New Melamine–Formaldehyde–Ketone Polymers. IV. Dissolution of Melamine in Reactive Solvents Prepared from Methyl Ethyl Ketone

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ABSTRACT: Reactive solvents of melamine were prepared from methyl ethyl ketone and formaldehyde in the presence of the catalyst triethylamine. The solubility of melamine in the resulting solvents was determined, and the mechanism of dissolution was explained with ^{1}H-NMR and IR spectroscopy. Preliminary experiments aimed at curing the melamine solutions in reactive solvents into melamine–formaldehyde–butanone resins are reported. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1496–1505, 2006
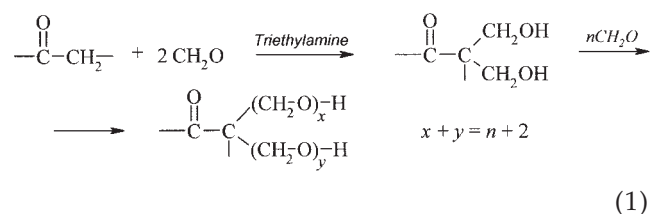
Key words: heteroatom-containing polymers; dissolution; reactive solvents; melamine; structure-property relations

INTRODUCTION

Melamine is an important raw material for the chemical industry. Its main advantages are (1) accessibility and low price (it is produced from urea), (2) the presence in the molecule of a chemically and thermally stable aromatic *s*-triazine ring with three amine groups, and (3) the lack of toxicity, color, and smell. The major application of melamine is in the production of melamine–formaldehyde resins.[1] Another application is in the production of polyetherols (obtained in reactions of melamine with oxiranes or alkylene carbonates) as components of polyurethane foams of improved thermal stability.[2–7]

The main disadvantage of melamine is its poor solubility in organic solvents. Success in sought-for better solvents of melamine could substantially broaden the applicability of melamine and modify the existing methods of processing resins based on melamine. Such attempts have been undertaken in recent years, namely through the preparation of so-called reactive solvents (RSs) of melamine. In these solvents, melamine not only dissolves physically but also reacts with the solvents and converts into better soluble intermediates. The RSs are obtained by the reaction of formaldehyde with various ketones.[8–16]

The reactions taking place in the system are presented in eq. (1) for a ketone fragment:

$$x + y = n + 2$$

(1)

Melamine dissolves in RSs to form resinlike reactive solutions that cure at elevated temperatures (>80°C) in the presence of acidic or basic catalysts.[10,13,14,16]

In this article, we describe new RSs of melamine prepared in reactions of methyl ethyl ketone (MEK) with an excess of formaldehyde. The solubility of melamine in the RSs was determined and the course of dissolution was followed with IR and ^{1}H-NMR spectroscopy. Preliminary attempts at curing melamine solutions are also reported. New melamine–formaldehyde–butanone resins were thus obtained.

EXPERIMENTAL

Chemicals

MEK [analytically pure (p.a.); Chempur, Piekary Śląskie, Poland], formalin (p.a.; Standard, Lublin, Poland), triethylamine (p.a.; Fluka, Buchs, Switzerland), and melamine (p.a.; Fluka) were used.

Synthesis of the RSs

The syntheses were carried out as described in ref. 15, except that MEK was used, not cyclohexanone. An RS obtained with a 1:*n* molar ratio of MEK to formaldehyde was coded as *n*-HMMEK (*n* = 1, 2, …, 12). The

TABLE I
Conditions of Synthesis and Mass Balance for a Series of Reactions Between MEK and Formaldehyde in the Presence of Triethylamine Catalyst

RS	Reaction temperature (°C)	Reaction time (h)	TEA amount (cm^3)	Ketone (g)	Formalin (g)	Formalin concentration (wt %)	Mass of product (g) Calcd.[a]	Found	Product yield (% wag)	Formal ketone/ CH$_2$O ratio in product
1-HMMEK	80	5.5	0.6	79.3	91.7	36.0	112.3	109.2	97.2	1:0.9
2-HMMEK	80	5.0	0.6	54.1	125.0	36.0	99.1	97.7	98.6	1:1.9
3-HMMEK	80	5.5	0.6	39.7	137.6	36.0	89.2	87.8	98.4	1:2.9
4-HMMEK	80	6.0	0.6	32.5	148.1	36.5	86.5	84.7	97.9	1:3.9
5-HMMEK	25	9.5	0.5	25.7	146.3	36.5	79.1	78.8	99.6	1:5.0
5-HMMEK	40	8.5	0.5	25.5	146.0	36.6	78.8	78.1	99.1	1:4.9
5-HMMEK	60	7.5	0.5	25.7	146.1	36.5	79.0	78.0	98.7	1:4.9
5-HMMEK	80	6.0	0.5	28.8	164.6	36.5	88.9	86.8	97.6	1:4.8
6-HMMEK	80	6.5	0.6	21.7	147.9	36.5	75.7	74.2	98.0	1:5.8
7-HMMEK	80	7.0	0.7	19.9	159.0	36.5	77.9	76.1	97.7	1:6.8
8-HMMEK	80	7.0	0.7	18.0	200.0	36.5	78.0	76.9	98.6	1:7.9
9-HMMEK	80	7.0	0.9	16.3	167.5	36.5	77.4	76.6	99.0	1:8.9
10-HMMEK	80	7.0	1.0	16.3	185.8	36.5	84.1	82.9	98.6	1:9.8
11-HMMEK	80	7.0	1.0	14.4	180.8	36.5	80.4	78.9	98.1	1:10.8
12-HMMEK	80	7.0	1.0	12.7	174.0	36.5	76.2	74.9	98.3	1:11.8

Conditions of distillation: p = 9–15 mmHg (12–20 hPa), t_{vapour} = 17–30°C, $t_{reaction\ mixture}$ = 17–50°C.
[a] Mass of adduct calculated as $m_{ketone} + m_{formaldehyde}$.

substrates were mixed in predetermined proportions, and the reaction carried out at 25, 40, 60, or 80°C for 5–9.5 h. Finally, the water and catalyst were distilled off under reduced pressure.

