

Preparation of New Polymers from Heterocyclic Compounds and Reactive Solvents of Melamine

Jacek Lubczak, Renata Lubczak, Iwona Zarzyka-Niemiec

Faculty of Chemistry, Rzeszów University of Technology, 35-959 Rzeszów, Poland

Received 16 July 2002; accepted 27 March 2003

ABSTRACT: Reactive solvents were obtained from reactions of acetone with formaldehyde. They were used for the dissolution of some heterocyclic compounds. When the dissolution of the obtained compounds was not possible, the structures of these compounds were modified to increase their solubility. The oligomers cured at 80–120°C in the

presence of an acidic catalyst. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3390–3401, 2003

Key words: heteroatom-containing polymers; structure-property relations

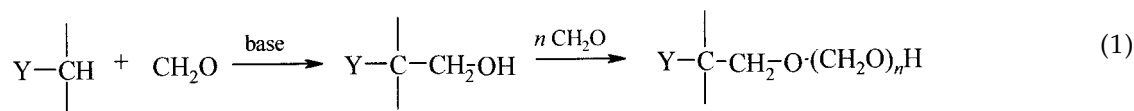
INTRODUCTION

The presence of 1,3,5-triazine rings in molecules furnishes polymers containing melamine with improved chemical and thermal stability as well as good electrical properties.¹ Despite this advantage, very little data can be found for applications of melamine in the preparation of polymers other than the classic melamine-formaldehyde resins. The reason might be the lack of efficient organic solvents that allow reactions involving this monomer to be carried out. Recently, Wirpsza and coworkers^{2,3} developed a new group of so-called reactive solvents (RSs) of melamine capable of dissolving melamine, mainly by reacting with it. Dissolved melamine is built into the structure of the solvent, and

this yields a thick, resinous liquid. Solutions of melamine can then be cured with acidic or basic catalysts to obtain new melamine-based polymeric materials with interesting properties. These new melamine-based polymers can be used to prepare highly water-resistant adhesives and thermostable foams.⁴

The effective RSs of melamine include hydroxymethyl derivatives of aliphatic compounds with strongly electronegative groups capable of activating the C—H link in the α position with respect to these groups.

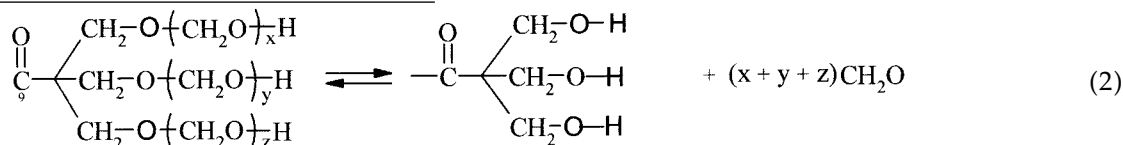
The RSs are prepared in a basic medium by the reaction of an excess of formaldehyde with the aforementioned α -C—H group



where Y stands for a strongly electronegative group such as $\text{C}=\text{O}$, $-\text{NO}_2$. Hence, the RSs are hydroxymethyl derivatives of ketones, aldehydes, and aliphatic nitro compounds containing oxymethylene bridges.² The solubility, or rather liquefiability, of mel-

amine increases with an increasing number of hydroxymethyl groups in the RSs.^{3,5}

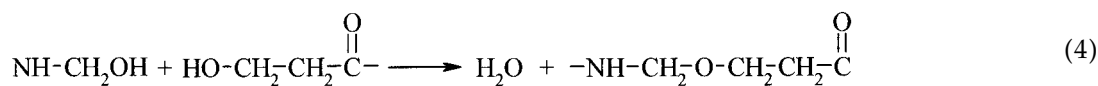
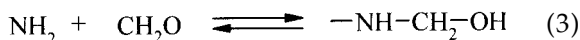
The solvents decompose when heated to about 105°C (regardless of the kind of starting solvent), and this yields free formaldehyde formed by the decomposition of semiacetal groups:³



Correspondence to: J. Lubczak (jml@prz.rzeszow.pl).

This is advantageous from the point of view of melamine dissolution because liberated formaldehyde reacts with it to yield *N*-(hydroxymethyl) groups, which can further react with the solvent.³

Water is formed during the condensation of hydroxymethyl groups of melamine with hydroxyl groups of an RS, and melamine is built into the structure of the RS.^{3,5}



During further heating, water evaporates from the system. The addition of extra water to the system improves the solubility of melamine. Hence, water acts in two ways: it physically dissolves melamine and facilitates the decomposition of semiacetal groups and the reaction of liberated formaldehyde with melamine.³

We expected that a similar method could be applied to the preparation of polymeric materials from heterocyclic compounds other than melamine but also containing —NH— groups. Among these compounds are isocyanuric acid (IA), barbituric acid (BA), uric acid (UA), melam, melem, melamine isocyanurate (MI), adenine, and guanine:

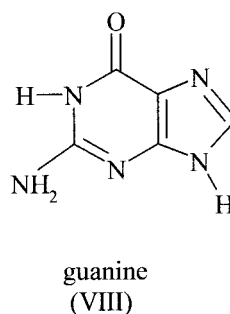
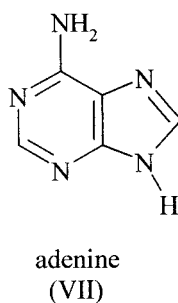
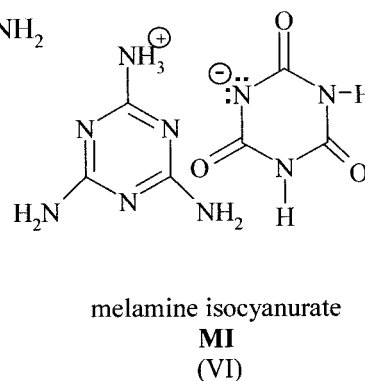
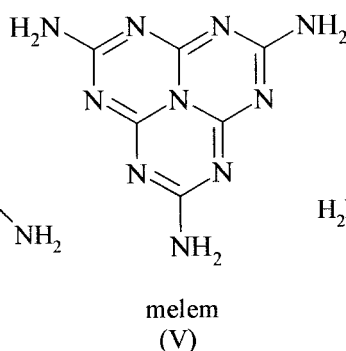
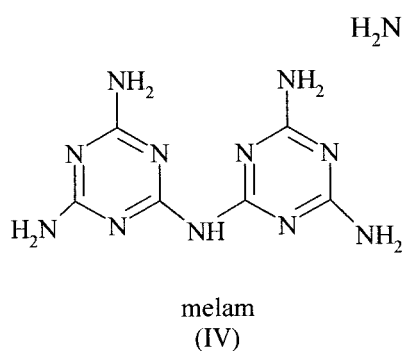
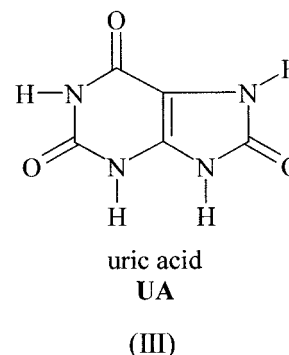
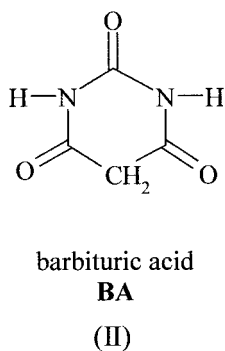
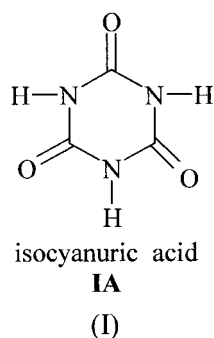


