

Application of Reactive Solvents of Melamine for Synthesis of Polyetherols with Perhydro-1,3,5-triazine Rings

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ABSTRACT: The application of reactive solvents (RSs), namely hydroxymethyl derivatives of acetone for digestion of isocyanuric acid, which is insoluble in most organic solvents except for DMSO, makes the substrate available for further conversions. At this step, the incorporation of perhydro-1,3,5-triazine ring into RS takes place. The obtained solutions were used for synthesis of polyetherols containing perhydro-1,3,5-

triazine rings in reaction with oxiranes: ethylene and propylene oxides. The polyetherols were then used to obtain foamed polyurethanes with enhanced thermal stability. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 776–785, 2011

Key words: heteroatom-containing polymers; oligomers; reactive processing; polyurethanes

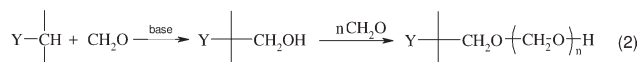
INTRODUCTION

The presence of 1,3,5-triazine ring of melamine in polymeric compounds possesses high thermal stability and good dielectrical properties.¹ Despite of these advantageous properties, there is not much literature considering the application of melamine for synthesis of polymers except for classical melamine–formaldehyde resins. The reason is presumably the poor solubility of melamine to perform reaction in solution. Melamine is soluble in multifunctional alcohol²; the solvents of choice were also hydroxymethyl derivatives of acetone. Wirpsza² has applied such a solvent obtained in reaction between acetone and 3 equiv of formaldehyde



as melamine solubilizers. The solubility of melamine in this solvent at 140°C is 150/100 g of solvent, that is, the 60 wt % solution can be obtained. Dissolving of melamine is accompanied by the reaction of melamine with the solvent, which results in the formation of resin-like reactive products, which upon heating in the presence of acidic or basic catalysts leads to polycondensation, gelling, and hardening of product. Further studies revealed that hydroxymethyl derivatives of aliphatic compounds containing additionally electron-withdrawing groups activating α C–H bonds lead to increase of the solubility of melamine in such solvent.^{3–8} The solvents were called reactive solvents (RSs) of melamine; they can

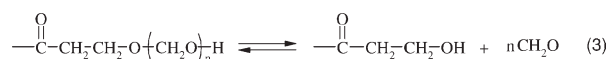
be obtained in the reaction of inserting of formaldehyde into activated C–H bond according to the scheme:



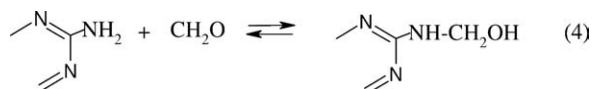
where activating Y is, for example, carbonyl or nitro group.

Thus, RSs of melamine are hydroxymethyl derivatives of keto-, aldo-, or nitro-aliphatic compounds. The reactions occurring upon dissolving of melamine were identified as:

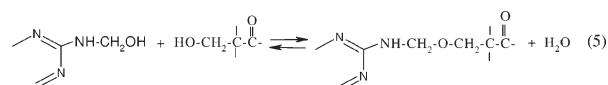
- in temperature above 80°C, the release of formaldehyde from RS takes place:



- in the next step, the product of formaldehyde elimination reacts with melamine to give hydroxymethyl derivatives of melamine:



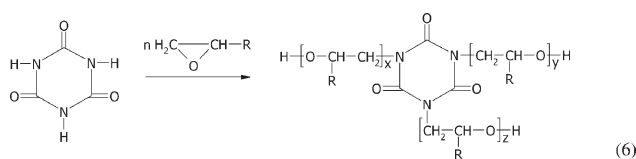
- then condensation of hydroxymethyl derivative of melamine with RS occurs:



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the presence of acidic or basic catalysts.^{6,7,10} Previously,¹¹ the attempts to obtain similar polymers were performed based on the strategy of digestion of azacycles in RS accompanied by reaction with formaldehyde and acetone. We have expected that similar polymers, containing other insoluble azacyclic compounds instead of melamine, such as isocyanuric acid (IA), barbituric and uric acids, and adenine can also be solubilized in RS. It has been found that only isocyanuric and barbituric acids follow the concept.¹¹

IA and melamine, all containing nitrogen atoms in the ring, are thermally resistant. Therefore, they were subjected to the reaction with oxiranes to obtain polyetherols^{12,13} and used further for synthesis of polyurethanes of enhanced thermal stability, for instance:



where $x + y + z = n$; n is the number of oxirane units attached to one molecule of IA.

