

New Melamine-Formaldehyde-Ketone Polymers: I. Synthesis of Reactive Solvents of Melamine from Selected Ketones

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ABSTRACT: Reactive solvents of melamine were prepared by reacting ketones with an excess of formaldehyde in the presence of triethylamine catalyst. The ketones used were cyclohexanone, cyclopentanone, acetophenone, benzoylacetone, biacetyl, or ethyl-methyl ketone. The structures of the resulting reactive solvents were studied by $^1\text{H-NMR}$. The best solubility of melamine was observed for the solvent

derived from ethyl-methyl ketone. Preliminary attempts at curing the melamine solutions yielded melamine-formaldehyde-ketone polymers. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1319–1332, 2005

Key words: reactive solvents; melamine; coatings; structure-property relations; heteroatom-containing polymers

INTRODUCTION

Melamine, a nontoxic and commercially available compound, is widely used in the chemical industry. It contains reactive amine groups and an aromatic *s*-triazine ring (thermally stable up to 360°C) that provides materials derived from it with excellent thermal stability and good dielectric properties.^{1–3} Melamine easily reacts with formaldehyde and with oxiranes yielding polyetherols containing *s*-triazine ring suitable for the synthesis of thermostable polyurethane foams.^{2,4,5}

In spite of these interesting advantages, literature data on applications of melamine in the synthesis of materials other than the classical melamine-formaldehyde resins is rather scarce. The reason might be that melamine is too poorly soluble in organic solvents to be a sufficiently interesting reagent.

The most commonly used solvents of melamine are water,² dimethyl sulfoxide,⁶ and polyhydroxyl alcohols⁷ that are capable of dissolving melamine to some extent. Melamine dissolves relatively well in formalin (above 80°C), but here the dissolution is accompanied by a chemical reaction leading to formation of hydroxymethyl derivatives and subsequently, to melamine-formaldehyde resins.

Applications of melamine could be considerably extended if suitable solvents could be found. Also, processing of its polymers could then be greatly facilitated. The attempts to find such solvents by Wirpsza^{7,8} led to some success. He discovered that melamine dissolves well in the products of reactions of formaldehyde with acetone or other ketones and called these products “reactive solvents of melamine.”^{7,8} His approach to this problem has already been the subject of several publications.^{9–12} It has been shown that melamine not only physically dissolves in the reactive solvents, but also reacts with them and forms a resin-like reactive system.^{8–10} The resulting solution, when heated and in the presence of acidic catalysts, condenses, yielding melamine-formaldehyde-ketone polymers.

In this article we describe new reactive solvents of melamine obtained by reacting various ketones with an excess of formaldehyde. The new products were tested as the reactive solvents of melamine at different temperatures. The resulting solutions were also cured in the presence of catalysts to obtain new melamine-formaldehyde-ketone polymers.

EXPERIMENTAL

Chemicals

Acetophenone (analytically pure (p.a.)), Avocado, Karlsruhe, Germany; Acetylacetone p.a., Aldrich, Milwaukee, WI; Benzoylacetone p.a., Avocado, Karlsruhe, Germany; Biacetyl p.a., Avocado, Karlsruhe, Germany; Cyclohexanone p.a., Chempur, Piekary Slaskie, Poland;

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Cyclopentanone p.a., Aldrich; Formalin pa., Standard, Lublin, Poland; Ethyl-methyl ketone p.a., Chempur; Melamine p.a., Fluka, Buchs, Switzerland.

Synthesis of reactive solvents

The reactive solvents were prepared in a three-necked 250 cm³ flask equipped with reflux condenser, thermometer, and mechanical stirrer, from predetermined amounts of ketones and formalin (33–33.5% of CH₂O). Typically, 1 mol of ketone was reacted with 1 to 5 mol of formaldehyde. (Some ketones, e.g., benzoylacetone or acetylacetone, reacted with formalin vigorously so that temperature in the flask rose to 100°C.) Triethylamine was then added to adjust pH to 11. The reaction was carried out at 80°C for 3–7 h. (Products of reaction of 1 mol of ethyl-methyl ketone with 5 mol of formaldehyde were obtained also at lower temperatures of 25°C, 40°C, and 60°C, by carrying out the reaction for appropriately longer times (7–9 h)). After that time water and catalyst were removed by distillation under reduced pressure (at 1200–2400 Pa, keeping the content of the flask at a temperature not exceeding 50°C).

Analytical procedures and spectral analysis

The course of reaction was followed by measuring the content of formaldehyde using the sulfite method.¹³ The mass of the reacting systems was controlled at each stage by weighing all substrates, postreaction mixture, and the product obtained after water and catalyst have been distilled off with an accuracy of ±0.1 g.

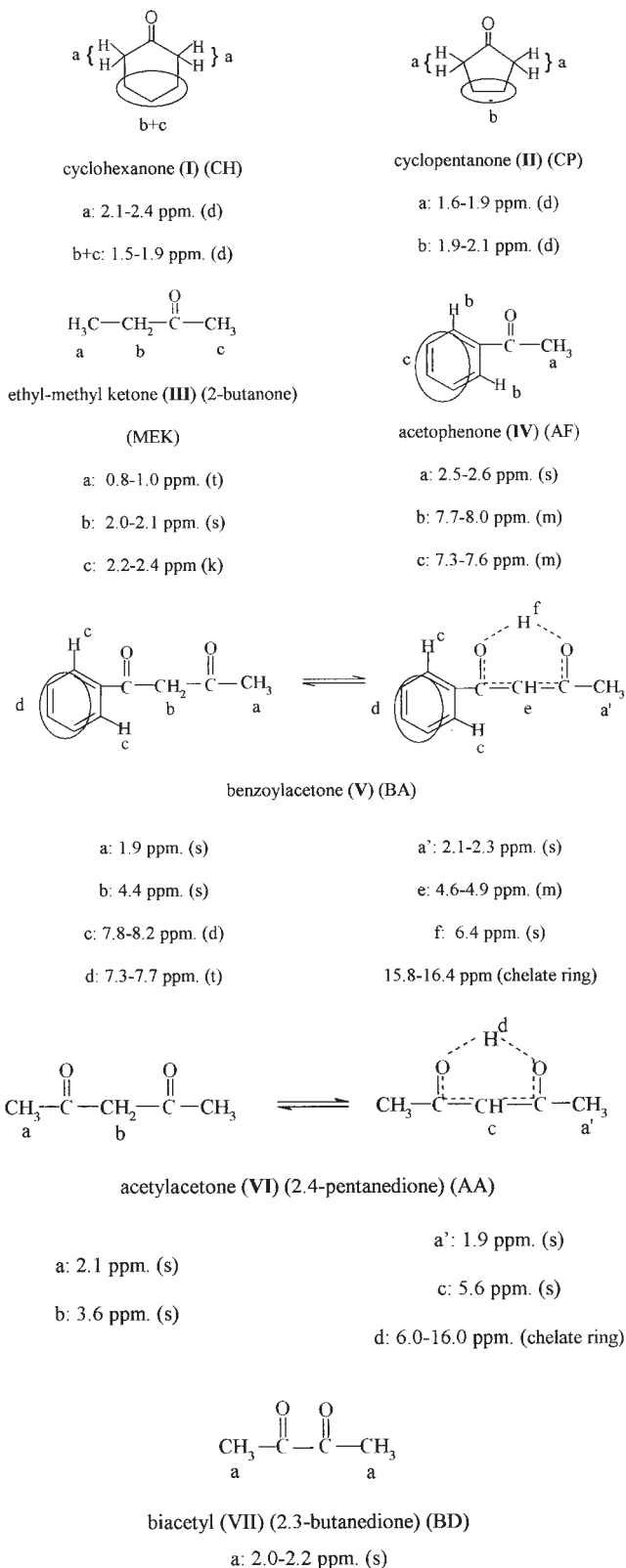
¹H-NMR spectra were recorded with a Tesla BS-587A spectrometer in d₆-DMSO with hexa-methyldisiloxane as an external standard. The chemical shifts, δ, are expressed in ppm.

