New Melamine–Formaldehyde–Ketone Polymers. II. Dissolution of Melamine in Reactive Solvents Prepared from Cyclohexanone

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ABSTRACT: Reactive solvents of melamine were prepared from cyclohexanone and excess of formaldehyde in the presence of triethylamine catalyst. The solubility of melamine in the solvents was evaluated and the mechanism of dissolution explained on the basis of ^{1}H-NMR and IR spectroscopy. Attempts to cure the melamine solutions resulted in melamine–formaldehyde–cyclohexanone polymers. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 77–85, 2005

Key words: heteroatom-containing polymers; melamine; reactive solvents; structure–property relations; H-NNR and IR spectroscopy

INTRODUCTION

The presence of *s*-triazine rings makes the polymers obtained from melamine relatively resistant against aggressive chemicals and heat, and with good dielectric properties.[1] Nevertheless, relatively little information has been published on melamine-containing polymers other than on the classical melamine–formaldehyde resins. The reason seems to be the very low solubility of melamine in organic solvents that limits the possibility of a broader use of this valuable and cheap chemical. The existence of a good solvent formelamine would extend its applications and also modify the methods of processing melamine-based polymers. An attempt to prepare such solvents (so-called reactive solvents of melamine) from acetone and formaldehyde were initiated by Wirpsza[2,3] and continued in our group.[4–7] Melamine reacts with a reactive solvent, in which it has been previously dissolved. Melamine and solvent thus constitute a reactive resinlike system that can be cured at elevated temperature (above 80°C) in the presence of acidic or basic catalysts.[4,5,7]

The obtained plastic materials can be used for water-resistant coatings, components of laminates, or components of thermostable polyurethane foams.

In this work new reactive solvents of melamine, by reacting cyclohexanone with excess of formaldehyde, have been thoroughly examined. Solubility of melamine in the solvents was determined and the course of dissolution was followed by IR and proton magnetic resonance (^{1}H-NMR) spectroscopy. Attempts to cure the melamine solutions in reactive solvents were also carried out, and new melamine–formaldehyde–ketone polymeric materials were obtained.

The methods of preparation of new polymeric materials from melamine solutions in reactive solvents will be the subject of a forthcoming article.

## EXPERIMENTAL

Chemicals

Cyclohexanone, formalin, ethyl methyl ketone, and melamine were obtained from Chempur (Gliwice, Poland), Standard (Warsaw, Poland), Chempur, and Fluka Chemie AG (Buchs, Switzerland), respectively.

Syntheses of reactive solvents of melamine

Into a trineck 250-cm³ flask, equipped with reflux condenser, thermometer, and mechanical stirrer, were placed predetermined amounts of cyclohexanone and formalin (33.0–36.5 wt % of CH_2O). Then, triethylamine was added in an amount sufficient to adjust the pH to 11. The molar excess of formaldehyde with respect to cyclohexanone ranged from $n = 1$ to $n = 12$. The symbol of the respective product is *n*-HMCH (e.g., 1-HMCH to 12-HMCH). The mixture of substrates was heated at 80°C for 5–6 h. After that time, water and triethylamine were distilled off under reduced

^{1}H-NMR	IR
	2940-2916 cm^{-1} $v_{C\text{-}H\ as}$ >CH_2, in ring, strong
	2883 cm^{-1} $v_{C\text{-}H\ sym}$ >CH_2 in ring, strong
	1716 cm^{-1} $v_{C=O}$, sharp, strong
a: 2.1-2.4 ppm, (δ)	1460 cm^{-1} δ_{CH2}, medium, scissors-like
b + c: 1.5-1.9 ppm, (δ)	1416 cm^{-1} $\delta_{CH2\text{-}C=O\ op}$, strong
	1170 cm^{-1} $v_{C\text{-}C}$, skeleton, sharp, strong
	996-944 cm^{-1} $\delta_{C\text{-}H}$, medium
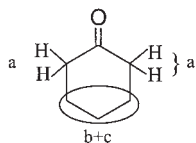
CH (**I**)

Scheme 1

pressure (1200–2400 Pa), to maintain the temperature in the reaction flask below 50°C.

Analytical methods and spectroscopy

The course of the reaction between cyclohexanone and formaldehyde was monitored by measuring the content of unreacted formaldehyde. The sulfite method was used.[8] The mass of the reacting system was controlled by careful weighing (accuracy to 0.1 g) of the substances. The weighing was carried out three times: before reaction, after reaction, and after distillation.

^{1}H-NMR spectra of the reactive solvents and solutions of melamine were recorded on a Tesla BS-587A spectrometer. The samples were dissolved in d_6-DMSO and contained hexamethyl-disiloxane as an internal reference. IR spectra were recorded by horizontal ATR on a Paragon 1000 FT spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT). The samples were in the form of thin films.