Chemical and spectral analyses

All chemicals were used and all ^{1}H-NMR and IR spectral analyses were carried out exactly as described in ref. 15,

except that MEK was used instead of cyclohexanone. Elemental analyses were conducted with a Carlo-Erba (Mediolan, Italy) EA-1108 analyzer, which recorded the contents of carbon and hydrogen. Electrospray ionization mass spectrometry (ESIMS) spectra were recorded on a Finnigan (Bremer, Germany) MAT 85S double-focus spectrometer. KI was used for ionization, and the flow rate of the moving phase (CH$_3$OH and tetrahydrofuran) was 5 μdcm^3/min. Positive ions were recorded in
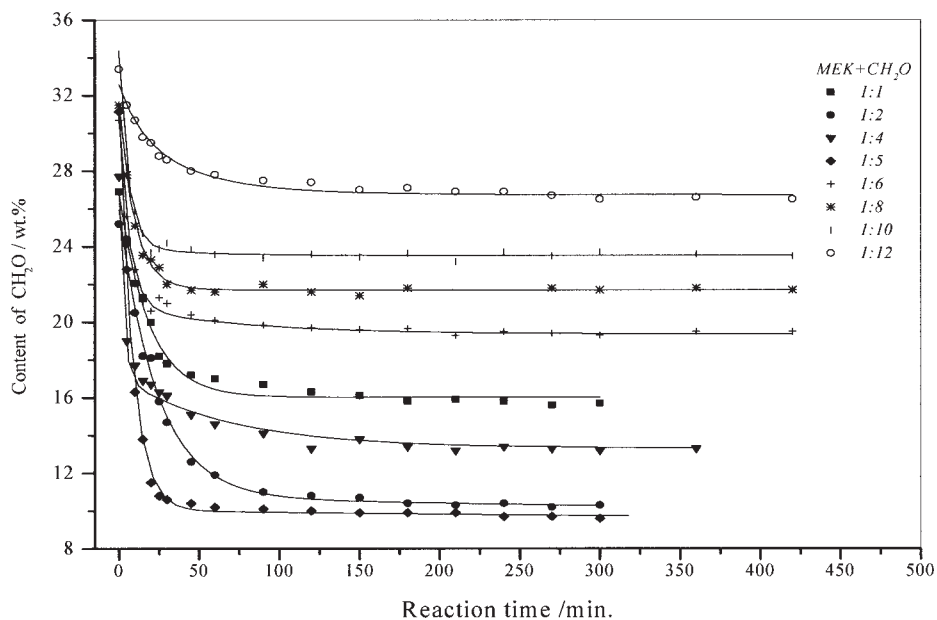

Figure 1 Free and weakly bonded formaldehyde versus the time of the reaction of 1 mol of MEK with 1–12 mol of formaldehyde at 80°C.
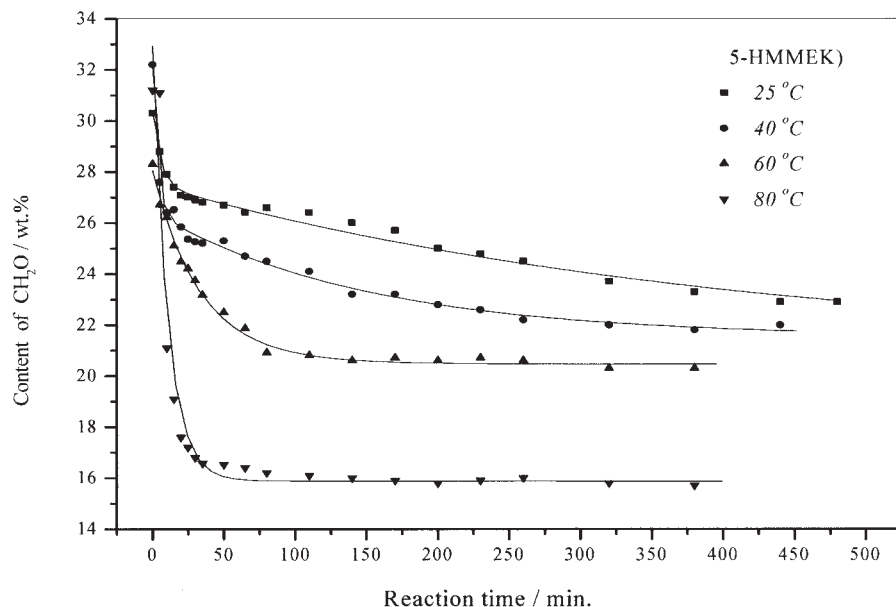
Figure 2 Free and weakly bonded formaldehyde versus time during the reaction of 1 mol of MEK with 5 mol of formaldehyde at various temperatures.

the m/z range of 200–2000. The samples were diluted to a concentration at the level of picomoles per decimeter cubed.

Physical properties of the RSs

The refractive index, density, viscosity, and surface tension of the RSs were measured[13] at 20°C.

Course of melamine dissolution in the RSs

The course of melamine dissolution was studied in detail for two RSs: 1-HMMEK and 5-HMMEK (pre-

pared with 1 or 5 mol of formaldehyde/mol of MEK, respectively). The procedure was exactly the same as that described in ref. 15. The RSs were diluted with 20 wt % water. The amount of dissolved melamine was 23.5 or 56.7 g/100 g of 1-HMMEK or 5-HMMEK, respectively. The dissolution time was 10 min, and ^{1}H-NMR and IR spectra were recorded 3, 5, 8, and 10 min after the beginning of dissolution.