Properties of reactive solvents

The physical properties of reactive solvents were measured at 20°C. These were the refractive index (Abbe refractometer), specific density (pycnometrically), viscosity (Höppler viscometer), and surface tension (ring detachment method). The amount of free and unstable (labile) formaldehyde was determined by the sulfite method.¹³

Solubility of melamine in reactive solvents and curing attempts

The solubility of melamine was measured by gradual and single introduction of melamine to a reactive solvent, or with addition of 10–40 wt % of water. The curing procedure was described in a previous paper.¹⁰



Scheme 1

RESULTS AND DISCUSSION

The study on hydroxymethyl derivatives of ketones was initiated anticipating that since melamine dis-

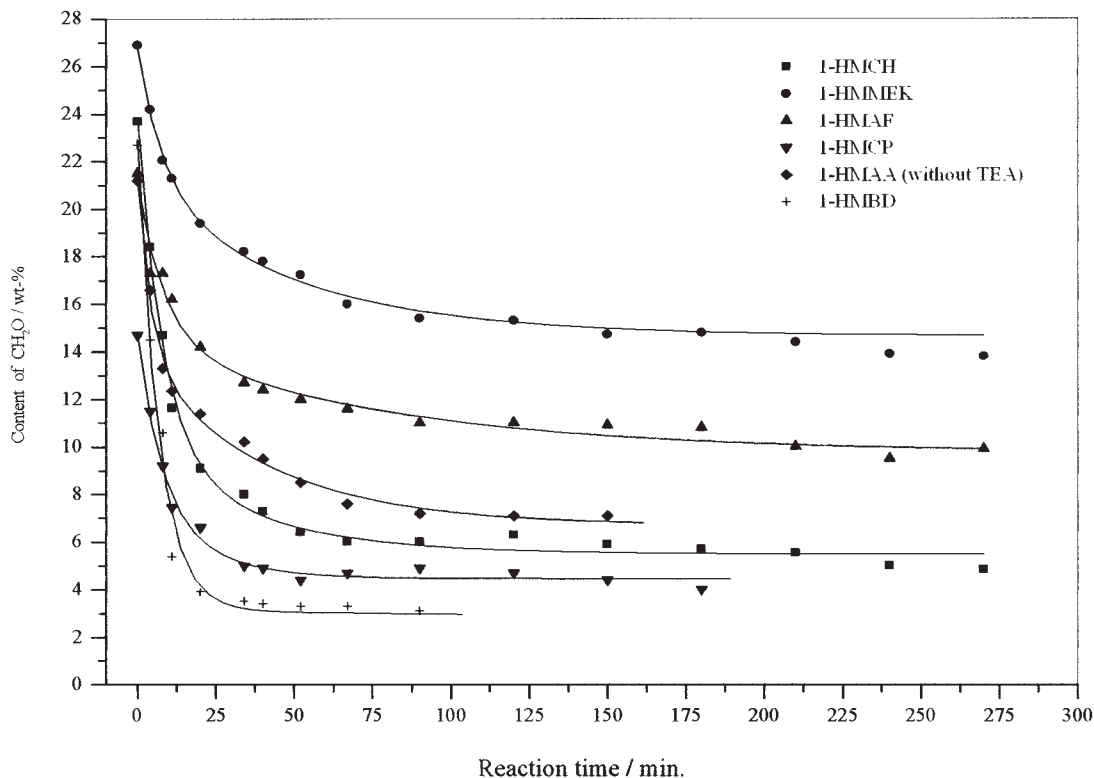


Figure 1 Unreacted formaldehyde versus time in the reaction with ketones. Molar ratio of ketone to formaldehyde 1 : 1. Temp. 80°C.

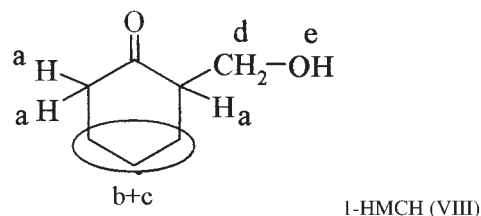
The reactive solvents are coded in this work with the symbol: *n*-HMketone (temp.) where *n* is the molar excess of formaldehyde over ketone (1 or 5) as used in the synthesis stage, *ketone* is the abbreviated ketone name coded with two capital letters as defined in Scheme 1, and temperature is specified in parentheses, if different from the standard 80°C. HM stands for *hydroxymethyl*.

In most cases the reactive solvents were thick transparent liquids (Table II), but some of them (e.g., 5-HM-MEK (40°C), 5-HMAA, and 5-HMAF) after 7–14 days became turbid, became thicker, and finally turned into semisolid or solid greasy substances. This was a reversible behavior since the substances became clear and liquid again after heating to 80–90°C.

The postreaction mixtures obtained from acetophenone or acetylacetone were two-phase systems. The organic phase was separated and distilled under reduced pressure to remove the remaining water.

The structures of the reactive solvents were analyzed using ¹H-NMR. In the spectra of the products of reaction of formaldehyde with cyclohexanone (I) (Fig. 4a,b), one observes a reduction in intensity of signals in the range 2.1–2.5 ppm due to reaction of α -methylene protons of cyclohexanone with formaldehyde (reaction 1). New signals appear instead at 3.1–3.7 ppm

due to methylene group protons in $-C-CH_2-OH$ (d) and hydroxyl protons (e) at 4.3 ppm. The actual ratio of signal areas a : (b + c) : d : e in the spectrum of 1-HMCH is 1.8 : 4.2 : 2.7 : 1 in contrast to the calculated 3 : 6 : 2 : 1.



It suggests that a part of cyclohexanone does not take part in the reaction. This is confirmed by the mass balance. The reason is the subsequent reaction of formaldehyde with newly formed hydroxyl groups. The reaction leads to semiacetals.

In the ¹H-NMR spectrum of 5-HMCH one observes, besides the signals from protons (a), (b + c), (d), and (e), the presence of signals from semiacetal methylene groups in the range 4.65–4.8 ppm (cf. eq. (3)) and a signal in the range 4.4–4.65 due to protons in polyoxy-methylene groups $-C-O-CH_2-O-C-$ (cf. eq. (4) and Table III).