Properties of reactive solvents

Properties of the reactive solvents, such as refractive index (Abbe refractometer), specific density (pycnometer), viscosity (Höppler viscometer), and surface tension (ring detachment method), were determined at 20°C. The amount of free and weakly bonded formaldehyde was also determined by the sulfite method.[8]

Dissolution of melamine in reactive solvents

The process of dissolution was studied by dissolving melamine in the reactive solvent (RS) prepared in the reaction of 1 mol of cyclohexane with 5 mol of formaldehyde (5-HMCH). Melamine (76.7 g) was dissolved in 100 g of RS containing 20 wt % of water. The time of dissolution was about 10 min. After 3, 5, or 7 min from the moment of mixing the RS with melamine, samples of liquid were withdrawn and their ^{1}H-NMR and IR spectra were recorded.
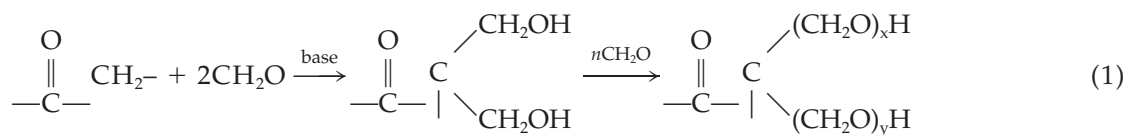
Solubility of melamine in reactive solvents and attempts to cure the solutions

The solubility of melamine in one-step or gradual introduction of melamine to RS, the solubility in RS containing 10–40 wt % of water, and curing attempts were determined as described previously.[5]

RESULTS AND DISCUSSION

Preparation of reactive solvents

The reactive solvents of melamine were prepared in reactions of 1 mol of cyclohexanone and 1–12 mol of formaldehyde in the presence of triethylamine catalyst. The reaction scheme was

$$\begin{array}{c} O \\ \parallel \\ -C- \end{array} CH_2- + 2CH_2O \xrightarrow{\text{base}} \begin{array}{c} O \\ \parallel \\ -C- \end{array} \begin{array}{c} \diagup CH_2OH \\ C \\ | \diagdown CH_2OH \end{array} \xrightarrow{n CH_2O} \begin{array}{c} O \\ \parallel \\ -C- \end{array} \begin{array}{c} \diagup (CH_2O)_xH \\ C \\ | \diagdown (CH_2O)_yH \end{array} \quad (1)$$

where $x + y = n + 2$.

Because of the initial molar ratio of reagents, the degree of substitution of α-hydrogen atoms in cyclohexanone molecules with hydroxymethyl groups was different. The course of reaction was followed by measuring the amount of unreacted formaldehyde by the sulfite method[8] (Fig. 1). After water and catalyst had been distilled off, the molar ratio of cyclohexanone to formaldehyde in the products was calculated from the

mass of product (Table I). In the experiments it was found that the reaction should not be carried out at temperatures higher than 80°C (this was the highest temperature below which triethylamine started to boil). Moreover, the removal of water should be carried out while keeping the temperature below about 50°C (under pressure not exceeding 2.4 kPa). Otherwise, as shown in Wirpsza et al.,[4] a slow dehydration of aldols to unsaturated ketones would take place. It eventually would re-
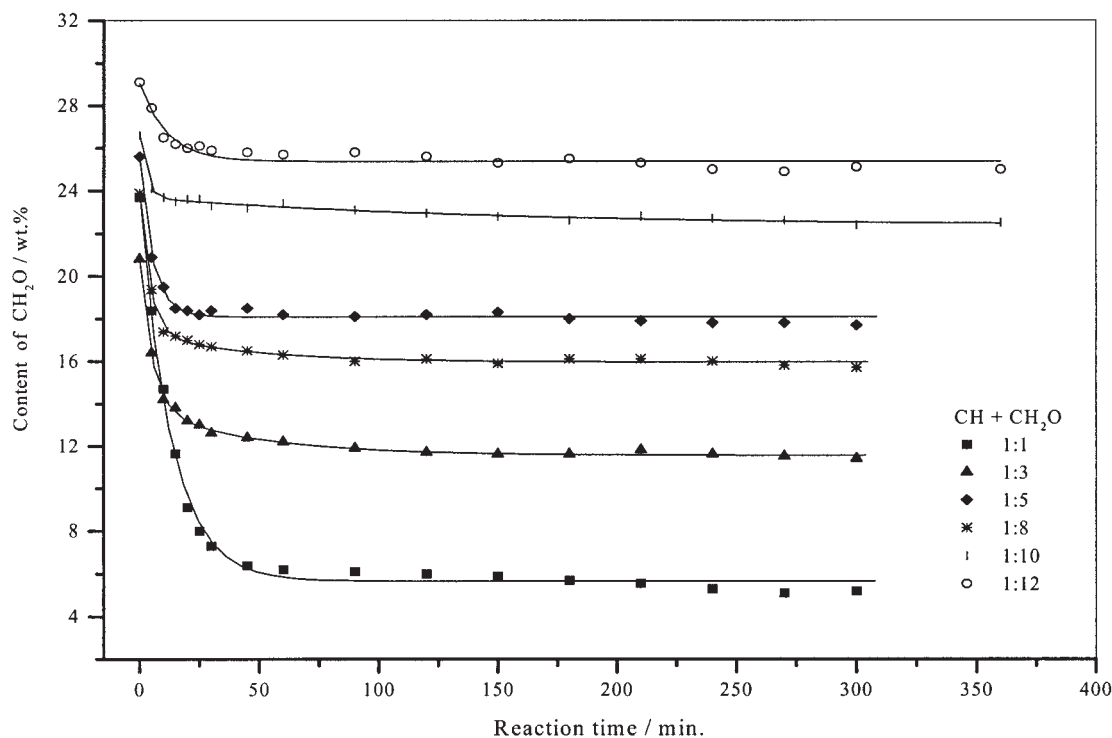
Figure 1 Amount of unreacted formaldehyde versus reaction time in the synthesis of reactive solvents (prepared from 1 mol of cyclohexanone and 1–12 mol of formaldehyde at 80°C.