Solubility of melamine and curing experiments

The solubility of melamine in the RSs was determined with the gradual introduction of melamine and with

TABLE II
Physical Properties of RSs of Melamine at 20°C

RS	Reaction temperature (°C)	Density (g/cm^3)	Surface tension $\times 10^{-3}$ (N/m)	Viscosity (Pa s)	Refractive index	CH$_2$O content (wt %)	Appearance after distillation under reduced pressure
1-HMMEK	80	1.056	39.0	0.08	1.4588	12.5	Clear, liquid, thick
2-HMMEK	80	1.109	43.1	0.15	1.4590	20.3	Clear, liquid, thick
3-HMMEK	80	1.134	43.3	0.19	1.4598	29.2	Clear, liquid, thick
4-HMMEK	80	1.148	43.9	0.20	1.4560	32.3	Clear, liquid, thick
5-HMMEK	25	1.176	43.2	0.16	1.4498	38.1	Clear, liquid, thick
5-HMMEK	40	1.170	42.5	0.19	1.4501	40.4	Clear, liquid, thick
5-HMMEK	60	1.164	40.9	0.20	1.4350	39.3	Clear, liquid, thick
5-HMMEK	80	1.166	46.0	0.25	1.4512	43.0	Clear, liquid, thick
6-HMMEK	80	1.170	46.7	0.54	1.4556	45.9	Liquid, thick
7-HMMEK	80	1.183	48.7	0.71	1.4574	47.5	Liquid, thick
8-HMMEK	80	1.201	49.3	0.64	1.4581	48.5	Greasy, semisolid[a]
9-HMMEK	80	1.208	61.2	0.82	1.4635	50.8	Greasy, semisolid[a]
10-HMMEK	80	1.214	61.9	0.92	1.4590	51.7	Greasy, upon storage solidifies[a,b]
11-HMMEK	80	1.287	62.8	1.16	1.4636	53.5	
12-HMMEK	80	—	—	—	—	55.3	Solidifies directly after distillation

[a] Semisolid or solid and greasy product that clarifies and become liquid again on heating.
[b] Properties determined just after distillation under reduced pressure.

^{1}H NMR   IR

$$H_3C—CH_2—\overset{\overset{\displaystyle O}{\|}}{C}—CH_3$$
a   b   c

a: 0.8-1.0 ppm,   2981 and 2883 cm^{-1} $\nu_{C-H\ asym\ \&\ sym}$ of -CH$_3$, strong,

b: 2.0-2.1 ppm,   2940 and 2909 cm^{-1} $\nu_{C-H\ asym\ \&\ sym}$ of >CH$_2$, medium,

c: 2.2-2.4 ppm   1718 cm^{-1} $\nu_{C=O}$, sharp, strong,

MEK (butan-2-one)   1461 cm^{-1} scissor vibr. of >CH$_2$, over asym. of -CH$_3$,

(I)   1417 cm^{-1} $\delta_{CH2-C=O\ op}$, strong,

1366 cm^{-1} $\delta_{CH3-C\ O}$, sharp, strong,

1173 cm^{-1} ν_{C-C}, skeleton, sharp, strong,

996÷944 cm^{-1} δ_{C-H}, medium.

Scheme 1

all the melamine introduced at once. The RSs were diluted with 10–40 wt % water (similarly to refs. 13 and 15). The preliminary curing experiments were carried out as described in ref 15.

RESULTS AND DISCUSSION
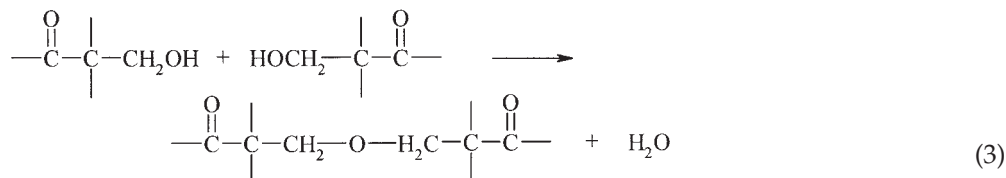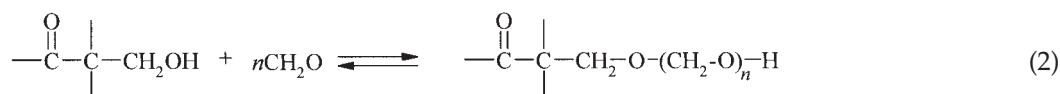
Synthesis of the RSs and their properties

The RSs were prepared in reactions of 1 mol of MEK with 1–12 mol of formaldehyde. The reactions were carried out at 80°C for 5–7 h in the presence of triethylamine as a catalyst (cf. Table I). Some reactions at a 1:5 molar ratio of MEK to formaldehyde were also carried out at a lower temperature of 25, 40, or 60°C.

Depending on the molar ratios of the reactants, compounds of different degrees of substitution of α protons in ketone molecules with hydroxymethyl groups were made. The final molar ratio of ketone to formaldehyde was established from the mass balance after the water and catalyst had been distilled off[13] (cf. Table I). The amount of free and unstably bonded formaldehyde was determined by sulfite method[17] to follow the course of the reaction (cf. Figs. 1 and 2). As the excess of formaldehyde with respect to MEK increased, so did the density, viscosity, surface tension, and content of free or weakly bonded formaldehyde. The refractive index remained essentially unchanged in the range of 1.43–1.46 (cf. Table II).

