Additional water present in the solvent facilitated melamine dissolution. Water seems to have two effects: (1) physically dissolves some melamine and (2) facilitates decomposition of hemiacetal groups and the reaction of released formaldehyde with melamine.

4. In the spectrum of 1-HMA, the ratio of surface areas under signals from protons of —CH_3 and $(\text{CH}_2)_2$ was 1 : 1.2. In the spectrum after melamine has been dissolved in this solvent, the ratio changed to 1 : 2.5. This indicates that the structure $\text{—NH—CH}_2\text{—O—CH}_2\text{—CH}_2\text{—C=O}$ was formed according to reaction (11) and yielded signals at 3.4–3.6 ppm. Support for this conclusion provides spectra of *s*-triazine polyetherols obtained from melamine or its hydroxymethyl derivatives and oxirane that have similar $\text{—CH}_2\text{—CH}_2\text{—O—}$ structures and signals in the same region.^{11,12}
5. By heating 1-HMA with melamine, the intensity of signals at 5.9–6.4 and 2.2 ppm increased, thus indicating formation of more methylvinyl ketone.
6. No methylvinyl ketone was formed during dissolution of melamine in 10-HMA (no signals at 5.9–6.4 and 2.2 ppm). Hy-

droxymethylmelamines formed in this solvent contained amino group substituted by two hydroxymethyls (a signal at 5.0 ppm). A release of free formaldehyde was observed during melamine dissolution (signal at 8.3 ppm).

IR spectra of melamine solutions in the reactive solvents (Fig. 3) fully confirmed the mechanism of dissolution. The intensity of bands in the range of 1660–1550 cm^{-1} (deformational vibrations of melamine amino groups) decreased due to reaction with formaldehyde. Another proof for incorporating melamine structure into that of the solvent provided the peak at 815 cm^{-1} due to vibrations of the *s*-triazine ring.

REFERENCES

1. Z. Wirpsza and J. Brzeziński, *Aminoplasty*, WNT Publrs, Warsaw, 1970.
2. M. Kucharski and J. Lubczak, *Acta Polym.*, **42**, 186 (1991).
3. E. Smolin and L. Rapoport, *s-Triazines and Derivatives*, Interscience, New York, 1967.
4. K. Sato, *Bull. Chem. Soc. Japan*, **40**, 1547 (1967).
5. Z. Wirpsza, *Polimery* (Warsaw), **41**, 456 (1996).
6. Z. Wirpsza and N. Pietruszka, *Polimery* (Warsaw), **52**, 538 (1997).
7. *Methoden der Organischen Chemie, Makromolekulare Stoffe II*, Georg Thieme Verlag, Stuttgart, 1963, p. 422.
8. T. Kastierina and L. Kalinina, *Chemical Analysis of Plastic Materials* (in Polish, translated from Russian), WNT, Warsaw, 1965, p. 138.
9. J. Lubczak, *Ind. J. Chem., Sect. B*, **33**, 125 (1994).
10. *The Aldrich Library of ¹³C and ¹H-NMR Spectra*, Vol. I, Ed. I, Ch. J. Pouchert and J. Behnke, Milwaukee, 1993.
11. J. Lubczak, *J. Appl. Polym. Sci.*, **58**, 559 (1995).
12. J. Lubczak, *Polimery* (Warsaw), **40**, 509 (1995).