duce the solubility of melamine in the resulting reactive solvents. Triethylamine facilitated formation of semiacetal groups at the expense of the direct reaction of cyclohexanone with melamine. The presence of semiacetals in the products turned out to be advantageous from the perspective of melamine dissolution.

In most cases the reactive solvents were viscous and clear liquids, but some of them (the products n-HMCH with $n > 7$) became turbid in 2 to 24 h after distillation; their viscosity increased and they even-

tually became semisolid or solid greaselike substances. One should point out that, when reheated to 80–90°C, the solid or semisolid reactive solvents again became transparent. The viscosity of the reactive solvents ranged from 0.1 to 1.9 Pa·s. They were heavier than water (density 1.1–1.6 g/cm^3) and had a surface tension ranging from 36.6 to 50 N/m. All these quantities were higher the more that oxymethylene groups were introduced per cyclohexanone molecule.

TABLE I
Synthesis Conditions and Mass Balance of the Reaction Between Cyclohexanone and Formaldehyde (at 80°C)

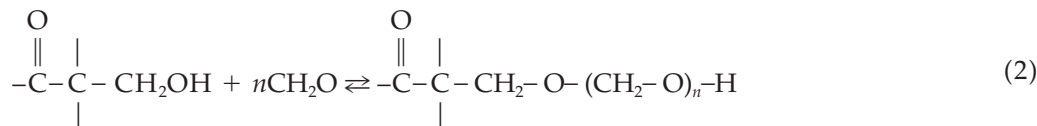| Reactive solvent | Reaction time (hours) | TEA amount (cm^3) | Mass balance | | | | | Product yield (% wag) | Formal ketone : CH$_2$O ratio in product |
			Ketone (g)	Formalin (g)	Formalin (concn. wt %)	Calcd[a]	Found		
1-HMCH	5.0	0.5	68.8	59.3	35.6	89.9	87.9	99.8	1 : 0.8
2-HMCH	5.0	0.5	49.1	84.5	35.5	79.1	77.9	98.5	1 : 1.9
3-HMCH	5.0	0.5	39.4	101.9	35.5	75.6	74.1	98.4	1 : 2.9
4-HMCH	5.0	0.5	39.3	135.5	35.5	87.4	86.4	98.8	1 : 3.9
5-HMCH	5.5	0.6	34.5	153.8	34.3	87.3	86.0	99.2	1 : 4.9
6-HMCH	5.5	0.6	29.4	157.4	34.3	83.4	82.1	98.4	1 : 5.9
7-HMCH	5.0	0.5	19.6	122.4	34.3	61.6	61.0	99.0	1 : 7.0
8-HMCH	5.0	0.6	24.5	166.7	36.0	84.5	83.1	98.3	1 : 7.8
9-HMCH	5.5	0.6	19.6	150.0	36.0	73.6	72.8	98.9	1 : 8.9
10-HMCH	5.5	0.7	19.6	166.7	36.0	79.6	78.6	98.7	1 : 9.8
11-HMCH	6.0	0.8	14.7	137.5	36.0	64.2	63.6	99.1	1 : 10.9
12-HMCH	6.0	0.8	14.7	150.0	36.0	68.7	67.7	98.7	1 : 11.8

[a] Mass of adduct calculated as: $m_{ketone} + m_{formaldehyde}$.

Analysis of the reaction course and structure of reactive solvents

The structure of reactive solvents was analyzed by ^{1}H-NMR and IR spectroscopy. The spectral characteristics of cyclohexanone are the following shown in Scheme 1.
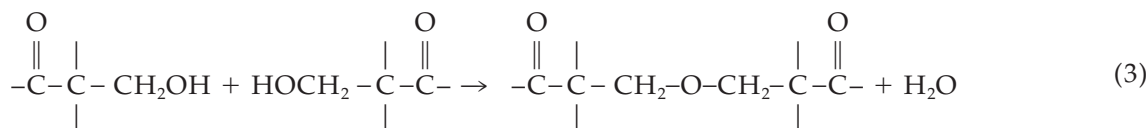
In ^{1}H-NMR spectra of the products of reaction between formaldehyde and cyclohexanone, one can observe a decrease of signal intensity in the range 2.1–2.4 ppm as a result of consumption of α-protons in cyclohexanone [reaction (1)]. One can also observe new signals appearing from methyl groups in $-C-CH_2-OH$ in the range 3.1–3.7 ppm (hereafter referred to as protons d) and from hydroxyl proton (e) at 4.3 ppm.