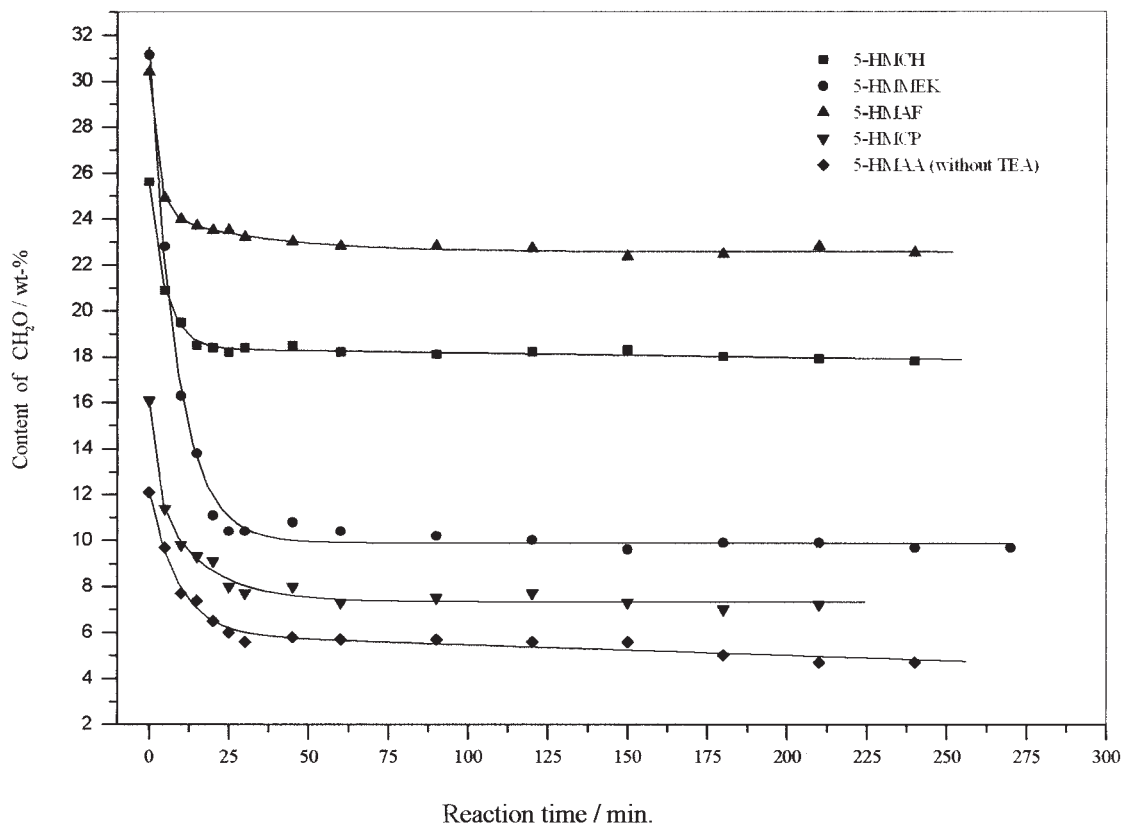


Figure 2 Unreacted formaldehyde versus time in the reaction with ketones. Molar ratio of ketone to formaldehyde 1 : 5. Temp. 80°C.

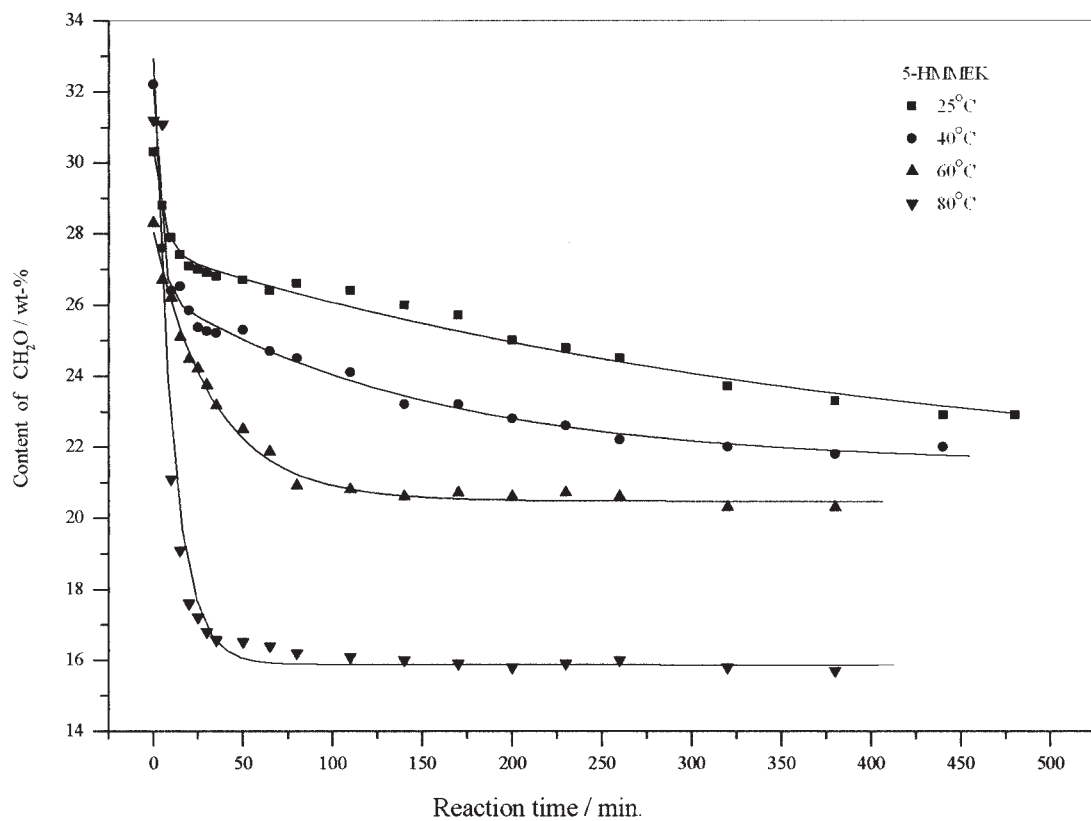


Figure 3 Unreacted formaldehyde versus time in preparation of 5-HMMEK at various temperatures.

TABLE II
Properties of the Reactive Solvents of Melamine (at 20°C)

No.	Reactive solvent (RS)	Density (g/cm ³)	Surface tension* 10 ⁻³ (N/m)	Viscosity (Pa·s)	Refractive index	CH ₂ O content (wt %)	Appearance after distillation under reduced pressure
1	1-HMCH	1.120	34.6	0.120	1.4672	3.0	clear, clean, liquid
2	5-HMCH	1.231	49.6	0.561	1.4641	28.1	clear, liquid, thick
3	1-HMCP	1.161	37.5	1.201	1.4773	1.8	clear, thick, liquid, light yellow
4	5-HMCP	1.245	45.4	1.207	1.4731	16.7	clear, thick, liquid, light yellow
5	1-HMMEK	1.056	38.9	0.077	1.4588	12.5	clear, liquid, thick
6	5-HMMEK (26°C)	1.176	43.7	0.114	1.4478	38.1	clear, liquid, thick
7	5-HMMEK (40°C)	1.162	39.7	0.142	1.4488	35.6	clear, liquid, thick
8	5-HMMEK (60°C)	1.154	38.9	0.156	1.4450	32.3	clear, liquid, thick
9	5-HMMEK (80°C)	1.168	46.7	0.254	1.4512	43.0	liquid, thick
10	1-HMAF	1.048	18.5	0.002	1.5282	5.4	clear, liquid, low viscosity
11	5-HMAF	1.123	47.8	0.006	1.5152	36.4	liquid, thick, turbid
12	1-HMAA (with TEA)	1.167	52.4	1.984	1.4872	2.7	clear, liquid, thick, yellow
13	5-HMAA (with TEA)	1.172	40.0	0.275	1.4590	23.0	clear, liquid, thick, yellow
14	5-HMAA (without TEA)		semisolid product		1.4613*	23.9*	turbid, creamy, semisolid

* Just after distillation under reduced pressure.