Unfortunately, the disadvantage of IA is lack of good solvents, which can be used as a medium for reactions of IA with oxiranes. That is why, despite good application properties, the aforementioned polyetherols and further obtained polyurethanes are not produced for manufacturing purposes. Researchers are still trying to find better solvents for IA. It seemed that RS of melamine could play the role, which not only dissolves IA and other azacycles but also reacts with them to form their hydroxymethyl derivatives well soluble in excess of oxiranes^{14,15} and could react further to give polyetherols with 1,3,5-triazine ring. There was no reported information on the use of RS for IA digestion in literature so far. Here, we report on synthesis of polyetherols containing perhydro-1,3,5-triazine ring with the use of RS of melamine as RS for IA. Thus, the fundamental difficulty, that is, insolubility of IA, has been avoided on the route of facile conversion of IA by the reaction of its hydroxymethyl derivatives with oxiranes.

EXPERIMENTAL

Syntheses

Syntheses of RS

A total of 34.8 g (0.6 mol) of acetone (pure, CHEMPUR, Piekary Śląskie, Poland), corresponding amount of formaline (34–36%, pure, POCH, Gliwice, Poland), and triethylamine (TEA, pure, Fluka, Buchs, Switzerland) to adjust the pH into about 11 (about 0.9 cm³ TEA) were placed in 250-cm³ round-bottom

flask equipped with reflux condenser, mechanical stirrer, and thermometer. The mixture was heated for 24–50 h at 40°C.⁹ Then, the catalyst and water were removed under reduced pressure ($p = 1467$ – 2133 Pa) keeping temperature below 50°C. The processes were conducted at acetone : formaldehyde ratio 1 : 2, 1 : 4, or 1 : 6; the ratio in product was as follows: 1 : 1.2, 1 : 3.3, or 1 : 5.0, respectively.

Digestion of IA in RS with stepwise addition of IA

IA was added in 0.1–0.2 g portions into 3.0 g of RS placed in 5-cm³ beaker. The mixture was stirred and heated at 90–100°C until dissolving of every portion of IA. The operation was ceased when mixture became viscous.

Digestion of IA in RS with one portion addition of IA

One portion addition was performed based on the results obtained in stepwise experiment. Previously found analytical sample was dissolved in 3 g of RS in 90–100°C temperature. To the obtained mixture, 0.1–0.4 g of IA was added. Attempts were made to dissolve IA to obtain a mixture, which was clear in room temperature. The solubility experiments were also conducted in the presence of water, which was added in amount of several weight percent of mass of RS. Addition of IA in one portion resulted in obtaining solution, to which additional 0.1–0.4 g of IA was added, the mixture was cooled down to room temperature, and no precipitation of IA occurred. The solubility experiments were also conducted in the presence of water, which was added in amount of several weight percent of mass of RS.

The miscibility of oxiranes with solution of IA in RS

To evaluate the miscibility of solution of IA in RS with oxiranes, ethylene oxide (EO) and propylene oxide (PO), 3 g of IA solution was mixed with 3 g of oxirane at 10°C, and addition of IA solution was continued until it became turbid. Only the homogeneous solution was then used for syntheses.

Syntheses of polyetherols from IA, RS, and oxiranes

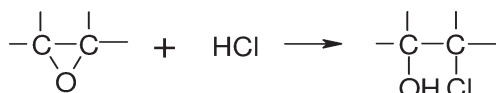
A total of 12 g of RS (of 1 : 3.3 acetone : formaldehyde ratio) was placed in 100-cm³ beaker, and 6.8 g of IA was added. The mixture was heated at 80–90°C until dissolving of IA (ca. 30 min). Then, the mixture was cooled down to 10°C (i.e., below boiling point of the applied oxiranes; b.p._{EO} = 14°C, b.p._{PO} = 34°C), and EO or PO was added (note), followed by addition of 0.5 cm³ TEA (catalyst). The mixture (consisting of IA dissolved in RS, TEA, and an

appropriate oxirane) was then placed in pressure reactor (0.6–0.7 MPa), where the mixture was heated at 50–55°C (in case of EO) or 50–60°C (in case of PO). The process was monitored by determination of not reacted epoxide groups.