In ^{1}H-NMR spectra of the addition product prepared at molar ratio 1 : 2 (cyclohexanone : formaldehyde) significant increases of signal intensities in the ranges 3.1–3.7 and 4.3–4.4 ppm were observed, compared with those in the products obtained at the molar ratio of reagents 1 : 1. Furthermore, the signal of somewhat smaller intensity observed at 4.55 ppm confirmed the presence of semiacetal groups $-O-CH_2-OH$ (0.24 mol/mol of RS). In IR spectra the corresponding band was present at 1029 cm^{-1}, attributed to asymmetric stretching vibrations in C—O—C grouping.

In the products of addition obtained from more and more formaldehyde per mole of cyclohexanone, a reduction of signal intensities, resulting from α-methylene protons at 2.1–2.5 ppm and attributed to hydroxyl protons, was observed. The signal from OH protons moved to 5.6 ppm and became broad; hydrogen bonds were formed in the products containing an increasing number of hydroxyl groups. In ^{1}H-NMR spectra of the reaction products, besides protons (a), (b + c), (d), and (e) defined above, new signals appeared in the range 4.65–4.8 ppm,[4] attributed to methylene protons of semiacetal groups $-O-CH_2-OH$ [Fig. 2(a)]:

$$-\overset{\overset{\textstyle O}{\|}}{C}-\overset{|}{\underset{|}{C}}-CH_2OH + nCH_2O \rightleftarrows -\overset{\overset{\textstyle O}{\|}}{C}-\overset{|}{\underset{|}{C}}-CH_2-O-(CH_2-O)_n-H \tag{2}$$

Furthermore, in the spectra of products with gradually increasing amounts of formaldehyde, a signal in the range 4.4–4.65 ppm appeared, attributed to protons in polyoxymethylene links[9] $-C-CH_2-O-CH_2-C-$that were formed in the linear condensation:

$$-\overset{\overset{\textstyle O}{\|}}{C}-\overset{|}{\underset{|}{C}}-CH_2OH + HOCH_2-\overset{|}{\underset{|}{C}}-\overset{\overset{\textstyle O}{\|}}{C}- \rightarrow -\overset{\overset{\textstyle O}{\|}}{C}-\overset{|}{\underset{|}{C}}-CH_2-O-CH_2-\overset{|}{\underset{|}{C}}-\overset{\overset{\textstyle O}{\|}}{C}- + H_2O \tag{3}$$

The intensity of signals, attributed to semiacetal and oxymethylene protons, increased with increasing number of moles of formaldehyde reacted with cyclohexanone. The intensities are presented in Table II.

The infrared spectra fully confirmed the conclusions drawn from analysis of ^{1}H-NMR spectra. In the spectrum of 1-HMCH (the product prepared from 1 mol of cyclohexanone and 1 mol of formaldehyde), strong bands appeared that were absent in the spectrum of cyclohexanone. These bands were attributed to the hydroxymethyl derivative of the ketone; that is, these were stretching vibrations of –OH group at 3387 cm^{-1} and deformational vibrations in the range 1449–1312 cm^{-1} as well as the stretching vibrations of C—O bonds in the range 1041–1025 cm^{-1}.

In IR spectra of the products containing increasing amounts of formaldehyde (Fig. 3), as the number of hydroxymethyl groups increased, the intensity of stretching vibrations of free hydroxyl groups (at 3390 cm^{-1}) decreased, which is explained by the formation of hydrogen bonds. The bands attributed to deformational vibrations of –OH group (in the range 1380–1310 cm^{-1}) were broadened, similar to that of the coupled C—O stretching vibrations (at 1020 cm^{-1}) and "ether" stretching bands at 1100 cm^{-1}.

All these spectra confirmed the formation of subsequent products of addition as well as of condensation products. The proportion of the latter increased, as did the excess of formaldehyde.

Based on these arguments and on the results of elemental analysis one can propose the following general equation describing the composition of the reactive solvents obtained from cyclohexanone as shown in Scheme 2:
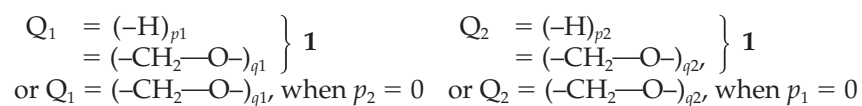

(II)
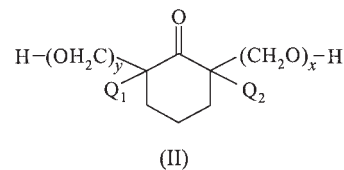
Scheme 2

Figure 2 ^{1}H-NMR spectrum of 5-HMCH (prepared from 1 mol of cyclohexanone and 5 mol of formaldehyde) (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.

where

$$Q_1 \; = (-H)_{p1} \atop = (-CH_2{-}O{-})_{q1} \Biggr\} \; \mathbf{1}$$
$$\text{or } Q_1 = (-CH_2{-}O{-})_{q1}, \text{ when } p_2 = 0$$

$$Q_2 \; = (-H)_{p2} \atop = (-CH_2{-}O{-})_{q2}, \Biggr\} \; \mathbf{1}$$
$$\text{or } Q_2 = (-CH_2{-}O{-})_{q2}, \text{ when } p_1 = 0$$

where $x + y + q_1 + q_2 = n$, and $5 \leq n \leq 12$, where n is the number of moles of formaldehyde per mole of cyclohexanone.