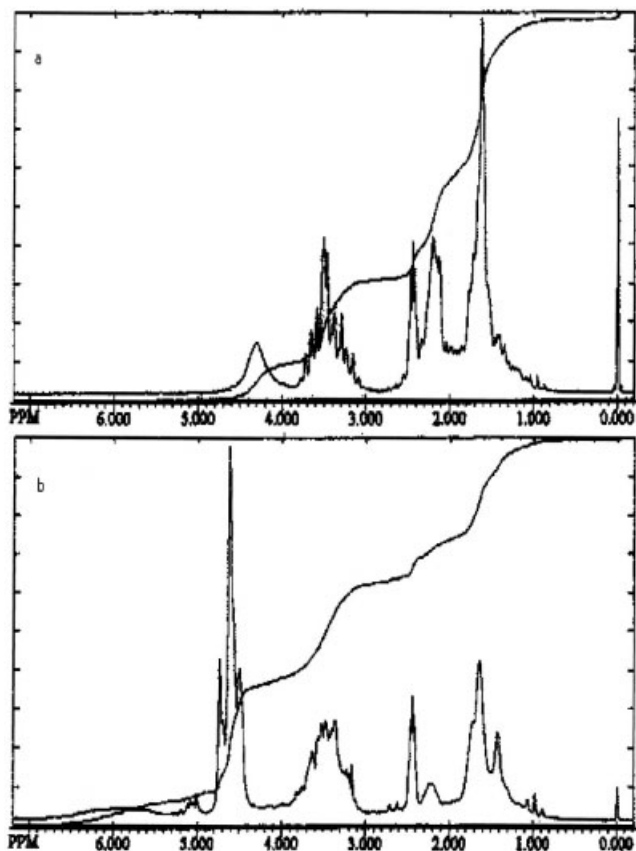


Figure 4 ¹H-NMR spectra in d₆-DMSO of the products of reaction between cyclohexanone and formaldehyde at the molar ratio of reagents: (a) 1 : 1 (1-HMCH); (b) 1 : 5 (5-HMCH).

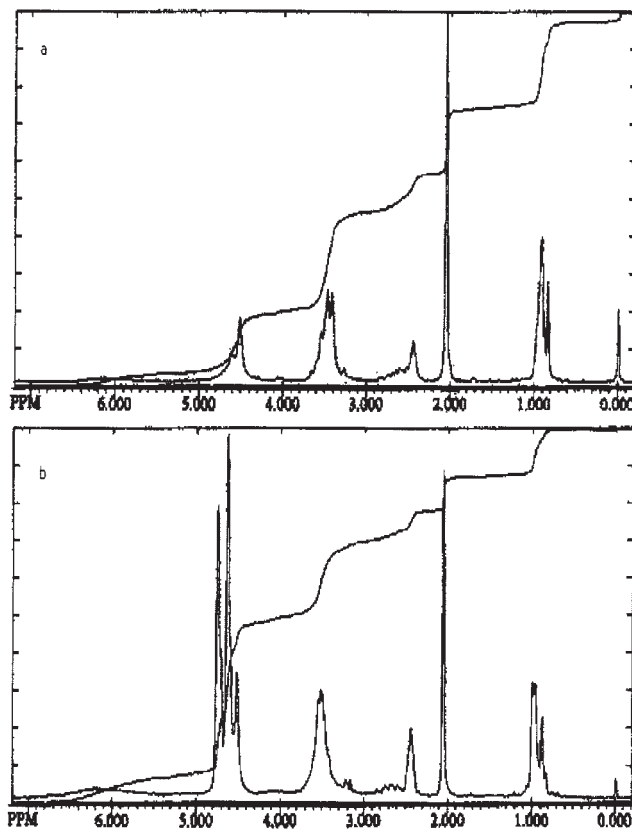
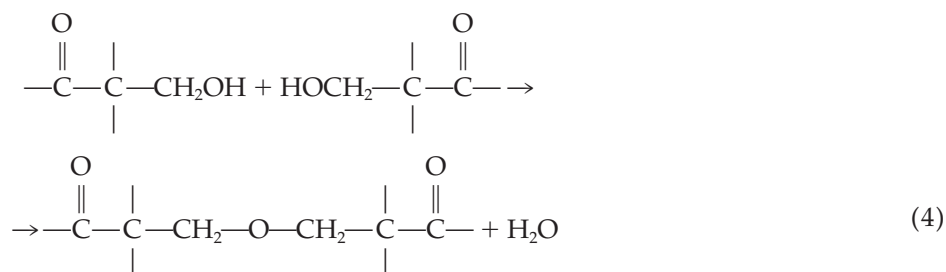
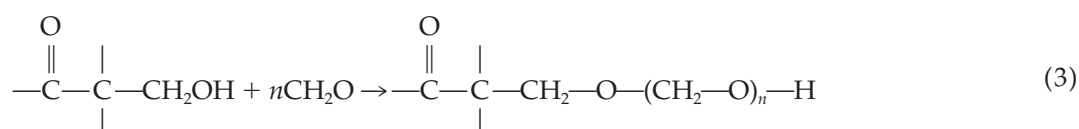


Figure 5 ¹H-NMR spectra in d₆-DMSO of the products of reaction between ethyl-methyl ketone and formaldehyde at the molar ratio of reagents: (a) 1 : 1 (1-HMMEK); (b) 1 : 5 (5-HMMEK).

TABLE III
Content of Hydroxyl Groups and Groupings Containing Unstable (Labile) Formaldehyde

No.	Reactive solvent (RS)	Content of groupings (mol/mol RS)		
		semiacetal —O—CH ₂ —OH	polyoxymethylene —C—CH ₂ —O—CH ₂ —C—	hydroxyl —OH
2	5-HMCH	1.23	1.33	2.22
4	5-HMCP	1.17	0.68	1.30
5	1-HMMEK	0.37	0.28	0.50
6	5-HMMEK (25°C)	1.20	1.50	2.00
7	5-HMMEK (40°C)	1.21	1.51	2.21
8	5-HMMEK (60°C)	1.24	1.46	2.26
9	5-HMMEK (80°C)	1.20	1.40	2.40
10	1-HMAF	0.20	0.07	0.50
11	5-HMAF	0.34	0.92	1.09

Numbers pertain to those in Tables I and II.