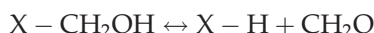
Note: To the mixture of RS and IA, 14.1 g (0.32 mol) or 21.2 g (0.48 mol) of EO or 18.5 g (0.32 mol) or 27.8 g (0.48 mol) of PO were added.

Analytical methods

Taking into account the fact that IA and hydroxymethyl derivatives are slightly acidic because of the presence of unreacted imide groups, the progress of reactions with oxiranes could be monitored by acidic number determined by alkacimetric method in obtained products. The progress of reactions of mixture IA–RS with oxiranes was monitored also by determination of epoxide number using hydrochloric acid in dioxane method.¹⁶ If there are epoxide groups in the system, then the following reaction takes place:

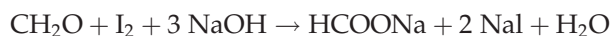


In this reaction, the excess of hydrogen chloride in dioxane is used, which is then titrated using sodium hydroxide. The reaction is continued until epoxide number 0 is achieved, in other words, when there are no more epoxide groups. Hydroxymethyl groups are weakly bounded with imide nitrogen atom, and they can dissociate in water giving free formaldehyde, according to:

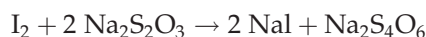


where X = –N, –O–.

The weakly bound formaldehyde (as hydroxymethyl groups) was determined in product using iodometric method,¹⁷ which uses the reaction with standardized iodine solution:



The excess of iodine is titrated with 0.1 M sodium thiosulfate:



In monitored processes, the excess of oxirane was used to obtain no more than 2–3% of weakly bounded formaldehyde. The larger amount would be unsuitable as in the process of obtaining of polyurethane foams, the evolution of formaldehyde caused uncontrolled foaming.

The ¹H-NMR spectra of products were recorded at 500 MHz Bruker UltraShield in DMSO-*d*₆ with hexamethyldisiloxane as an internal standard. IR spectra were registered on PARAGON 1000 FT IR Perkin Elmer spectrometer in ATR technique.

Studies of physical properties of polyetherols

The following properties of polyetherols have been determined: pycnometric density,¹⁸ refractive index, Höppler viscosity, and surface tension by ring detach method¹⁹ in temperature range 20–80°C.

Foams preparation

Attempts of foaming the polyetherols were carried out in small 250-cm³ test cups at room temperature as follows: to 10 g of a polyetherol, 0.1 g of surfactant (Silicon 5340, pure, Houdry Hüls), 0.09–0.3 g of TEA catalyst, and 0.1–0.3 g of water were added. After careful mixing of the components, a weighed amount of 4,4'-diphenylmethane diisocyanate (pure, Merck-Schuchardt, Hohenbrunn, Germany), containing about 30 wt % of trifunctional isocyanates, was added. The amount of isocyanate was optimized to obtain the best properties of foams. The composition was vigorously mixed until it started creaming (for definition see Table V). From the foams thus obtained samples for testing were cut out after about 48 h of seasoning.

Studies of foams properties

The following properties of foams were determined: apparent density,²⁰ water uptake,²¹ linear shrinkage²² including determination of changes in linear dimensions before and after heating at 100°C for 4 h, flammability,²³ thermal stability as the mass loss after heating at 150, 175, and 200°C for a month, and compression strength.²⁴

RESULTS AND DISCUSSION

Three RSs were obtained from acetone and formaldehyde. Based on mass balance and determination of weakly bound formaldehyde (in hemiacetal groups), the molar ratios acetone : formaldehyde in products were as follows: 1 : 1.2; 1 : 3.3, and 1 : 5.0, respectively. The solubility of IA in RS was studied stepwise and later in one portion addition of IA into RS followed by continued addition of IA until maintaining mixture homogeneous. The stepwise addition was accompanied by partial decomposition of RS, which limited the solubility of IA depending on RS used. It was found that the more the weakly bound formaldehyde in RS was, the higher the solubility of IA was. The solubility data for IA in RS are collected in Table I. The RS with high formaldehyde