TABLE I
Highest Solubility of Heterocyclic Compounds in RS 8-HMA

Heterocyclic compound	Solubility (g/100 g of RS introduced)	Loss weight of RS on heating (wt %)	Solubility (g/100 g of RS left)	Concentration of heterocycle (wt %)	Time of dissolution (min)	Appearance
IA	62.3	17.1	75.2	42.9	12	Clear
BA	53.5	15.2	63.1	38.7	10	Slightly opaque
UA	3.5	23.9	4.6	4.4	10	Slightly opaque
Melem	<1	24.8	<1.3	—	No solubility	—
Melam	<20	25.0	<26.6	21.0	No solubility	Opaque
MI	9.5	30.0	13.6	12.0	10	Slightly opaque
Adenine	62.3	22.1	80.0	44.4	10	Clear
Guanine	0.0	32.0	—	—	No solubility	—

Attempts have been made by colleagues in our laboratory⁵ to apply some of the aforementioned compounds to the preparation of new polymeric materials with an RS obtained from cyclohexanone and acetone. We, however, were successful in preparing new polymers from melamine only, following the known procedures.³ We had no success with other heterocyclic compounds.

In this work, we examine some possible ways of avoiding the difficulties encountered before, and we try to explain the reasons why the desired products have not been formed or have had limited stability.

EXPERIMENTAL

Syntheses

Synthesis of the RSs

The RSs from acetone and formaldehyde were obtained as described in ref. 3. Products were obtained in which the molar ratio of acetone to formaldehyde was 1:1, 1:4, or 1:8.

Preparation of melam, melem, and MI

The compounds were obtained with the procedures described in refs. 6–8. The products were identified by their elemental analysis.

ELEM. ANAL. Calcd. for melam: C, 30.64%; N, 65.55%; H, 3.83%. Found: C, 30.31%; N, 65.92%; H, 3.26%. ELEM. ANAL. Calcd. for melem: C, 33.03%; N, 64.22%; H, 2.75%. Found: C, 32.91%; N, 64.34%; H, 2.28%. ELEM. ANAL. Calcd. for MI: C, 28.24%; N, 49.41%; H, 3.53%. Found: C, 27.95%; N, 49.05%; H, 3.41%.

Synthesis of the hydroxymethyl derivatives of the heterocyclic compounds

Into a three-necked, 250-cm³, round-bottom flask equipped with a reflux condenser, a thermometer, and a stirrer, 0.05 mol of a heterocyclic compound (melem, MI, UA, adenine, or guanine) and an appropriate amount of formalin (36%) were added. The content of the flask was heated at the boiling point (ca. 96°C) until the heterocyclic compound dissolved and then for another 30 min. The reaction mixture was cooled to room temperature, and if a precipitate was formed, it was filtered off, washed with water, and dried out at less than 40°C. Otherwise, water was distilled off under reduced pressure (1.5–2.1 kPa; temperature of boiling mixture ≤ 50°C) to obtain a solid or semisolid resin.

The amount of formalin was adjusted so that the formaldehyde content was stoichiometric with respect to the amount of —NH— groups in the heterocyclic

TABLE II
Highest Solubility of Heterocyclic Compounds in RS 8-HMA Containing 30 g of Water per 100 g of RS

Heterocyclic compound	Solubility of heterocycle		Loss of mass of the system during dissolution of heterocycle (wt %)	Concentration of heterocycle (wt %)	Time of dissolution (min)	Appearance
	g/100 g of starting RS + H ₂ O	g/100 g of final RS + H ₂ O				
IA	55.1	90.2	38.9	47.4	15	Slightly opaque
BA	86.0	97.1	11.4	49.3	8	Clear
UA	40.9	52.4	22.0	34.4	15	Clear
Melem	< 1	< 1	—	—	—	No solubility
Melam	100	133.3	25.0	—	10	Clear
MI	7.8	11.7	43.8	10.5	15	Clear
Adenine	35	44.9	22.1	31.0	10	Initially clear, but precipitate appeared after a while
Guanine	—	—	32.4	—	—	No solubility

TABLE III
Conditions of Synthesis of *N*-(Hydroxymethyl) Derivatives of Some Heterocyclic Compounds in Reaction with Formalin

Heterocyclic compound	CH ₂ O/heterocycle molar ratio	Reaction conditions		Remark	Product appearance
		Temperature (°C)	Time (h)		
Melem	6–45	95	48	No reaction	—
UA	4	85	48	No reaction	—
	6	95	0.75	Dissolved, and soon precipitate dropped down	White powder
	7	85	0.1	Dissolved	semisolid resin: % CH ₂ O _{found} = 52.3, % CH ₂ O _{calcd} = 55.4
IM	9	95	48	No reaction	—
	10	95	3	Dissolved during 2.5 h, then solution slowly became opaque and gels	—
	15	95	0.75	Dissolved	Semisolid resin dissolved in RS containing 14 wt % H ₂ O

compound. Attempts with larger amounts of formalin were made when the stoichiometric amount was insufficient to dissolve the compound.