Immediately after the reaction, the RSs were usually thick, transparent liquids (Table II). Some of them, however, such as 8-HMMEK and those prepared with even larger formaldehyde excess, became turbid after 2–24 h and turned into semisolid or even solid, grease-like substances. They turned back into transparent liquids after heating to 80–90°C.

Course of the formation of the RSs

The composition and structure of the RSs were determined by elemental analysis and ^{1}H-NMR, IR, and ESIMS spectra. The spectral characteristics of MEK are given in Scheme 1. In ^{1}H-NMR spectra of the products of the reactions with a continuously increasing excess of formaldehyde [successive products; Figs. 3(a–e)], one can observe a clear reduction of the signal intensity from methylene protons (b; in the range of 2.0–2.1 ppm) due to a reaction with formaldehyde. Furthermore, with an increasing number of moles of reacted formaldehyde per mole of MEK, the intensity of the signal from methylene protons in —O—CH$_2$—OH groups (4.65–4.8 ppm)[10] also increases as well the signal at 4.4–4.65 ppm due to methylene protons in —C—CH$_2$—O— groups.[18] This indicates that more and more subsequent products are being formed [cf. reactions (2) and (3)]:
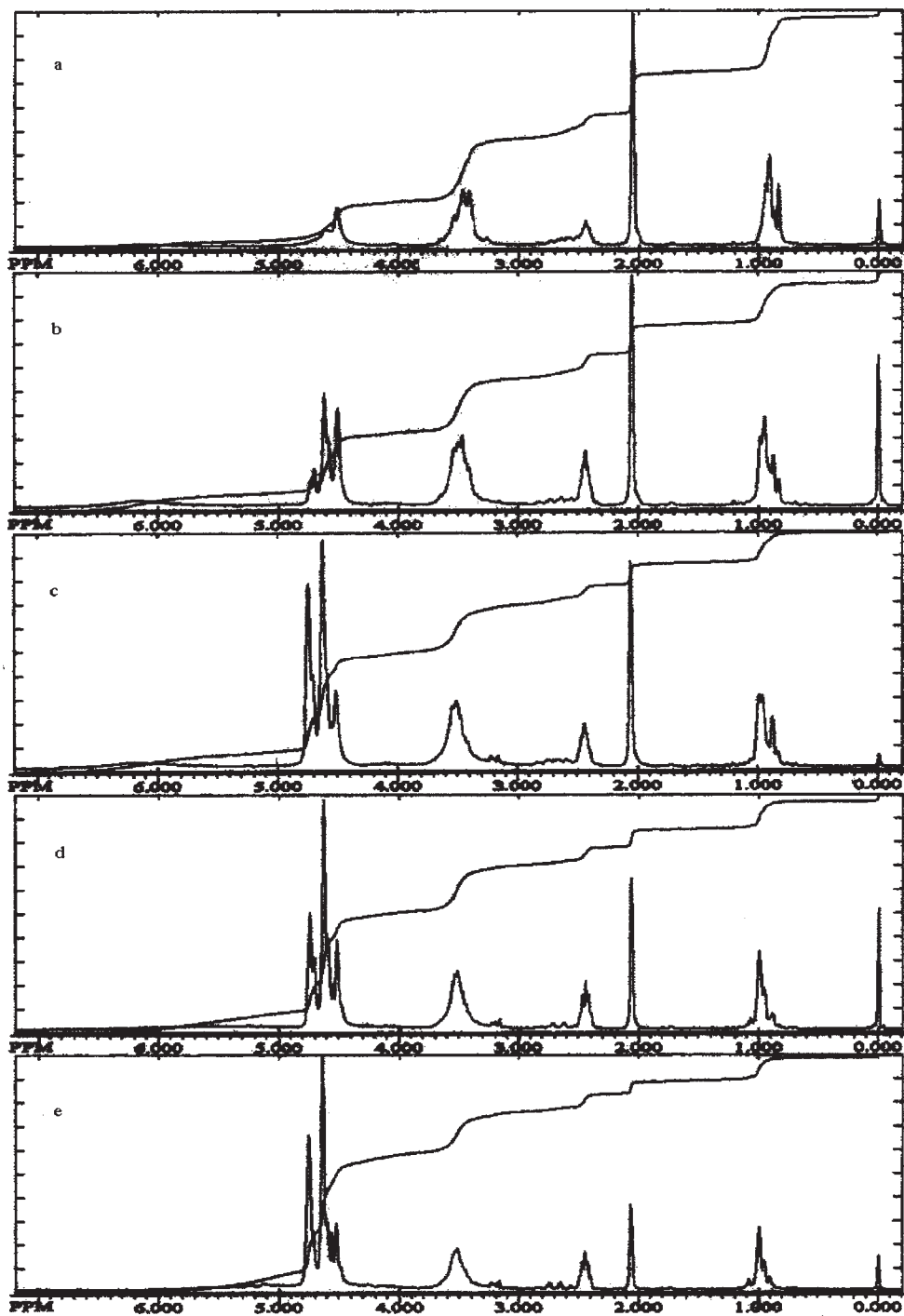
$$—\overset{\overset{\displaystyle O}{\|}}{C}—\overset{|}{\underset{|}{C}}—CH_2OH\ +\ nCH_2O\ \rightleftarrows\ —\overset{\overset{\displaystyle O}{\|}}{C}—\overset{|}{\underset{|}{C}}—CH_2—O—(CH_2-O)_n—H \qquad (2)$$

$$—\overset{\overset{\displaystyle O}{\|}}{C}—\overset{|}{\underset{|}{C}}—CH_2OH\ +\ HOCH_2—\overset{|}{\underset{|}{C}}—\overset{\overset{\displaystyle O}{\|}}{C}— \longrightarrow$$

$$—\overset{\overset{\displaystyle O}{\|}}{C}—\overset{|}{\underset{|}{C}}—CH_2—O—H_2C—\overset{|}{\underset{|}{C}}—\overset{\overset{\displaystyle O}{\|}}{C}—\ +\ H_2O \qquad (3)$$

Figure 3 ^{1}H-NMR spectra (in DMSO-d_6) of RSs prepared in reactions of 1 mol of MEK with (a) 1, (b) 3, (c) 5, (d) 8, and (e) 12 mol of formaldehyde.