TABLE I
Dissolution of IA in RS Obtained from Acetone and Formaldehyde

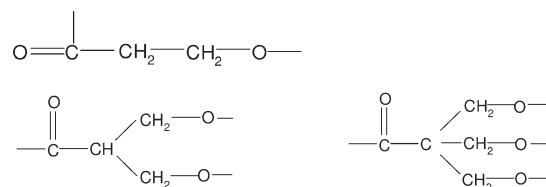
Initial molar ratio, acetone : CH ₂ O	Molar ratio, acetone : CH ₂ O in RS	Amount of water (g/100 g RS)	Amount of dissolved IA (g/100 g RS)	Notes on IA dissolution and solvent of IA with oxiranes mixing
1 : 2	1 : 1.2	—	50	IA not dissolves up to 120°C
1 : 4	1 : 3.3	—	50	IA is well soluble at 80°C within 5 min; the solution is infinitely miscible with PO and EO
1 : 4	1 : 3.3	—	57	Good dissolving of IA, homogeneous mixture, slightly turbid
1 : 6	1 : 5	3.3	50	Well soluble, the solution is infinitely miscible with PO and EO
1 : 6	1 : 5	—	50	See above
1 : 6	1 : 5	—	57	The solution slowly homogenizing with PO after heating, slightly turbid

content was not used for synthesis of polyetherols because of very high viscosity of solutions of IA in these solvents. Therefore, after estimation of maximum solubility of IA in 90–100°C, the concentration of IA was decreased into 90% of maximum solubility, and such solution was used for syntheses. The solution of IA thus obtained was homogeneous, and addition of oxirane at room temperature did not cause any precipitation. Table I contains also the data on solubility of ternary system IA : RS : oxiranes.

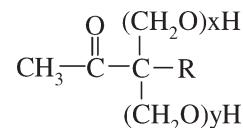
The studies were aimed at synthesis of polyetherols with large contribution of perhydro-1,3,5-triazine units to obtain polyetherols and further polymers with good thermal stability. Generally, the best RS should be those containing the least weakly bound formaldehyde, and they are good solubilizers for IA. Solubility studies indicated that in ternary mixtures the solubility can be either infinite or in some cases the homogeneity is lost and mixture becomes turbid (Table I). Therefore, for further studies, the RS with acetone : formaldehyde (Ac : CH₂O) ratio 1 : 1.2 was not used because of limitation of solubility of IA. Finally, the Ac : CH₂O ratio 1 : 3.3 was used in which the solubility of IA was 50/100 g RS. This solution is infinitely miscible with oxiranes. The syntheses of polyetherols: EO and PO in the presence of TEA led to polyetherols of IA : RS : oxirane ratio 1 : 1.4 : 6 and 1 : 1.4 : 9 (Table II). The molar ratio of substrates incorporated in product was estimated on the basis of initial mass of substrate applied. The reaction was continued until disappearance of oxirane in closed reactor, and isolated

products showed that no mass loss occurred. The yield was 100%. The resin, light-yellow products contained 2–3 wt % of weakly bound formaldehyde.

Structure of polyetherols was elucidated on the basis of ¹H-NMR and IR examination (Figs. 1–4). The resonances at 2.1 ppm in the ¹H-NMR spectrum of RS (Fig. 1) originate from methyl group protons of acetone unit built into RS. The resonances in the 3.3–3.7 ppm region were assigned to methylene and methine protons in:



The group of signals at 4.5–4.6 ppm belongs to methylene protons of (CH₂O)_x. The hydroxyl proton signal could be seen at 6.3 ppm. Based on ¹H-NMR spectrum, the general formula of RS is as follows:



where R = —H or —CH₂OH, and $x + y = n - 1$; n is the number of CH₂O moles attached to one mole of acetone.

The ¹H-NMR spectrum of IA and RS reaction mixture proved clearly the dissolution of IA in RS; the

TABLE II
Conditions of Obtaining of Polyetherols

Entry	Oxirane	Molar ratio, IA : RS : oxirane	Temperature (°C)	Time of reaction (h)
1	EO	1 : 1.4 : 6	50–55	17
2	EO	1 : 1.4 : 9	50–55	39
3	PO	1 : 1.4 : 6	55–60	32
4	PO	1 : 1.4 : 9	50–55	40