Dissolution of the heterocyclic compounds in the RSs

The solubility of the heterocyclic compounds in the RSs at 95–100°C was determined as described in ref. 3. It consisted of the gradual or immediate introduction of the heterocyclic compounds directly into the RSs (Table I). Alternatively, 20–30 wt % water-diluted RSs were added (Table II).

Analysis of the products

The amount of unstable formaldehyde present in the form of *N*- and *O*-(hydroxymethyl) groups in the products of the reaction of UA or adenine with formaldehyde was determined iodometrically.⁹ A procedure analogous to that used in determining the *N*- and *O*-hydroxymethyl derivatives of melamine and UA was used.^{10,11} ¹H-NMR spectra of the hydroxymethylation products and the mixtures of RSs with gradually dissolving heterocyclic compounds were recorded on a BS587A 80-MHz spectrometer (Tesla, Brno, Czechoslovakia) in an acetone-*d*₆ or deuterated dimethyl sulfoxide (DMSO-*d*₆) solution.

Attempted curing of the polymer solutions

To a solution usually containing the largest possible amount of a dissolved heterocyclic compound dissolved in 2 g of an RS, hydrochloric acid (36%; 1–6 wt % with respect to the solvent) was added, and the mixture was stirred with a glass rod at 100°C until the

mixture gelled (the resin lost its fluidity and tended to detach from the rod). Attempts to cure the resins placed on glass platelets were also made via heating at 80–140°C for 30 min to 11 h.

RESULTS AND DISCUSSION

Dissolution of the heterocyclic compounds

The dissolution experiments involving RSs were carried out with compounds I–VIII. The compounds were hardly soluble in organic solvents and contained —NH— and/or —NH₂ groups in their structure. The presence of groups similar to those in melamine suggested a similar mechanism of dissolution of the compounds in the RSs. The first RS tested was that obtained by the reaction of 1 mol of acetone with 8 mol of formaldehyde (8-HMA) at 40°C. This was the best solvent for melamine.³ The results of the experiments are presented in Tables I and II. The best solubility in the solvent was found for IA and BA. The solubility of melam was improved 5 times after 30% water was added to the RS. Here, use was made of the earlier observation that melamine solubility considerably increased when the RS was diluted with water.³ The solubility of melam seems similar to that of melamine, just as their structures are similar. In the case of UA, the addition of water caused the solubility to increase over 10 times, and the solubility of BA increased 1.5 times. However, the solubility of adenine decreased (Table II). The dissolution procedure was carried out until a clear solution was obtained.

In summary, the data indicate that melam, BA, and IA were quite soluble in the RSs, whereas the other compounds were poorly (UA) or very poorly soluble (MI, melem, adenine, and guanine) even after water was introduced into the solvents.

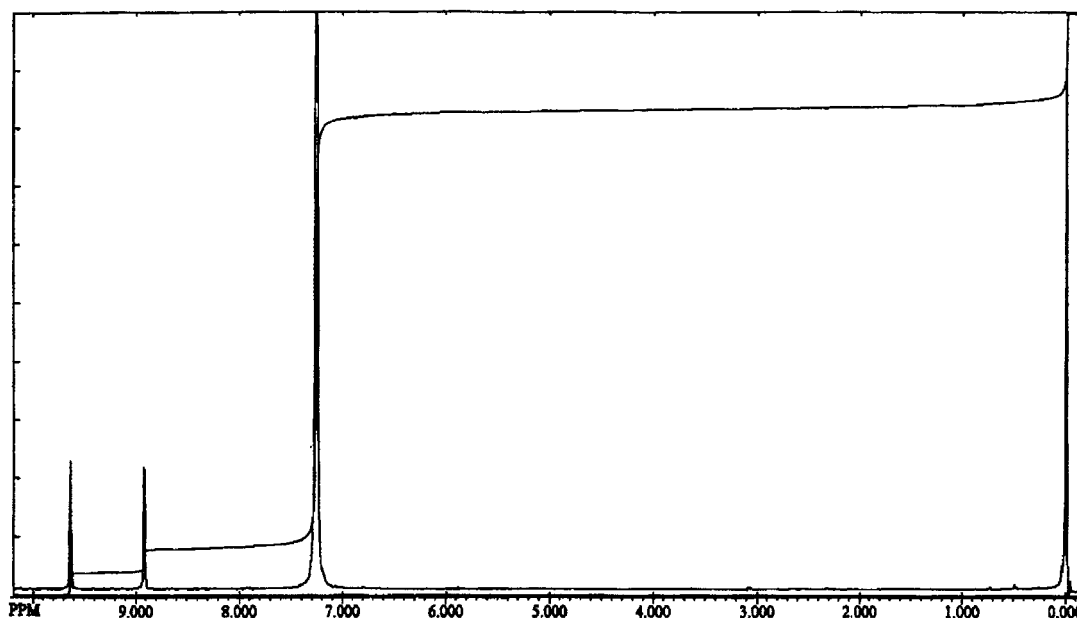
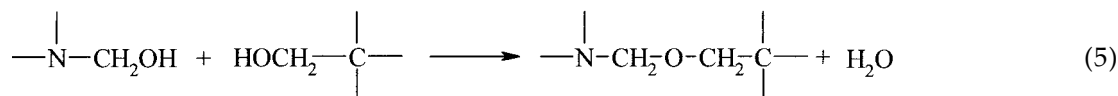


Figure 1 $^1\text{H-NMR}$ spectrum of adenine (with $\text{D}_2\text{O-D}_2\text{SO}_4$ as a solvent).

Modification of the structures of the heterocyclic compounds for improved solubility in the RSs

Attempts were made to improve the solubility of UA, MI, melem, adenine, and guanine in the RSs according

to the following reasoning. If the dissolution takes place according to reactions (4) and (5),



then the very short time of dissolution determined by the poor stability of the RSs at the applied temperatures (10–20 min) is insufficient for *N*-hydroxymethyl derivatives to be formed. Hence, the compound does not dissolve. To verify this, one should first obtain the derivative in question and then introduce it into the RSs and check whether or not it builds into the solvent structure. A stoichiometric amount of formaldehyde was used with respect to all ---NH--- groups in a given compound. When this amount was insufficient to dissolve the compound, an excess of formaldehyde was used.