In the spectra of RS 5-HMMEK [Fig. 3(c)] and the higher hydroxymethyl derivatives [8-HMMEK and 12-HMMEK, Fig. 3(d,e)], one can observe a clear reduction of the intensity of the signal due to —OH protons in the range of 5.9–6.5 ppm, which indicates the possibility that RS molecules underwent a condensation reaction.

From ^{1}H-NMR spectra, we have estimated the fraction of hydroxyl groups and that of groupings con-

taining weakly bonded formaldehyde as well as the amount of formaldehyde that reacted with methyl (O=C—CH$_3$) or methylene (O=C—CH$_2$—) groups (Table III).

The mass spectrum (ESIMS) of RS 9-HMMEK revealed that the product was a mixture of hydroxymethyl derivatives containing various amounts of substituted formaldehyde. In ESIMS spectra, one can see signals from ions separated by a constant mass of

TABLE III
Chemical Compositions of RSs Prepared from MEK and Formaldehyde

| RS | Reaction temperature (°C) | Number of CH$_2$O moles (mol/mol RS) that reacted with | | Fractions of groups (mol/mol RS)[a] | | |
		Methyl (CH$_3$—C═O)	Methylene (—CH$_2$—C═O)	Semiacetal (—O—CH$_2$—OH)	Oxymethylene (—C—CH$_2$—O-CH$_2$—C)	Hydroxyl (—OH)
1-HMMEK	80	0.17	0.75	0.27	0.23	0.50
2-HMMEK	80	0.23	0.60	0.64	0.39	0.86
3-HMMEK	80	0.26	0.72	0.50	0.75	1.17
4-HMMEK	80	0.27	0.62	0.90	1.15	1.60
5-HMMEK	25	0.24	0.60	1.20	1.50	2.00
5-HMMEK	40	0.25	0.58	1.21	1.51	2.21
5-HMMEK	60	0.26	0.53	1.24	1.46	2.26
5-HMMEK	80	0.26	0.48	1.20	1.40	2.40
6-HMMEK	80	0.27	0.45	1.75	1.59	2.25
7-HMMEK	80	0.31	0.48	1.75	1.69	2.37
8-HMMEK	80	0.40	0.70	1.69	1.78	2.25
9-HMMEK	80	0.46	0.70	1.75	1.63	3.00
10-HMMEK	80	0.50	0.70	2.43	1.82	3.18
11-HMMEK	80	0.43	0.85	1.89	1.89	3.05
12-HMMEK	80	0.45	0.73	2.70	2.20	3.33

[a] Protons (a) of MEK not participating in the reactions were taken as reference signals (cf. Table I).

$m/z = 30$, that is, a formaldehyde molecule. Its interpretation is presented in Table IV.

In IR spectra of the successive products of the reaction between increasing amounts of formaldehyde and MEK, beside the bands present in MEK itself (I), extra bands characteristic of primary alcohols were observed at (1) 3389 cm^{-1} ($\nu_{O—H}$; polyassociates, strong) and (2) 1284 cm^{-1} ($\nu_{O—H}$; medium) integrated with $\nu_{C—O}$ at 1018 cm^{-1} (diffused, strong). The presence of these bands proves the formation of hydroxymethyl derivatives of MEK. Another strong band appeared at 1112 cm^{-1} due to the stretching vibration of ether links (C—O—C), confirming the presence of the subsequent products [reactions (2) and (3)].

On the basis of this reasoning and the results of elemental analysis of the products (Table V), a general equation representing the structure of the RSs prepared from MEK and an excess of formaldehyde is shown in Scheme 2.

Dissolution of melamine in the RSs

The mechanism of melamine dissolution in the RSs prepared in this work seems identical to that of dissolution in the analogous RSs prepared from other ketones.[10,15] That is, at an elevated temperature, formaldehyde is released from semiacetal groups of RS (the intensity of the signal in the range of 3.2–3.7 ppm

TABLE IV
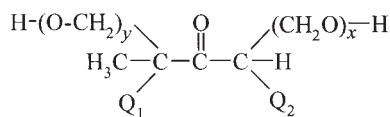**Interpretation of ESI MS Spectrum of the RS Prepared from 1 mol of MEK and 9 mol of Formaldehyde (9-HMMEK)**

RS	MS signal (m/z)	Signal relative intensity (%)	Expected structure of molecular ion	Calculated molar mass (g/mol)
	214.8	8	4-HMMEK + Na$^+$	215.0
	244.8	18	5-HMMEK + Na$^+$	245.0
	274.9	30	6-HMMEK + Na$^+$	275.0
	304.9	66	7-HMMEK + Na$^+$	305.0
	334.9	89	8-HMMEK + Na$^+$	335.0
	365.0	100	9-HMMEK + Na$^+$	365.0
	395.0	96	10-HMMEK + Na$^+$	395.0
9-HMMEK	425.0	83	11-HMMEK + Na$^+$	425.0
	455.0	67	12-HMMEK + Na$^+$	455.0
	485.1	41	13-HMMEK + Na$^+$	485.0
	515.0	30	14-HMMEK + Na$^+$	515.0
	545.1	18	15-HMMEK + Na$^+$	545.0
	575.2	11	16-HMMEK + Na$^+$	575.0
	629.3	5	18-HMMEK + Na$^+$	635.0