Dissolution of melamine in reactive solvents

The course of dissolution of melamine was studied for the products of reaction of 1 mol of cyclohexanone with either 1 mol (1-HMCH) or 5 mol of formaldehyde (5-HMCH). The time dissolution was about 6 min for 1-HMCH and about 8 min for 5-HMCH. After 2, 3.5, and 5 min for 1-HMCH (after 3, 5, and 7 min for 5-HMCH) from the start of dissolution, samples of solution were withdrawn and their ^{1}H-NMR and IR spectra were recorded.

TABLE II
Content of Hydroxyl Groups and the Groupings Containing Unbound Formaldehyde
in the Reactive Solvents (RS) Calculated from ^{1}H-NMR Spectra

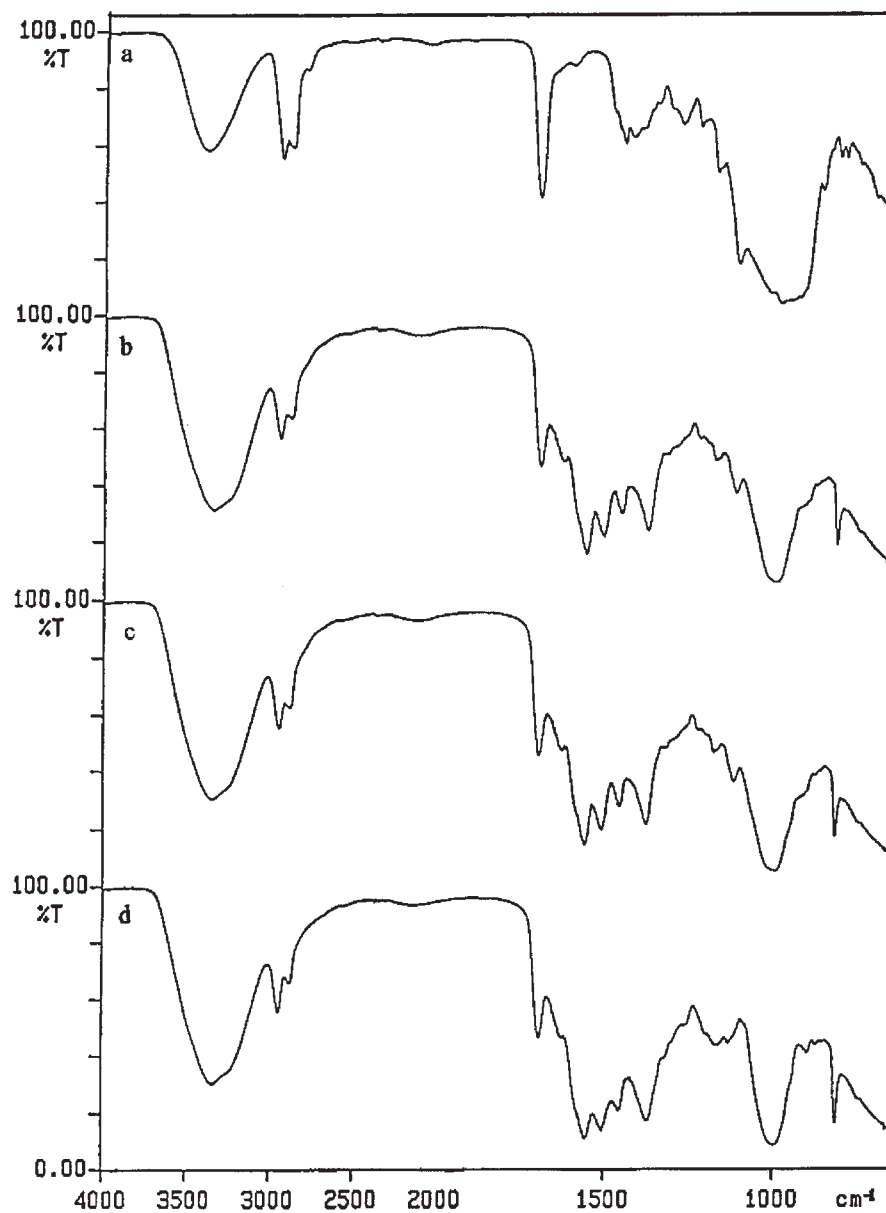| Reactive solvent	Fraction of grouping (mol/mol RS)		
	Semiacetal $-O-CH_2-OH$	Oxymethylene $-C-CH_2-O-CH_2-C-$	Hydroxyl $-OH$
2-HMCH	0.24	—	1.52
3-HMCH	0.52	0.41	1.19
4-HMCH	1.17	0.81	1.90
5-HMCH	1.23	1.33	2.22
6-HMCH	1.38	1.38	2.13
7-HMCH	1.07	1.73	2.38
8-HMCH	1.11	1.78	2.67
9-HMCH	1.71	2.28	3.71
10-HMCH	1.58	2.24	3.43
11-HMCH	2.43	2.16	3.24
12-HMCH	2.40	3.20	3.80