It was found that neither a stoichiometric excess nor a large excess of formaldehyde was sufficient to obtain *N*-hydroxymethyl derivatives of melem even after prolonged reaction times (48 h; Table III). The other hard-to-dissolve compounds, that is, UA and MI, reacted with formaldehyde to form the derivatives in question. At molar ratios of UA to formaldehyde in the range of 1:4 to 1:6, an *N,N',N'',N'''*-tetrakis(hydroxymethyl) derivative of UA was formed¹¹ that was poorly soluble in a medium containing an RS (it consisted of 12.5 g of the derivative per 100 g of the RS containing 30 wt % water). Only a formaldehyde con-

centration as high as 7 mol/mol of UA provided a product soluble in formalin. The product had the form of a semisolid resin that was quite soluble in the RS. MI behaved in a similar manner. It did not dissolve in formalin unless the molar excess of formaldehyde became about 10-fold. Then, MI slowly dissolved but soon gelled. Only a 15-fold excess of formaldehyde yielded a product that was sufficiently soluble in the RS as long as 14–15% moisture was still left in the compound after the water was distilled off.

The behavior of adenine was different. It dissolved in formalin at 95°C in a few minutes, but then a white solid precipitated from the solution. The solid also formed at a higher molar ratio of formaldehyde to adenine (8:1 or 10:1). The solid did not dissolve during further heating (for 2 days). Hence, the stepwise procedure failed as a method of obtaining higher derivatives of adenine.

The reaction of adenine with formaldehyde was followed chemically (by the measurement of the amount of weakly bonded formaldehyde) and by $^1\text{H-NMR}$ analysis of the products. From the formaldehyde contents, it follows that the solid precipitate obtained at a molar ratio of adenine to formaldehyde

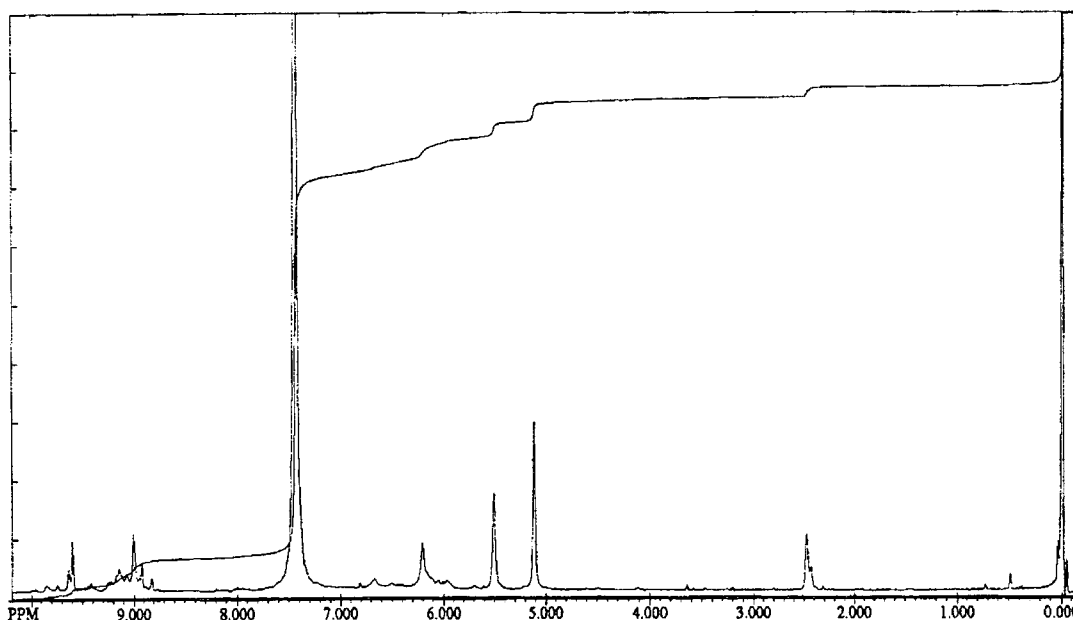
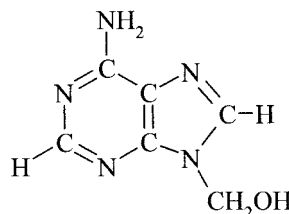
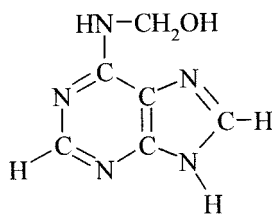


Figure 2 $^1\text{H-NMR}$ spectrum of the product of the hydroxymethylation of adenine (with $\text{D}_2\text{O-D}_2\text{SO}_4$ as a solvent).

of 1:4 was a monosubstituted hydroxymethyl derivative ($\% \text{CH}_2\text{O}_{\text{calcd.}} = 18.2$, $\% \text{CH}_2\text{O}_{\text{found}} = 19.5$). Unfortunately, the derivative was poorly soluble in solvents, including deuterated ones, such as $\text{DMSO-}d_6$. Hence, its spectrum was made in heavy water containing some D_2SO_4 . In the spectrum of adenine in the same solvent (Fig. 1), no signals from amino protons could be seen, unlike its spectrum in $\text{DMSO-}d_6$ (cf. ref. 12),

but two signals of CH= groups could be seen at 8.9 and 9.7 ppm. The same signals were present in the spectrum of the hydroxymethyl derivative of adenine (Fig. 2) in addition to signals due to methylene protons at N -hydroxymethyl groupings, at 5.1 ppm (due to $\text{N6-CH}_2\text{-OH}$, compound IX) and 5.5 ppm (due to $\text{N9-CH}_2\text{-OH}$, compound X),¹³ suggesting that two monohydroxymethyl derivatives were present:



The ratio of the two derivatives was 1:1, as follows from the intensity ratios of the signals at 5.1 and 5.5 ppm. Signals at 6.1 ppm from methylene protons in poly(methylene glycol) $\text{HO-(CH}_2\text{-O)}_n\text{-OH}$ and at 2.2 ppm from -CH_3 protons in acetone were also present in the spectrum. The latter was used to precipitate hydroxymethyl derivatives of adenine. The formation of N -(hydroxymethyl)adenines was confirmed by an IR spectrum (Fig. 3), in which a strong signal from associated hydroxyl groups appeared in the range of $3250\text{--}3500\text{ cm}^{-1}$ and bands due to deformational vibrations of -OH groups at 1068 and 1218 cm^{-1} appeared that were absent in the spectrum of pure adenine.¹⁴