The reactions between cyclopentanone (II) or ethylmethyl ketone (III) and 1 or 5 mol of formaldehyde proceed similarly to that between cyclohexanone and formaldehyde (Fig. 5, a,b), except that in the ¹H-NMR spectrum of 1-HMMEK, one observes a signal from protons of methylene groups in the range 4.7–4.8 ppm formed in the subsequent reaction of formaldehyde with hydroxymethyl derivative of the ketone (reaction per eq. (3)). Formation of these semiacetal groups is advantageous from the point of view of melamine dissolution, as will be shown later. In the range 5.8–6.4 ppm one observes a broad signal due to hydroxyl protons that form polyassociates. The spectrum recorded with heavy water (D₂O) has no signal in the range 5.8–6.4 ppm proving that signal to be due to mobile —OH protons of —C—CH₂—OH. The signal in the range 4.6–4.8 ppm becomes reduced in the presence of D₂O. This indicates that it is due to not only methylene group protons, but also due to “nonassociated” hydroxyl groups.

In the ¹H-NMR spectrum of the product of reaction between 1 mol of ethyl-methyl ketone and 5 mol of formaldehyde (5-HMMEK) prepared at room temper-

ature, one observes a further decrease of methylene proton signal (Fig. 5b).

Furthermore, with temperature increase, the signals from methylene groups in —C—O—CH₂—OH (4.65–4.8 ppm) or —C—O—CH₂—O—C—(4.4–4.65 ppm) groups also increase. This suggests that, as expected, a higher amount of the products of subsequent reactions with formaldehyde are formed than for 1-HMMEK (cf. reactions per eqs. (3) and (4)). In the product 5-HMMEK obtained at 80°C, the signals due to OH groups in the range 5.9–6.5 ppm are significantly reduced, thus indicating that under these conditions a condensation reaction between molecules of the reactive solvent takes place (cf. Table III).

In the case of acetophenone (IV), at the molar ratio 1 : 1, substitution of all hydrogen atoms in methyl group (CH₃—C = O) with hydroxymethyl groups does not occur. The spectrum indicates that a mixture of unchanged acetophenone and monosubstituted derivative (1-HMAA) is formed. The reason might be the poor solubility of acetophenone in the reaction medium. To obtain a reactive solvent from acetophenone, an excess of formaldehyde should be used, for example, 5 mol of CH₂O per mole of AF.

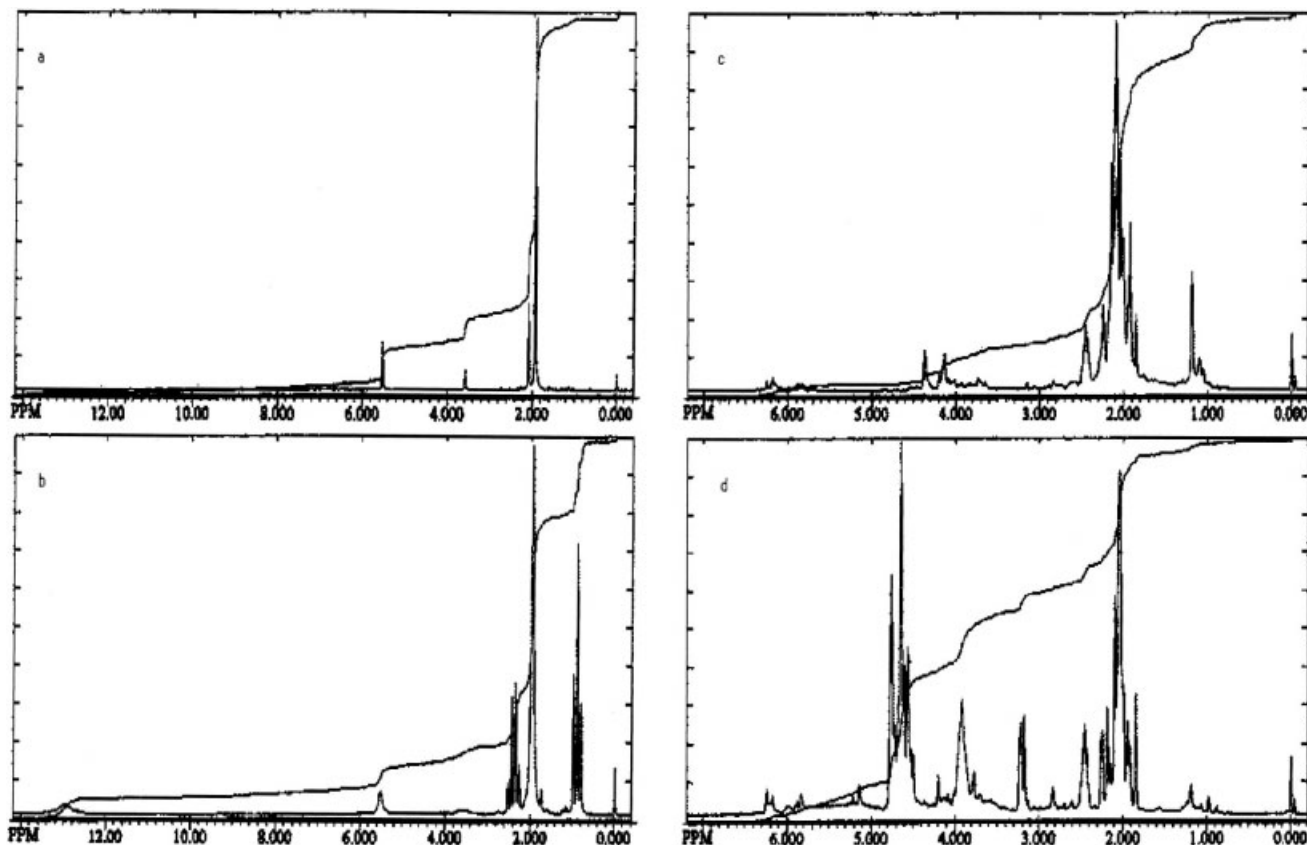


Figure 6 $^1\text{H-NMR}$ spectra in d_6 -acetone of the products of reaction between formaldehyde and (a) acetylacetone, (b) acetylacetone and triethylamine (TEA). $^1\text{H-NMR}$ spectra in d_6 -DMSO of the products of reaction of acetylacetone with formaldehyde (TEA catalyst): (c) 1 : 1 (1-HMAA), (d) 1 : 5 (5-HMAA).

In the $^1\text{H-NMR}$ spectrum of benzoylacetone (V), the presence of both keto and enol forms of this compound is seen. The fraction of enol form calculated from the spectrum is 83%.

The course of reaction of formaldehyde with ketones that constituted a mixture of ketonic and enolic forms was carried out with acetylacetone as an example. Pure acetylacetone (VI) also constitutes a mixture of two tautomeric isomers. The content of the enolic form considerably exceeds that of the ketonic one and is $\sim 75\%$ in d_6 -acetone and $\sim 64\%$ in d_6 -DMSO. The presence of triethylamine (used as the catalyst of reaction with formaldehyde) shifts the equilibrium towards the enolic form (Fig. 6a,b). In the $^1\text{H-NMR}$ spectrum, the signals due to methylene protons and of methyl groups in enolic form (at 3.8 and 2.2 ppm, respectively) disappear. Hence, in the presence of triethylamine, acetylacetone reacts with formaldehyde with its enolic form. Formaldehyde addition takes place directly to hydroxyl groups of this form and mostly $-\text{O}-\text{CH}_2\text{OH}$ groups are being formed (Fig. 6c,d). The spectrum of the product of reaction between 1 mol of acetylacetone with 5 mol of formaldehyde (5-HMAA) clearly confirms the course of reaction. A signal from $-\text{O}-\text{CH}_2\text{OH}$ groups at 4.8 ppm is clearly

seen, whereas the signal from $-\text{C}-\text{CH}_2\text{OH}$ groups in the range 3.6–4.2 ppm is rather small.