Figure 3 IR spectrum of 5-HMCH (prepared from 1 mol of cyclohexanone and 5 mol of formaldehyde) (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.
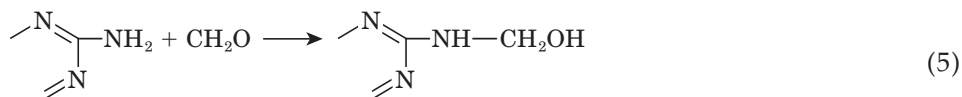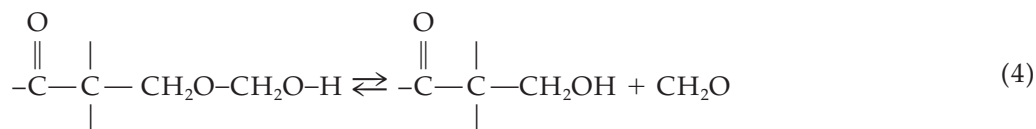
Dissolution of melamine in 1-HMCH

In the ^{1}H-NMR spectrum of melamine only one signal from protons in –NH$_2$ groups was present in the range 6.5–6.6 ppm. In spectra of the samples withdrawn during dissolution in 1-HMCH, besides the signals characteristic for the solvent itself, an additional peak appeared at 5.9 ppm, attributed to the –NH$_2$ groups of melamine. A signal from condensation water was present at 3.4 ppm, which was partly covered by signals from methylene protons. In the succeeding samples withdrawn after 2, 3.5, and 5 min one could observe: (1) an increase of the signal in the range 3.1–3.8 ppm, attributed to methylene protons in –C—CH$_2$OH (indicating a release of some formaldehyde from O-hydroxymethyl groups) and (2) clear reduction of signal intensity in the range 4.2–4.4 ppm from hydroxyl groups in –C—CH$_2$OH (indicating their consumption in the condensation).

IR spectra confirmed the course of the melamine dissolution deduced from ^{1}H-NMR spectra. In the spectrum of the mixture obtained by dissolution of melamine in 1-HMCH, compared with that of the solvent itself, there is a clear increase of intensity and broadness of the band (at 3390 cm^{-1}) attributed to stretching vibrations of "associated" –OH and –NH$_2$ groups. This is also the range at which C—H bonds and water absorbed energy. There also appeared deformational bands of –NH group at 1630 cm^{-1} (primary amines) and at 1550 cm^{-1} (secondary amines).

Dissolution of melamine in 5-HMCH

As mentioned earlier, the presence of subsequent products formed in reactions (2) and (3) could be seen in the spectra of solvent 5-HMCH. The respective peaks were absent in the spectra of 1-HMCH. The course of dissolution of melamine in 5-HMCH (followed by recording ^{1}H-NMR and IR spectra) is illustrated in Figures 2 and 3. In the ^{1}H-NMR spectrum of the solution obtained after 3 min, signals appeared that were attributed to the following protons [Fig. 2(b)][10]: (1) in the range 7.1–7.6 ppm from secondary amino group –NH–in the grouping –NH—CH$_2$OH, (2) at 6.2 ppm (singlet) from "free" amino group of melamine, (3) at 4.9 ppm from methylene group in –NH—CH_2OH, (4) in the range 3.7–4.2 ppm from methylene group in –C–CH_2OH, and (5) in the range 4.65–4.8 ppm. A decrease of signal intensity from methylene protons in –O—CH$_2$OH grouping in the reactive solvent was also observed.

In the spectra of the next solution (withdrawn after 5 or 7 min of dissolution), the signal intensity from secondary amino groups in the range 7.1–7.6 ppm, as well as from methylene protons in –C—CH$_2$OH in the range 3.7–4.2 ppm, increased. This indicated the release of formaldehyde from O-hydroxymethyl groups of the reactive solvent. The reduction of signal intensity from methylene protons in O-hydroxymethyl groups (–O—CH$_2$OH) and appearance of new signals from N-hydroxymethyl group protons (–N—CH_2OH) indicated that the following reactions took place in the system during melamine dissolution:

$$-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{|}{\underset{|}{C}}-CH_2O-CH_2O-H \rightleftarrows -\overset{\overset{\displaystyle O}{\|}}{C}-\overset{|}{\underset{|}{C}}-CH_2OH + CH_2O \qquad (4)$$

$$\text{N}{=}{-}NH_2 + CH_2O \longrightarrow \text{N}{=}{-}NH—CH_2OH \qquad (5)$$

In short, melamine dissolution took place by formation of its hydroxymethyl derivatives. The signals from protons in water molecules formed during melamine dissolution appeared in ^{1}H-NMR spectra at 3.7 ppm. This signal intensity increased, as did