The excessive heating of hydroxymethyl derivatives of adenine for many hours with over a 10-fold excess of formaldehyde did not lead to the dissolution of these compounds. This helps us to understand the types of reactions taking place during the dissolution of adenine in an RS. First, an equimolar mixture of monohydroxymethyl derivatives was formed that dissolved in the RS. Then, upon heating, the solvent released formaldehyde, which left the system without reacting with the derivatives. The composition of the solvent thus changed, and the derivatives finally precipitated from it. This was seen particularly well when the solution was poured onto a glass plate and ex-

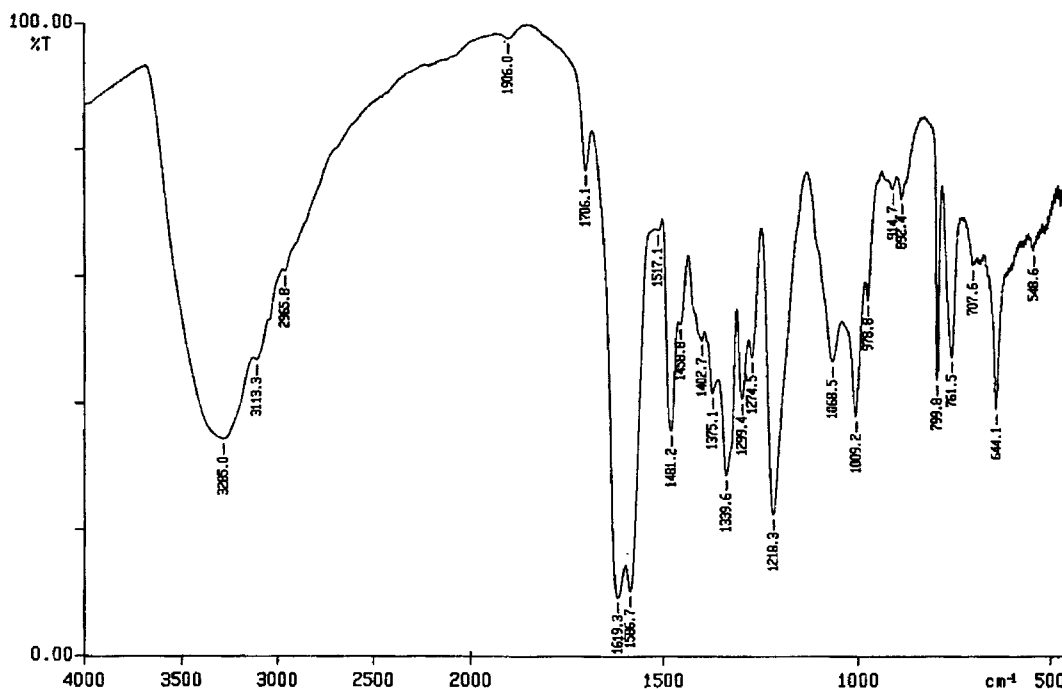


Figure 3 IR spectrum of the product of the hydroxymethylation of adenine.

posed to 120°C for several hours. Consequently, the resulting coating had poor water resistance.

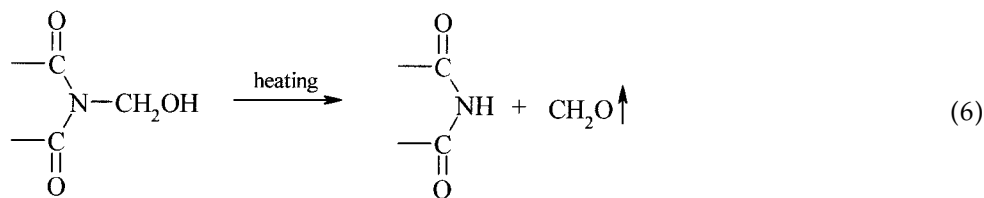
Attempts at preparing higher hydroxymethyl derivatives of adenine became positive only after the application of a 15-fold molar excess of formaldehyde. Solutions were then obtained that, after water was distilled off, were transparent or slightly opaque. This procedure, however (i.e., a large excess of formaldehyde with respect to adenine), excluded the possibility of applying the RS route to the preparation of polymeric materials. The content of adenine would then be too small to provide the material with any sensible properties.

Curing of solutions of the heterocyclic compounds in the RSs

Solutions of the heterocyclic compounds in the RSs were cured with hydrochloric acid similarly to mel-

amine solutions.⁵ To solution of the heterocyclic compounds, 1–6 wt % concentrated (36 wt %) hydrochloric acid was introduced (with respect to the amount of the RSs). The samples of the solutions were poured onto acetone-washed glass plates and cured at 80–140°C (Table IV). The solutions used in the curing experiments were those containing the highest amounts of dissolved heterocycles or containing 100 g of their hydroxymethyl derivatives in 100 g of an RS.

Solutions of IA were incurable with hydrochloric acid, even at temperatures as high as 100–140°C and with 3 wt % HCl with respect to RS. The reason was the instability of the *N*-hydroxymethyl groupings in IA,¹⁵ which decomposed at elevated temperatures with the restoration of the imide structure:



Solutions of melam in the RSs cured under these conditions very well. The coatings of the best quality were obtained with this compound. The curing of solutions of *N*-hydroxymethyl derivatives of UA and MI in the RS prepared from 1 mol of acetone and 8 mol of formaldehyde yielded highly blistered coatings. The reason might be a too large amount of formaldehyde

present in the RS in the form of *O*-hydroxymethyl groups that did not react with *N*-hydroxymethyl derivatives of heterocycles but decomposed at high temperatures, releasing gaseous formaldehyde. If this reasoning is correct, the use of an RS prepared with a smaller excess of formaldehyde should improve the quality of the coatings. Indeed, the solutions obtained

TABLE IV
Preliminary Results of the Coating Formation

Hetero-cyclic compound	Acetone/CH ₂ O molar ratio in RS	Water (g/100 g of RS)	Solubility of heterocyclic compound (g/100 g of RS)	Amount of aqueous HCl (wt %)	Curing conditions		Coating appearance
					Temperature (°C)	Time (h)	
IA	1:8	—	70	1	120	0.5	Uncured
			70	3	105	2.0	White powder precipitated
			70	3	140	2.0	White powder precipitated
			65	1	120	0.5	Cured, blistered
UA	1:8	30	75	3	105	2.0	Uncured
			75	3	140	2.0	Cured, blistered
Melam	1:8	30	150	2	120	0.5	Cured, no blisters
HMUA	1:4	30	125	4	100	5.0	Cured, no blisters
HMMI	1:4	—	100	3	110	3.0	Cured

HMUA = product of the reaction of 1 mol of UA with 7 mol of CH₂O;

HMMI = product of the reaction of 1 mol of MI with 15 mol of CH₂O.

by the dissolution of 100 g of the *N*-hydroxymethyl derivative of UA or MI in a solvent in which the molar ratio of acetone to formaldehyde was 1:4 (4-HMA) yielded, after being heated at 100–110°C for 3–5 h with 3–4 wt % HCl, well cured clear coatings free of blisters (Table IV).