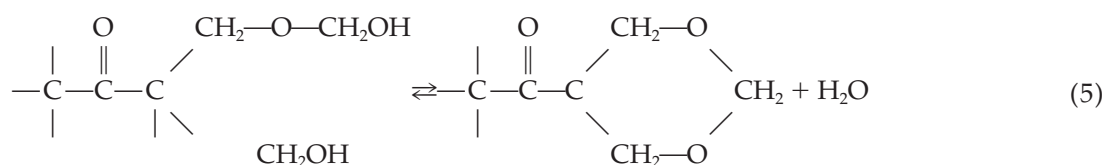
Biacetyl (butane-2,3-dione) (VII) occurs in ketonic form only. It can be deduced from $^1\text{H-NMR}$ spectra that substitution of methyl group takes place easily (in reaction with formaldehyde), but the products have an unpleasant smell of rotten butter and, as will be shown later, do not dissolve melamine well. For these reasons, they were not studied any further.

In the next step, melamine was introduced to the freshly prepared reactive solvents. The solubility was determined by gradual introduction of melamine into the solvents (Table IV), by dissolving melamine in one step (Table V), and by dissolving melamine in the solvent diluted with 10–40 wt % of water (Table VI).

The solubility of melamine was found to depend on the kind of ketone and the type of hydroxymethyl derivative of the ketone. A criterion of solvent quality was the amount of melamine dissolved in the solvent. This amount was found to be higher when melamine was introduced into the solution in small portions, each after the previous one had fully dissolved (Table IV). The reason was the cyclization reaction and self-condensation of the solvent molecules according to the reactions:

TABLE IV
The Maximum Solubility of Melamine in Reactive Solvents at Its Gradual Introduction (no water added)

No.	Reactive solvent (RS)	Amount of mel added R_{Mel} (g/100g initial amount of RS)	Solubility R'_{Mel} (g/100g final amount of RS)	Percentage of Melamine (wt %)
1	1-HMCH	3.8	3.8	3.7
2	5-HMCH	26.4	25.3	25.0
3	1-HMCP	3.6	4.1	3.9
4	5-HMCP	7.2	8.0	7.4
5	1-HMMEK	20.6	19.9	19.3
6	5-HMMEK (25°C)	24.4	28.3	22.0
7	5-HMMEK (40°C)	28.3	27.8	26.4
8	5-HMMEK (60°C)	27.4	26.6	24.9
9	5-HMMEK (80°C)	28.6	27.4	26.7
10	1-HMAF	3.3	3.6	3.5
11	5-HMAF	17.5	20.5	17.0
12	1-HMAA (with TEA)	3.3	3.5	3.4
13	5-HMAA (with TEA)	18.8	23.2	18.8
14	5-HMAA (without TEA)	10.6	12.0	10.7



or

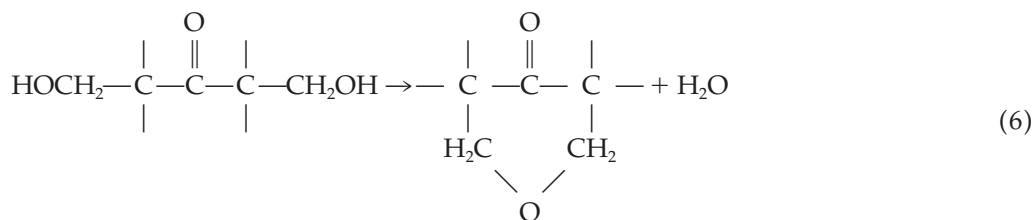


TABLE V
The Maximum Solubility of Melamine in Reactive Solvents at One Step Introduction (no water added)

No.	Reactive solvent (RS)	Amount of Mel added R_{Mel} (g/100g initial amount of RS)	Solubility R'_{Mel} (g/100g final amount of RS)	Percentage of Melamine (wt %)
1	1-HMCH	3.8	3.8	3.7
2	5-HMCH	30.4	29.3	22.5
3	1-HMCP	4.3	3.6	3.5
4	5-HMCP	11.2	10.3	7.4
5	1-HMMEK	20.6	19.9	17.1
6	5-HMMEK (25°C)	32.2	31.9	27.5
7	5-HMMEK (40°C)	36.2	35.8	28.6
8	5-HMMEK (60°C)	32.8	31.4	27.2
9	5-HMMEK (80°C)	33.6	32.4	27.8
10	1-HMAF	3.4	3.4	3.1
11	5-HMAF	25.2	24.3	21.9
12	1-HMAA (with TEA)	3.4	3.1	3.0
13	5-HMAA (with TEA)	23.2	22.6	20.4
14	5-HMAA (without TEA)	17.3	17.1	16.2

TABLE VI
The Maximum Solubility of Melamine in Reactive Solvents Containing Water

No.	Reactive solvent (RS)	Water added (wt %)	Amount of Mel added R_{Mel} (g/100g initial amount of RS)	Solubility R'_{Mel} (g/100g final amount of RS)	Percentage of compound (wt %)
1	1-HMCH	10	3.8	3.7	3.4
		15	4.3	4.2	3.8
		20	3.2	3.0	2.9
		25	3.6	3.1	3.0
		30	4.1	3.9	3.5
		35	7.0	5.7	5.4
		40	6.7	5.2	5.0
2	5-HMCH	10	39.2	42.7	29.9
		15	56.2	57.7	36.6
		20	69.9	69.8	41.1
		25	79.4	76.3	43.3
		30	86.5	71.4	44.5
		35	96.7	88.7	47.0
		40	103.2	90.8	47.6
3	1-HMCP	10	3.9	3.8	3.6
		15	3.7	3.6	3.4
		20	4.2	3.9	3.8
		25	7.6	6.8	6.4
		30	7.3	6.5	6.3
		35	7.4*	6.3	5.9
		40	18.6	19.4	16.2
4	5-HMCP	15	26.6	26.3	20.8
		20	38.3	37.4	27.2
		25	49.1	46.6	31.8
		30	61.4	55.5	35.7
		35	72.1*	67.5	40.3
		40	23.5	23.0	19.9
		15	23.5	23.2	20.2
5	1-HMMEK	20	30.3	30.1	23.5
		25	33.1*	32.4	24.4
		10	42.1	42.1	27.7
		15	54.8	49.2	32.3
		20	65.4	60.1	35.3
		25	77.0	66.8	40.0
		30	88.5	78.3	43.9
6	5-HMMEK (25°C)	35	96.1	84.7	45.5
		40	103.6	86.8	46.5
		10	46.3	47.6	32.2
		15	57.7	56.7	36.2
		20	69.5	67.4	40.3
		25	77.1	68.0	40.5
		30	81.8	70.1	41.2
7	5-HMMEK (40°C)	35	92.3	74.4	42.7
		40	99.8	79.5	44.4
		10	41.9	42.1	29.7
		15	55.3	37.9	61.0
		20	63.9	59.7	37.4
		25	75.1	70.7	41.4
		30	83.7	73.8	42.5
8	5-HMMEK (60°C)	35	97.1	78.8	43.7
		40	102.6	79.6	44.3
		10	39.5	42.4	29.8
		15	49.8	51.8	34.1
		20	57.0	58.4	36.9
		25	69.1	69.7	41.1
		30	84.5	72.6	42.1
9	5-HMMEK (80°C)	35	95.7	75.1	43.2
		40	102.6	77.3	43.7
		10	7.1	7.3	6.8
		15	3.7	3.3	3.2
		10	7.1	7.3	6.8
		15	3.7	3.3	3.2
		10	1-HMAF	15	3.7