the dissolution time. The presence of water proved that the competitive condensation reaction between hydroxymethyl derivatives of melamine and hydroxymethyl groups in the reactive solvent took place:
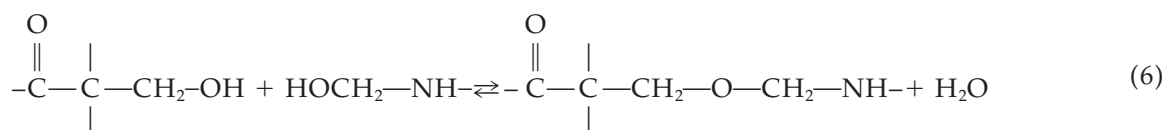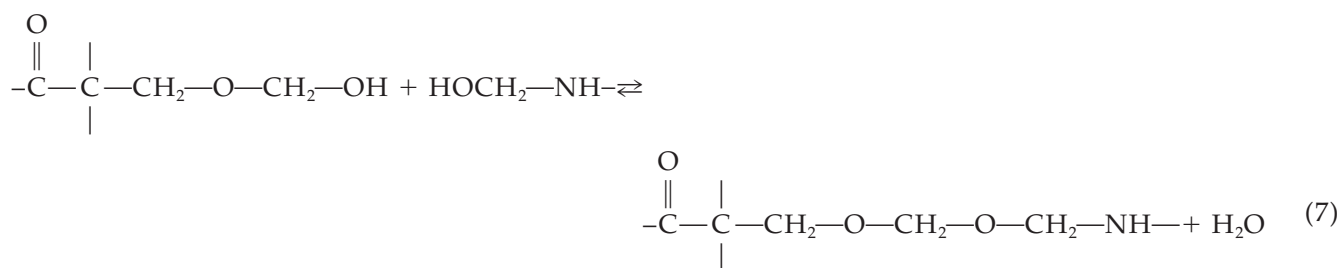
$$-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{|}{\underset{|}{C}}-CH_2-OH + HOCH_2—NH– \rightleftarrows -\overset{\overset{\displaystyle O}{\|}}{C}-\overset{|}{\underset{|}{C}}-CH_2—O—CH_2—NH–+ H_2O \qquad (6)$$

TABLE III
Highest Amount of Melamine Dissolved in Anhydrous Cyclohexanone-Based
**Reactive Solvents: Stepwise Introduction of Melamine**

Reactive solvent	Amount of Mel added R_{Mel} (g/100 g initial amount of RS)	Solubility R'_{Mel} (g/100 g final amount of RS)	Percentage of melamine (wt %)
1-HMCH	3.8	3.8	3.7
2-HMCH	26.9	26.6	25.2
3-HMCH	23.8	23.1	22.5
4-HMCH	25.2	24.9	24.3
5-HMCH	26.4	25.3	25.0
6-HMCH	25.7	24.6	24.0
7-HMCH	21.7	20.3	19.9
8-HMCH	26.7	25.7	24.9
9-HMCH	25.4	24.6	24.0
10-HMCH	30.0	29.4	28.6
11-HMCH	26.5	24.3	23.4
12-HMCH	31.0	30.0	25.9

or that melamine amino groups reacted with semi-acetal groups of the reactive solvent:

$$-\overset{\overset{\textstyle O}{\|}}{C}-\overset{\overset{\textstyle |}{}}{\underset{|}{C}}-CH_2-O-CH_2-OH + HOCH_2-NH- \rightleftarrows$$

$$-\overset{\overset{\textstyle O}{\|}}{C}-\overset{\overset{\textstyle |}{}}{\underset{|}{C}}-CH_2-O-CH_2-O-CH_2-NH- + H_2O \quad (7)$$

One cannot exclude that condensation between like groups in hydroxymethyl melamine derivative also took place under the dissolution conditions:

$$(8)$$
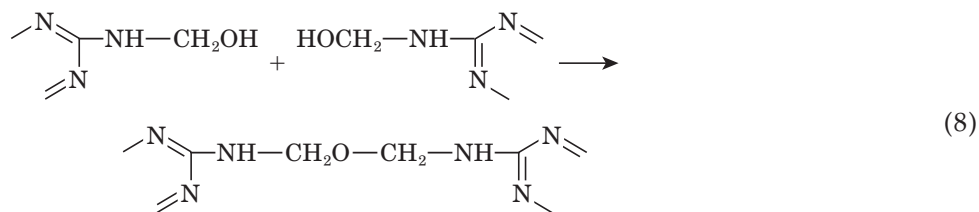
In the IR spectrum of the mixture obtained by dissolution of melamine in 5-HMCH [Fig. 3(b)–(d)] clear changes were observed, compared to the spectrum of the reactive solvent [Fig. 3(a)] itself. In the range 3500–3300 cm^{-1} one could observe a significant increase of both intensity and broadness of the bands attributed to stretching vibrations of the "associated" –OH and –NH$_2$ groups as well as the appearance of bands at (1) 1650 and 1550 cm^{-1} (δ_{NH} in primary and secondary amino groups, respectively), (2) at 1490 cm^{-1} (δ_{OH} in primary alcohols) conjugated with ν_{C-O} at 1150 cm^{-1}, (3) at 1350 cm^{-1} (ν_{C-N} in amines, (4) at 1050 cm^{-1} (ν_{C-O} in ethers), and (5) at 814 cm^{-1} (s-triazine ring).

The presence of all the bands fully confirmed the course of dissolution process deduced from the ^{1}H-NMR spectra.