Further experiments were carried out with BA and *N*-hydroxymethyl derivatives of UA and MI. The effects of the following parameters were tested on the visual quality of the coatings: the type of RS, the catalyst (HCl) content (1–6 wt %), the curing temperature (80–120°C), and the time (2–24 h). The results obtained with *N*-hydroxymethyl derivatives of UA dissolved in 4-HMA (Table V) can be summarized as follows:

- It was undesirable to cure solutions above 100°C; not fully cured coatings were then obtained, even after a long exposure time (up to 6 h).
- Increasing the temperature to 120°C reduced the curing time to about 3 h, but the coatings were blistered.
- With 4 wt % HCl and at 100–110°C, we obtained well cured coatings, but they were slightly blistered, particularly in thick layers.
- Reasonable coatings could be obtained with an RS prepared with an acetone/formaldehyde molar ratio of 1:1 (MHMA), 4 wt % catalyst, a curing temperature of 95–100°C, and a curing time of 3–6 h.

Even better surface coatings were obtained by the curing of solutions of *N*-hydroxymethyl derivatives of MI in 4-HMA. With 4 wt % HCl with respect to the RS

and a curing temperature of 100–110°C for 4 h, we obtained well cured coatings not containing blisters.

With BA as the coating base, the best results were obtained with MHMA as the RS and with solutions containing less than the highest amount of UA, that is, 50 g/100 g of RS. The best curing conditions were 95°C, 5 wt % HCl, and 6 h of heating (Table V). More details on the preparation and properties of the coatings obtained with this method involving RSs will be reported in another publication.

Analysis of the process of the dissolution of the heterocyclic compounds in the RSs and the curing of the solutions

The mechanism of the dissolution or more strictly the dissolution of the heterocyclic compounds was analyzed in detail for BA, melam, and *N*-hydroxymethyl derivatives of UA. In the ¹H-NMR spectrum of BA [Fig. 4(a)], two signals were present: at 11.0 ppm from protons of imide groups and at 3.4 ppm from protons of methylene groups. In solutions of the same acid in an RS, the intensity of the signal at 11.0 decreased, and a new signal appeared at 5.1 ppm [Fig. 4(b,c)]. This suggests that the dissolution of BA took place mostly via the reaction of imide groups with formaldehyde coming from the RS.¹⁶

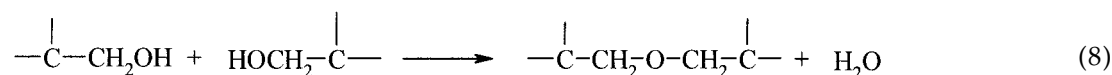
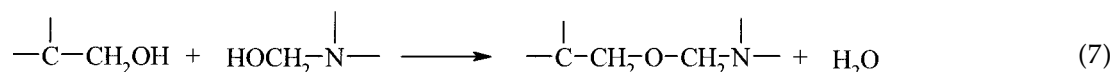
The instability of hydroxymethyl links in BA that decomposed according to eq. (6) was the reason why upon heating at high temperatures, the cured compositions lost formaldehyde. However, *C*-hydroxymethyl derivatives formed in small quantities (a decrease in the intensity of the signal at 3.4 ppm in the

TABLE V
Coatings from Heterocyclic Compounds and RSs

Compound	Type of RS	Solubility of heterocyclic compound (g/100 g of RS)	Amount of aqueous HCl (wt %)	Curing conditions		Coating appearance
				Temperature (°C)	Time (h)	
HMUA	4-HMA	100	2	80	6	Not fully cured
				100	+2	Not fully cured
				120	+3	Cured, blistered
			2	100	2	Not fully cured
				120	+3	Cured, blistered
				120	3	Cured, slightly blistered
				100	6	Cured, blistered
	MHMA	100	4	110	3	Cured, slightly blistered
				85	5.5	Not fully cured, slightly blistered
				90	3	Not fully cured, slightly blistered
			4	95	3	Not fully cured, slightly blistered
				95	6	Not fully cured, slightly blistered
				105	2	Not fully cured, slightly blistered
				110	8	Cured, blistered
HMMI	4-HMA	100	5	95	16	Not fully cured
				100	6.6	Not fully cured
			4	85	5.5	Not fully cured, no blisters
				90	3	Not fully cured, no blisters
				95	7	Cured
				100	4	Cured, no blisters
				110	4	Cured, no blisters
	MHMA	50	5	100	4	Cured, no blisters
				100	4	Cured, no blisters
				110	4	Cured, no blisters
			2	80	4	Not fully cured,
				100	+2	Not fully cured, blistered
				100	2	Not fully cured,
				120	+3	Cured, heavily blistered
BA	4-HMA	75	4	80	7.5	Not fully cured, blistered
				85	4.5	Not fully cured, blistered
				120	2	Not fully cured, blistered
			6	80	4	Not fully cured,
				100	+2	Not fully cured, blistered
				100	2	Not fully cured,
				120	+3	Cured, heavily blistered
MHMA	50	5	80	4	Not fully cured,	
			100	+2	Not fully cured, blistered	
			100	2	Not fully cured,	
		2	80	4	Not fully cured,	
			100	+2	Not fully cured, blistered	
			100	2	Not fully cured,	
			120	+3	Cured, heavily blistered	

30% water with respect to the total mass of used. HMUA = product of the reaction of 1 mol of UA with 7 mol of CH₂O; HMMI = the product of the reaction of 1 mol of MI with 15 mol of CH₂O.

¹H-NMR spectrum was observed) were probably responsible for the curing reactions:



The blistering was caused by formaldehyde evolving from the system when the viscosity of the polymer solution increased.