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TABLE V
Results of Elemental Analysis for RSs Prepared in Reactions of MEK and Formaldehyde at 80°C

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	Elemental analysis					
	C (wt %)		H (wt %)		O (wt %)	
RS	Calcd	Found	Calcd	Found	Calcd	Found
1-HMMEK	58.82	51.51	9.80	9.17	31.38	39.32
2-HMMEK	54.54	48.80	9.09	8.11	36.37	43.08
3-HMMEK	51.85	52.22	8.64	8.03	39.51	39.75
4-HMMEK	50.00	49.06	8.33	7.73	41.67	43.21
5-HMMEK	48.65	49.76	8.12	8.28	43.24	41.96
6-HMMEK	47.62	46.33	7.94	8.12	44.44	45.55
7-HMMEK	46.81	45.58	7.80	8.06	45.39	46.36
8-HMMEK	46.15	46.71	7.69	7.73	46.15	46.15
9-HMMEK	45.61	46.20	7.60	7.91	46.79	45.89
10-HMMEK	45.16	45.10	7.53	7.96	47.31	46.94
11-HMMEK	44.78	43.15	7.46	8.07	47.76	48.79
12-HMMEK	44.44	42.11	7.41	7.97	48.15	49.93

decreases), and *N*-hydroxymethyl derivatives of melamine appear in the system (signals at 4.9 and ca. 7.2 ppm from protons in —NH—CH_2—OH and —NH—CH$_2$—OH group, respectively).[19] Then, *N*-hydroxymethyl groups in melamine derivatives condense with *C*-hydroxymethyl ones in the RSs (signal at ca. 4.5 ppm) to yield a resinlike solution capable of further condensation in the presence of an acid catalyst.

The evidence for melamine being built into the RS molecules is the appearance of an 814-cm^{-1} band in IR spectra that is characteristic for vibrations of an *s*-triazine ring. Melamine dissolution is also accompanied by the formation of its *N,N*-bis(hydroxymethyl) derivatives. These can clearly be identified in NMR spectra of melamine solutions (Fig. 4) in which, beside the signals from protons of methylene groups in —NH—CH$_2$OH groups (4.9 ppm), a signal at 5.1 ppm appears from the structure —N(CH$_2$OH)$_2$.

$$\text{H-(O-CH}_2)_y \diagdown \quad \underset{\|}{\overset{O}{}} \quad \diagup (\text{CH}_2\text{O})\overline{}_x\text{-H}$$
$$\text{H}_3\text{C—C—C—C—H}$$
$$\diagup \quad\quad\quad \diagdown$$
$$Q_1 \quad\quad\quad Q_2$$

(II)

where:

$$Q_1 = (-H)_{p_1}$$
$$= (-CH_2-O-)_{q_1}$$

$$\left.\right\} \quad 1$$

$$Q_2 = (-H)_{p_2}$$
$$= (-CH_2-O-)_{q_2}$$

$$\left.\right\} \quad 1$$

$$or \ Q_2 = (-CH_2-O-)_{q_2}, \ if \ p_1 = 0$$

$x + y + q_1 + q_2 = n$, where : $\quad 5 \leq n \leq 12$

n — is the number of moles of formaldehyde per 1 mole of MEK,

Scheme 2

Melamine solutions

As a measure of the quality of the hydroxymethyl derivatives of ketones called RSs, the amount of melamine dissolved in 100 g may serve. It was determined in two ways: by the gradual addition of melamine to the solution (Fig. 5) or by the addition of melamine in one portion (Fig. 6). Furthermore, water was added to an RS in the concentration of 10–40 wt % (Fig. 7). Hence, the number of combinations in which various amounts of melamine could be dissolved was substantial. As in previous cases,[14,15] the amount of melamine dissolved depended on (1) the procedure of melamine dosage, (2) the presence and amount of water in the RS, and (3) the kind of hydroxymethyl derivative of MEK. By introducing melamine in one portion (as calculated from the results of portionwise dissolution), one may dissolve up to several percent more melamine than by its gradual introduction (Fig. 7).

The amount of melamine dissolved in an RS considerably increases when water is introduced in the concentration of 10 wt % with respect to the RS. The solubility is further enhanced when the concentration of water is increased up to 40 wt % in 5% intervals (Fig. 7).

The melamine dissolution ability of a solvent increases with an increasing molar excess of formaldehyde over MEK used in its synthesis and the amount of water added to it (Fig. 7).

Among the RSs prepared from MEK, the best melamine solubility was in products obtained with molar ratios of ketone to formaldehyde equal to 1 : 5, 1 : 8, 1 : 10, and 1 : 12 (102.6, 101.0, 110.8, and 123.8 g, respectively, in 100 g of an RS containing 40 wt % water; Fig. 7).

A further increase in the molar excess of formaldehyde in an RS (>12-fold) did not improve the melamine solubility.