Dissolution of melamine in reactive solvents in the presence of water

The solubility of melamine was determined by a stepwise (Table III) and single introduction of melamine (Fig. 4) as well as after adding to the solvent 10–40 wt % of water (Fig. 4). All the parameters, such as the kind of hydroxymethyl derivative of cyclohexanone, method of melamine introduction, and presence of
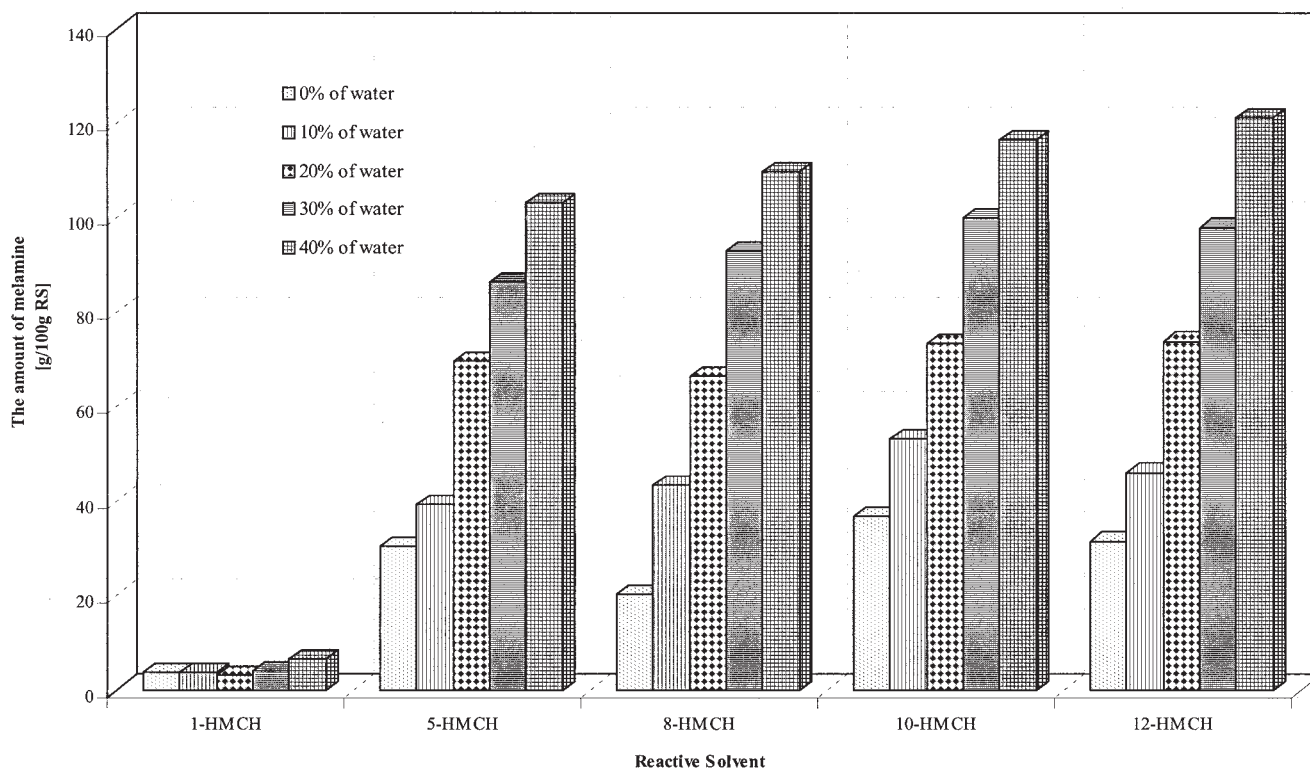
Figure 4 Solubility of melamine in reactive solvents (containing water) prepared from 1 mol of cyclohexanone and 1, 5, 8, 10, and 12 mol of formaldehyde (single introduction of melamine).

water in reactive solvent, did affect the solubility of melamine.

We have found that the amount of dissolved melamine is smallest when introduced in small portions (each next portion added after previous one had dissolved; cf. Table III). The reason was that cyclization and linear condensation reactions were taking place between solvent molecules themselves.[5,7] Introduction of melamine in one portion (in the amount determined in the stepwise procedure) allowed several more percent of melamine by weight to be dissolved (Fig. 4). Introduction of water to the reactive solvent before the dissolution process (in the amount 10–40 wt %) further improved melamine solubility (cf. Fig. 4). Interestingly, the more water that was added, the greater the amount of melamine that was dissolved. However, when the amount of water in the reactive solvent exceeded 40 wt %, no increase of melamine solubility was observed.

The ability of melamine to dissolve in reactive solvents increased with the number of moles of formaldehyde that reacted with cyclohexanone (Fig. 4). The best results were recorded for the solvents in which the molar ratios of cyclohexane to formaldehyde were 1 : 5, 1 : 8, 1 : 10, and 1 : 12. The solubility of melamine was (in grams per 100 g of reactive solvent) 103.2, 109.9, 116.6, and 121.2 g, respectively, in the presence of 40 wt % of water.

The solutions obtained in this way contained 47.3–50.7 wt % of melamine. The amount of formaldehyde exceeding 12 mol per mole of cyclohexanone did not improve melamine solubility.

Preliminary attempts were made to cure the melamine solutions in reactive solvents. The solutions were cured in the presence of acidic catalysts at 120°C and the final products had very good water resistance.

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