In the ¹H-NMR spectrum of melam, just one signal was present [Fig. 5(a)] due to all the protons of $\begin{array}{c} | \\ -\text{NH} \\ | \end{array}$ groups. The signal was reduced in the spectrum of the product of its reaction with formaldehyde, and signals appeared at 5.1 [$-\text{N}(\text{CH}_2\text{OH})_2$] and at 4.7 ppm

$\begin{array}{c} | \\ -\text{NH}-\text{CH}_2\text{OH} \\ | \end{array}$).^{16,17} Similar signals were present in the spectrum of melamine in an RS [Fig. 5(b)].

The mechanism of the dissolution of these two (as well as other) heterocyclic compounds was similar. First, *N*-hydroxymethyl derivatives were formed that later reacted with *C*-hydroxymethyl groups of the RS. Thus, the heterocycles were built into the structure of the RS. When the *N*-hydroxymethyl

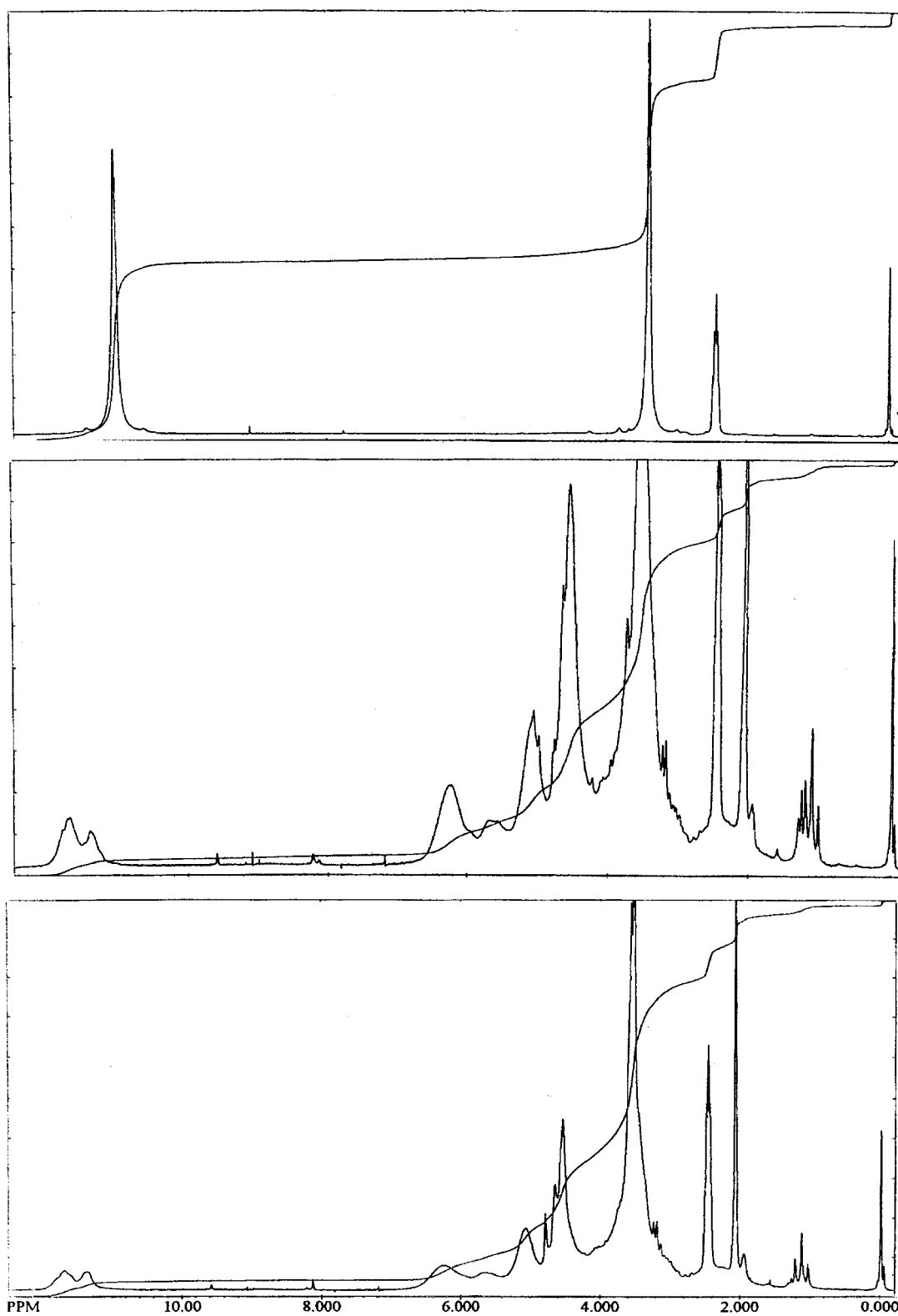


Figure 4 $^1\text{H-NMR}$ spectra of (a) BA and (b,c) mixtures obtained by the dissolution of BA in RS 8-HMA at 105°C for 2 and 10 min, respectively.