Preliminary experiments on the curing of melamine solutions in RSs were also carried out. The solutions
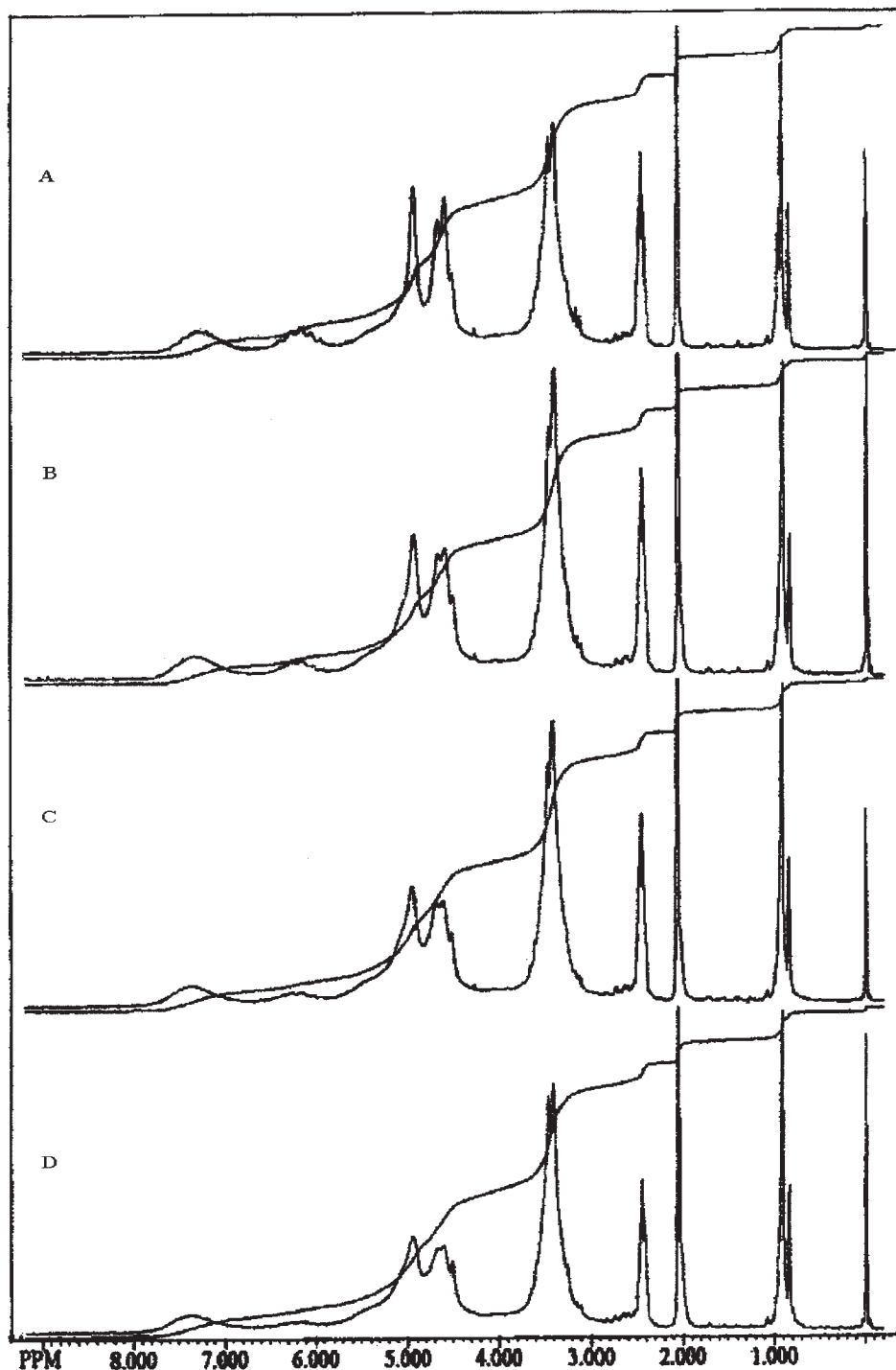
Figure 4 ^{1}H-NMR spectra (in DMSO-d_6) of melamine solutions in 5-HMMEK recorded after (A) 3, (B) 5, (C) 8, and (D) 10 min.

did harden in the presence of acidic catalysts at 120°C, and the products had excellent stability against water. The preparation and properties of new polymers prepared from melamine solutions in RSs will be the subject of a forthcoming article.

CONCLUSIONS

Hydroxymethyl derivatives of MEK are formed in reactions of the ketone with formaldehyde in a basic medium. These derivatives are excellent solvents of melamine and are called RSs of melamine.

The best melamine dissolution occurs in RSs obtained from reactions of 1 mol of MEK with 5, 8, 10, or 12 mol of formaldehyde.