TABLE VI Continued

No.	Reactive solvent (RS)	Water added (wt %)	Amount of Mel added R_{Mel} (g/100g initial amount of RS)	Solubility R'_{Mel} (g/100g final amount of RS)	Percentage of compound (wt %)
		20	3.9*	3.4	3.3
		10	34.0	35.6	26.2
		15	43.0	42.9	30.0
		20	59.1	56.2	36.0
		25	67.6	63.1	38.7
		30	73.2	76.2	43.2
		35	81.1	68.1	40.5
11	5-HMAF	40	85.6	77.5	43.4
		20	3.6	3.2	3.1
		25	3.7	3.2	3.1
		30	3.0	3.3	3.1
12	1-HMAA (with TEA)	35	7.4*	6.8	5.7
		10	27.5	29.9	23.0
		15	27.4	26.5	20.9
		20	28.1	27.2	21.4
		25	27.8	37.5	27.3
		30	28.2	25.0	20.0
		35	27.6	23.5	19.0
13	5-HMAA (with TEA)	40	27.6	23.1	18.8
		10	22.4	21.7	17.8
		15	24.8	23.7	19.1
		20	28.5	25.9	20.6
		25	27.1	23.6	19.1
		30	30.1	24.4	19.6
		35	30.0	23.6	19.1
14	5-HMAA (without TEA)	40	29.3	22.6	18.4

* Further introduction of water does not improve the solubility.

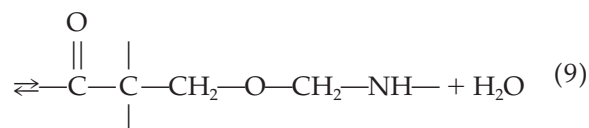
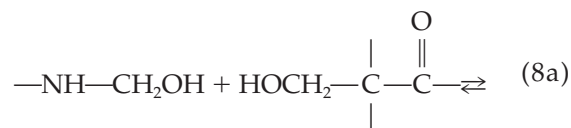
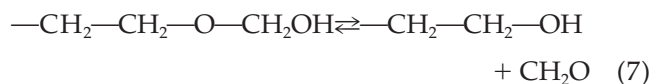
Formation of these structures reduces the content of hydroxymethyl groups in the structure of reactive solvent, but does not reduce melamine solubility, because at elevated temperature 1,3-dioxane groups (cf. reaction per eq. (5)) are unstable and first decompose and then react with melamine.

Introduction of melamine in one portion (in the amount determined by the gradual method) makes possible dissolution of several percent more melamine by weight (Table V).

The reactive solvents with 1 : 1M ratio of components were synthesized to adjust preparation conditions and to check on the reactivity of various ketones in the reaction with formaldehyde. In the case of reactive solvents obtained in reactions of 1 mol of ketone with 1 mol of formaldehyde (e.g., 1-HMMEK, 1-HMCP, 1-HMAA, or 1-HMAF), addition of water does not improve melamine solubility. The reason seems to be the small amount of semiacetal groups in the reactive solvents. Increasing the amount of water may only dissolve additional melamine to a negligible extent.

The reactive solvents obtained from 1 mol of ketone and 5 mol of formaldehyde exhibit much better melamine solubility. The reason is the presence of O-hydroxymethyl groups. Introduction of water to these derivatives usually further improves this property (cf. Table VI). At elevated temperature (above 90°C) the

O-hydroxymethyl groups decompose, releasing formaldehyde, which then reacts with melamine (per eqs. (7) and (8)). The resulting hydroxymethyl derivatives of melamine condense with hydroxymethyl derivatives of the reactive solvent, thus improving melamine solubility (per eq. (9)).¹⁴



The changes in melamine solubility with the differing ways of introducing it clearly indicate that the dissolution is accompanied by chemical reaction (per eqs. (7)–(9)). Water seems to play a double role. It dissolves

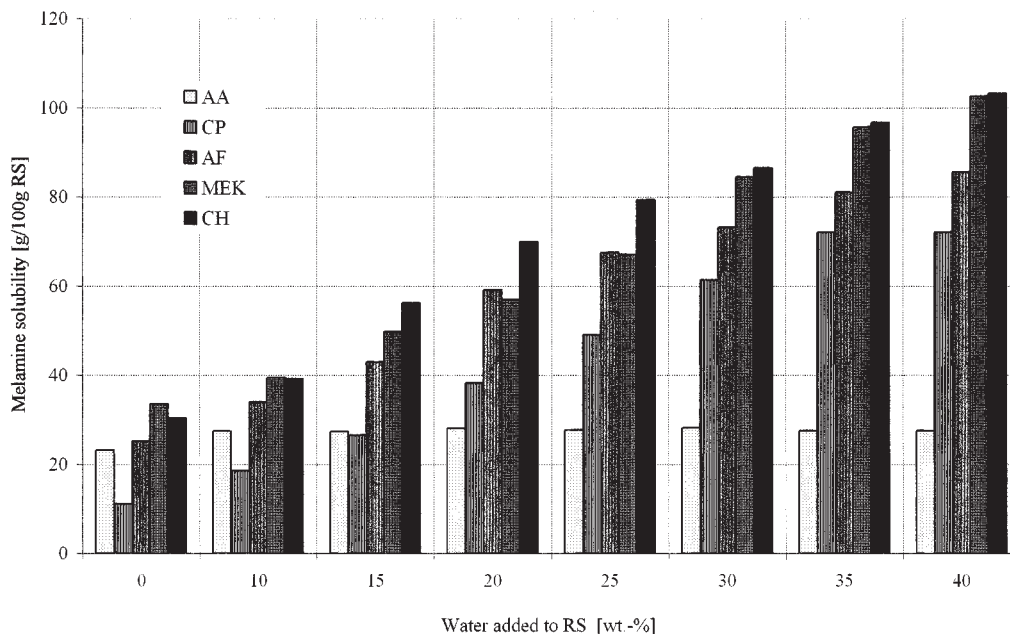


Figure 7 Solubility of melamine in the reactive solvents (containing water) prepared from 1 mol of ketone and 5 mol of formaldehyde.

some melamine, and facilitates decomposition of semiacetal groups and hence the reaction between melamine and formaldehyde.

The highest amount of melamine introduced in one portion (in g per 100 g of reactive solvents (RS)) dissolved in the solvent derived from ethyl-methyl ketone (5-HMMEK) at 40°C (36.2). Slightly less melamine dissolved in other reactive solvents: 5-HMCH (30.4), 5-HMAA (23.2), and 5-HMAF (25.2) (Table IV).