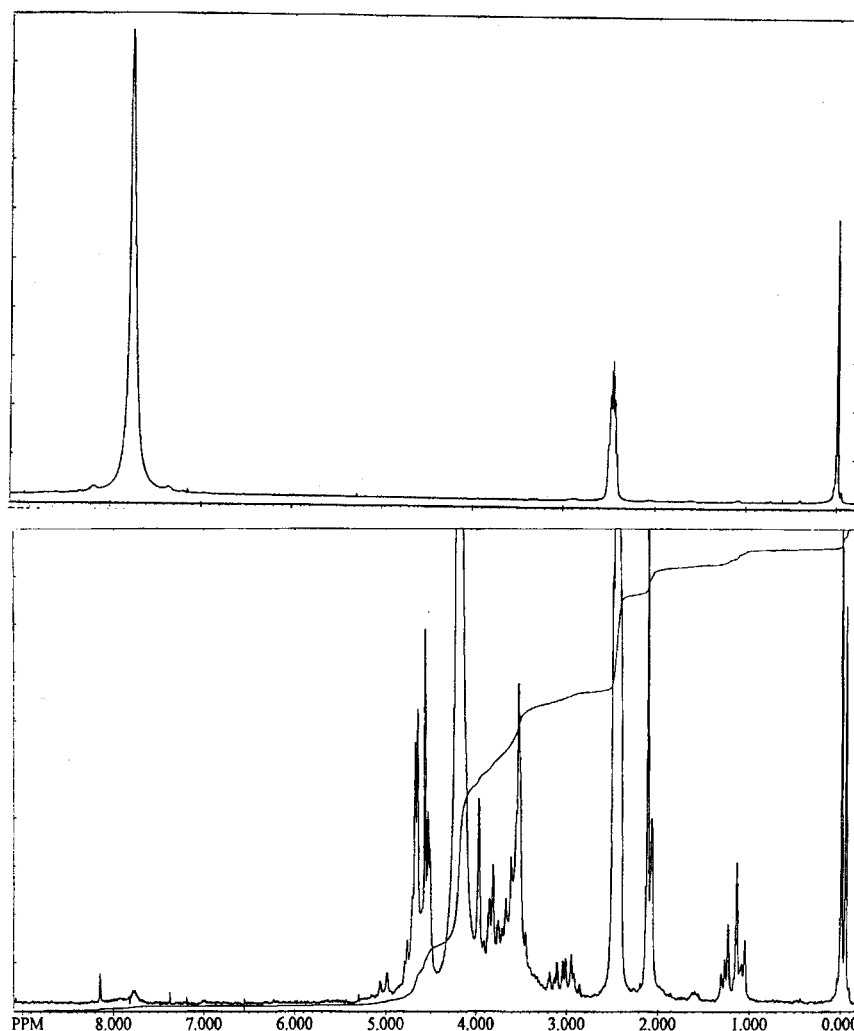


Figure 5 $^1\text{H-NMR}$ spectra of (a) melam and (b) a mixture obtained by the dissolution of melam in RS 8-HMA for 10 min at 105°C .

groups were thermally unstable and decomposed at an elevated temperature (100°C) to unblock —NH— groups, the heterocycle dropped back into the solution (e.g., for the curing of an IA solution: in the $^1\text{H-NMR}$ spectrum of the decomposition product, a signal at 12 ppm appeared due to the imide protons of IA).

If, however, during the heating of a heterocycle in the RS, no *N*-hydroxymethyl derivatives were formed because of, for example, a too short exposure time limited by solvent stability, dissolution did not take place, just as for melam. The only way to overcome this problem and build the heterocycle into the structure of the RS was to prepare the *N*-hydroxymethyl derivative of the compound beforehand (by its reaction with formaldehyde) and then dissolve the derivative in the RS. This was the case for UA. In the $^1\text{H-NMR}$ spectrum of the product of the reaction of 1 mol of UA with 7 mol of formaldehyde, three signals were present:¹⁰ at 5.65 ppm from hydroxyl protons,

at 5.15 ppm from methylene protons in the $\text{—NH—CH}_2\text{OH}$ groupings, and at 4.65 ppm from methylene protons in the $\text{—O—CH}_2\text{—OH}$ groupings.

The spectrum clearly indicated that with a formaldehyde excess with respect to reactive —NH— groups, semiacetal groups were present that easily decomposed at elevated temperatures, releasing formaldehyde.

For the dissolution of such a compound, we did not have to use a solvent that also contained semiacetal groups. To dissolve hydroxymethyl derivatives of heterocyclic compounds, it was sufficient to use a solvent containing less formaldehyde, such as 4-HMA or MHMA.

CONCLUSIONS

Heterocyclic compounds containing nitrogen atoms dissolved in RSs of melamine as long as they had at

least one >NH group. The dissolution proceeded by the reaction of formaldehyde released from the solvent with >NH groups to form *N*-hydroxymethyl groups.

Polymers were formed from the solutions of heterocycles in RSs by the condensation of the *N*-hydroxymethyl groups with hydroxyl groups present in the RSs. In some cases, the poor stability of *N*-hydroxymethyl groups at elevated temperatures led to the restoration of the heterocycles without the formation of polymeric structures. The stability depended on the acidic character of the >NH groups. The more acidic the groups were, the lower the stability was of the *N*-hydroxymethyl derivative. This observation may help to discriminate between nitrogen-containing heterocyclic compounds capable of forming new polymeric materials.

Sometimes, the formation of *N*-hydroxymethyl derivatives in reactions with RSs was too slow with respect to the decomposition rate of the solvents accompanied by formaldehyde release out of the system. Then, the only way of preparing a polymer-forming material was to synthesize an *N*-hydroxymethyl derivative beforehand in a direct reaction of heterocycle with formaldehyde (formalin) and a subsequent reaction of the derivative with an RS, preferably obtained with a small excess of formaldehyde.

The lack of solubility of a heterocycle or the insolubility of its *N*-hydroxymethyl derivatives in formalin

made the preparation of polymers from that compound impossible.

References

1. Wirpsza, Z.; Brzeziński, J. *Aminoplasty*; WNT: Warsaw, 1970.
2. Wirpsza, Z. *Polimery* 1996, 41, 456.
3. Wirpsza, Z.; Kucharski, M.; Lubczak, J. *J Appl Polym Sci* 1998, 67, 1039.
4. Wirpsza, Z.; Pietruszka, W. *Polimery* 1997, 52, 538.
5. Kucharski, M.; Głowacz-Czerwonka, D. *J Appl Polym Sci* 2002, 84, 2650.
6. Galperin, W. A.; Finkelsztajn, A. J.; Gawryłowa, N. K. *Ż Org Chim* 1971, 7, 2431.
7. Smolin, E.; Rapoport, L. *S-Triazines and Derivatives*; Interscience: New York, 1967.
8. Rukiewicz, O. S.; Zagranicznyj, W. J.; Sacharowa, E. Deposited Doc SPSTL 9th, 1980, 974; *Chem Abstr* 1982, 9791335e.
9. Kastierina, T. N.; Kalinina, L. S. *Chemical Analysis of Plastics* (in Polish); WNT: Warsaw, 1965.
10. Lubczak, J. *J Appl Polym Sci* 1997, 65, 2589.
11. Cisek-Cicirko, I.; Lubczak, J. *J Appl Polym Sci* 2000, 77, 2667.
12. Lubczak, R. *J Appl Polym Sci* 2002, 86, 489.
13. Nowak, M.; Rostkowska, H.; Łapiński, L.; Kwiatkowski, J.; Leszczyński, J. *J Phys Chem* 1994, 98, 2813.
14. Nowak, M.; Łapiński, L.; Kwiatkowski, J.; Leszczyński, J. *J Phys Chem* 1996, 100, 3527.
15. Kucharski, M.; Lubczak, J.; Rokaszewski, E. *Chem Stos* 1983, 27, 65.
16. Duliban, J.; Galina, H.; Lubczak, J. *Appl Spectrosc* 1996, 50, 528.
17. Sato, K. *Bull Chem Soc Jpn* 1967, 40, 1547.