Melamine solutions in RSs can be cured with acidic catalysts at 120°C to obtain new melamine–formaldehyde–ketone resins.
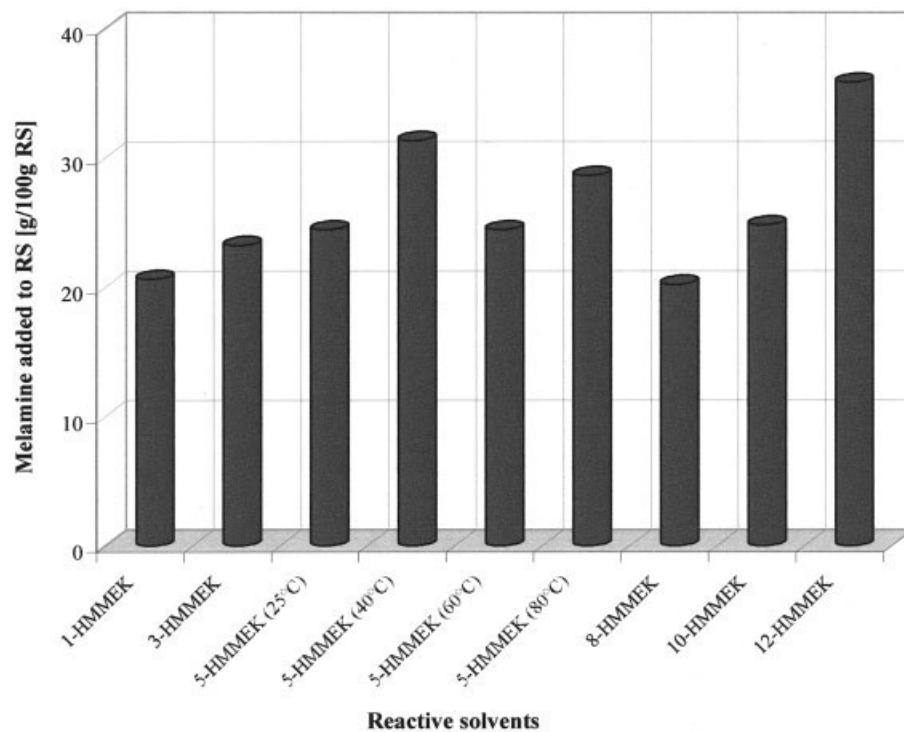
Figure 5 Solubility of melamine (introduced gradually) in different hydroxymethyl derivatives of MEK.
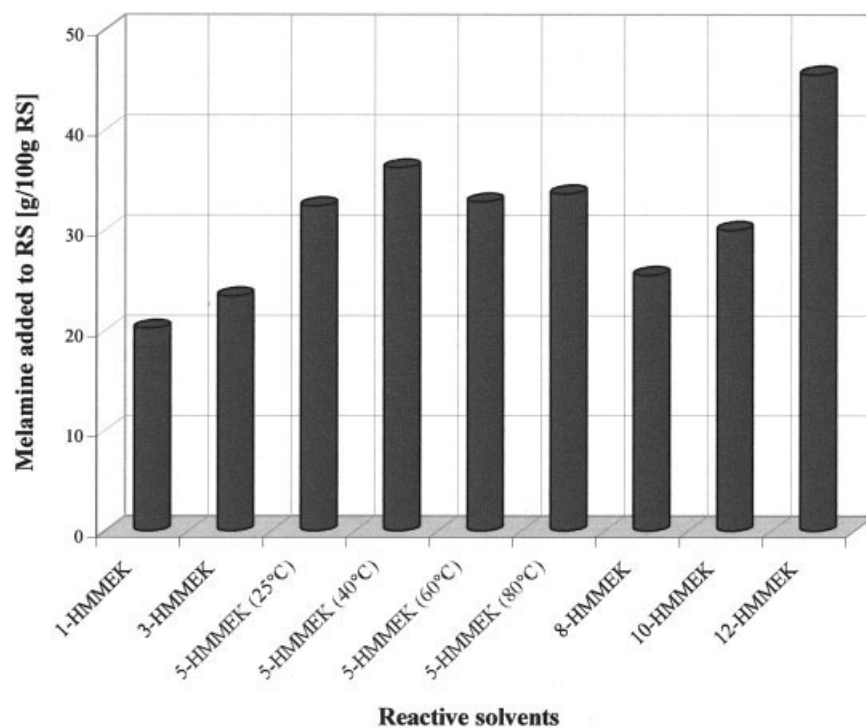

Figure 6 Solubility of melamine (introduced in one portion) in different hydroxymethyl derivatives of MEK.
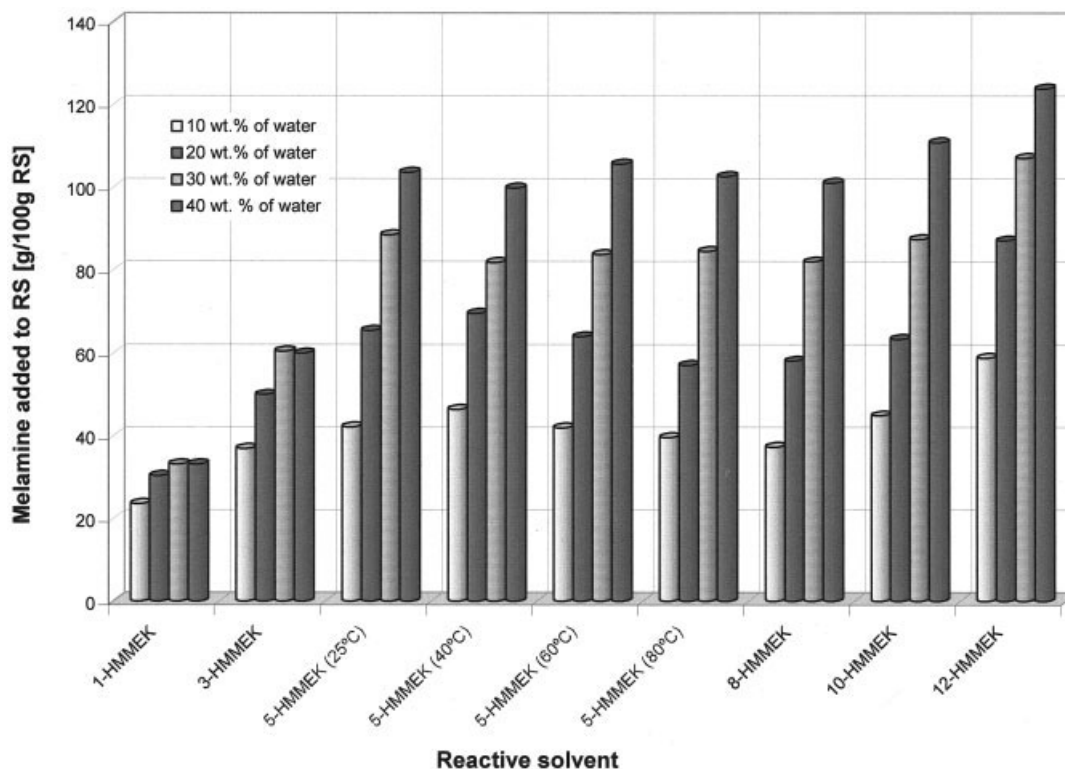
Figure 7 Solubility of melamine (introduced in one portion) in different hydroxymethyl derivatives of MEK with different amounts of water.

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