One observes considerable improvement in melamine solubility after introducing to the reactive solvent 10 wt % of water (and then also by increasing the amount of water by 5 wt % portions) (Table V). In the presence of 10 to 40 wt % of water, the solubility of melamine was very high in all RS obtained from ethyl-methyl ketone. In (5-HMMEK) obtained at different temperatures and diluted with 40 wt % of water, the solubility of melamine in g/100 g of RS was 103.6 (25°C), 99.8 (40°C), 102.6 (60°C), and 102.6 (80°C). In 5-HMCH diluted with 40 wt % of water, the solubility was 103.2 g/100 g of RS. Good solubility power was also observed for 5-HMAF (solubility 85.6). It was noticed that when the amount of dissolved melamine was approaching 100 g per 100 g of RS, after several hours the solution became opalescent.

In the reactive solvents obtained from acetylacetone, mostly the semiacetal groups $-O-CH_2OH$ are present. This fact significantly affects the process of melamine dissolution. Formaldehyde freed from the semiacetal groups at elevated temperature reacts with melamine, converting the latter into hydroxymethyl derivatives (per eqs. (7) and (8)). Since in the RS obtained from this ketone, no semiacetal groups are then left, it cannot further condense with hydroxymethyl derivatives of

melamine (per eq. (9)) and the solubility of melamine in this RS is reduced. Furthermore, when dissolving melamine in the reactive solvents obtained from acetylacetone, it is difficult to determine melamine solubility since the RS itself is not fully miscible with water (when its amount is 30 or 40 wt %). The melamine solubility in this RS was not high, anyhow, and the attempts of curing them also failed; the coatings were yellow, turbid, and slightly blistered.

Consequently, further experiments were carried out with RS exhibiting the highest melamine solubility, that is, 5-HMCH, 5-HMMEK, 5-HMAF, and 5-HMAA (Fig. 7).

Attempts were made to cure the solutions of melamine in reactive solvents. The solutions were all cured at 120°C, but the time of curing was varied (from 30 to 120 min). The catalysts were concentrated HCl (36%), HCOOH (80%), and CH_3COOH (80%), used in the amounts 0.5, 1.0, and 2.0 wt %. Attempts at curing without catalyst were also performed.

No cured products were obtained from melamine solutions in reactive solvents obtained by using equimolar ratio of reagents (ketone and formaldehyde) because of low melamine solubility and lack of gelation.

As shown in Table VII, the melamine solutions in the reactive solvent yield transparent and slightly opalescent (5-HMAF), light-yellow and transparent (5-HMCP), or colorless, transparent, and hard (5-HMCH or 5-HMMEK) coatings.

Further studies of the properties of melamine-formaldehyde-ketone resins and cured products will be limited to the reactive solvents prepared from cyclohexanone (I), cyclopentanone (II), ethyl-methyl ketone (III), and acetophenone (IV).

TABLE VII
Curing of Melamine-Formaldehyde-Ketone Resins at 120°C

Reactive solvent (RS)	Catalyst		Water Added (wt %)	Melamine added (g/100g RS)	Curing Time (min)	Appearance of coatings
	Type	Amount (%wag.)				
5-HMCH	-	-	30	66.6	30 ÷ 60	hard, transparent
			20	76.8	30 ÷ 90	
5-HMCP	-	-	30	59.2	30 ÷ 120	transparent, smooth yellowish, transparent, smooth
			20	63.7	30 ÷ 90	
5-HMMEK (25°C)	-	-	30	83.2	30 ÷ 120	colorless, smooth, transparent
5-HMEK (40°C)	-	-	20	59.8	30 ÷ 90	
5-HMMEK (60°C)	-	-	20	62.8	30 ÷ 120	colorless, smooth, transparent
			-	26.5	30 ÷ 120	colorless, smooth, excellent adhesion
5-HMMEK (80°C)	-	-	20	56.8	30 ÷ 90	colorless, smooth, hard
			30	69.9	30 ÷ 120	colorless, smooth, brittle
		0.5	30	99.8		very brittle, milky white
			20	49.9		
			60.0		30 ÷ 60	very brittle
				69.9		30 ÷ 60
			25	83.3	30 ÷ 60	rough surface
				89.9		
		1	30	99.9	30 ÷ 90	very hard, transparent
			20	49.9		brittle, transparent
			20	59.9		
			25	69.9		
			25	83.3	30 ÷ 60	brittle, transparent
				90.0		
5-HMCH	Concd. HCl	2	30	99.9	30 ÷ 90	hard, transparent
			20	49.9		smooth, very hard, transparent
			20	59.9		brittle, cracks inside
			30	69.9	30 ÷ 60	hard, pearl-like
5-HMCP	Concd. HCl	2	20	33.1		
			30	59.8	30 ÷ 120	transparent, yellowish, blisters
		0.5	1			transparent, smooth
			2		30 ÷ 120	transparent, smooth, cracks
			0.5	63.3	30 ÷ 120	transparent, smooth
			1	82.3		
5-HMMEK (25°C)		2	30	79.3	30 ÷ 120	smooth, slightly opalescent
			20	59.4	30 ÷ 90	
5-HMEK (40°C)		0.5	30	70.1	30 ÷ 120	transparent, smooth
			20	63.2	30 ÷ 90	smooth, slightly opalescent, brittle
5-HMMEK (60°C)	Concd.	0.5	30	82.7	30 ÷ 120	transparent, smooth, slightly opalescent
5-HMMEK (80°C)	HCl	0.5	30	68.5	30 ÷ 60	transparent, hard, slightly rough
			20	33.1	90 ÷ 120	
5-HMCP			30	60.1	90 ÷ 120	transparent, smooth, yellowish
5-HMMEK (40°C)				72.9	60 ÷ 120	transparent, smooth
5-HMMEK (60°C)		0.5	30	85.0	30 ÷ 120	transparent, smooth, scratches
			0.5	50.5	30 ÷ 120	smooth, slightly opalescent, yellowish
		1				
			2	20	26.6	30 ÷ 120
5-HMAF	80% HCOOH	0.5	30	50.0	30 ÷ 120	smooth opalescent
5-HMMEK (26°C)			30	83.0		transparent, smooth
			20	60.7		transparent, rough
5-HMMEK (40°C)		0.5	30	73.1	30 ÷ 120	transparent, smooth
			0.5	57.1	30 ÷ 120	transparent, hard, rough
5-HMMEK (80°C)	80% CH ₃ COOH	30	2	69.5	30 ÷ 120	transparent, hard, smooth

CONCLUSION

In reactions of ketones with formaldehyde in basic medium, multihydroxyl derivatives are formed that are capable of dissolving (or liquefying) melamine. The best solubility power is the solvent obtained in the

reaction of 1 mol of cyclohexanone (or ethyl-methyl ketone) with 5 mol of formaldehyde. The products obtained by dissolving melamine in the reactive solvents are potential raw materials in the synthesis of a new group of condensation polymers. The solutions

can be cured with acidic catalysts at 120°C, to obtain new melamine-formaldehyde-ketone polymers. Further results will be the subject of forthcoming papers.

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