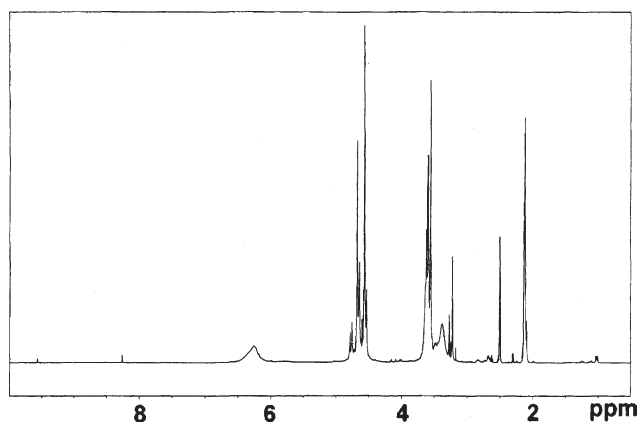


Figure 1 The $^1\text{H-NMR}$ spectrum of RS (acetone to CH_2O ratio 1 : 3.3).

release of formaldehyde from oxymethylene units occurs, accompanied by a decrease of the resonances within 4.5–4.6 ppm, followed by the reaction of imide groups of IA. The *N*-hydroxymethyl group formation demonstrates a resonance at 5.2 ppm from methylene protons (Fig. 2).¹⁴

In the $^1\text{H-NMR}$ spectra of polyetherols, the resonances of protons of oxyethylene groups incorporated into the structure of RS and IA are also present; for instance, methylene proton signals in 3.0–3.4 region in the products obtained from PO (Fig. 3) and resonances at 4.6 ppm assigned to methine protons. As follows from the spectra in the 1.0–1.4 ppm, the opening of PO leads to two products: the normal (I) and abnormal (II) ones²⁵:

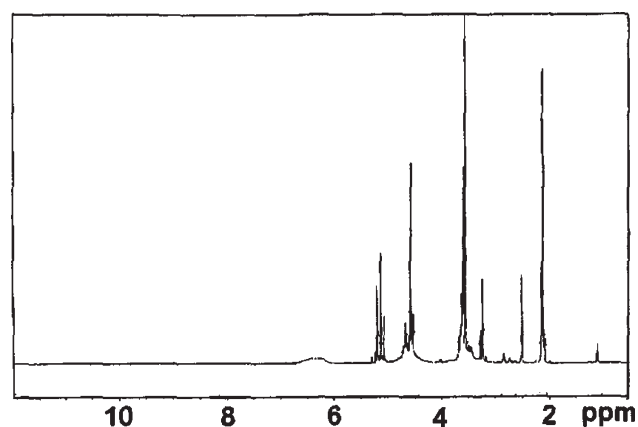
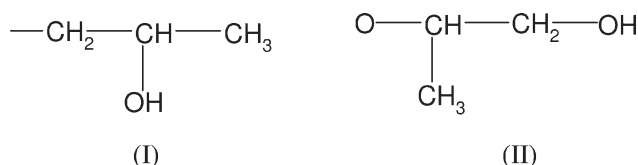


Figure 2 The $^1\text{H-NMR}$ spectrum of reaction mixture; IA in RS.

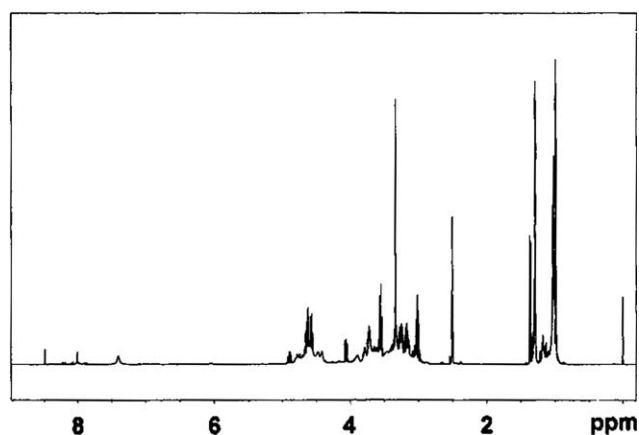


Figure 3 The $^1\text{H-NMR}$ spectrum of polyetherol obtained from IA, RS, and PO (IA : RS : PO ratio 1 : 1.4 : 6 (ratio acetone : CH_2O in RS = 1 : 3.3)).

Based on integral intensity of methyl proton resonances at 1.0 and 1.4 ppm, the percentage of normal groups (I) in polyetherol is about 33 mol %. Also, it can be concluded that *N*-hydroxymethyl groups of derivative of IA are involved in the reaction with oxiranes, which is demonstrated by disappearance of the resonance at 5.2 ppm.

IR spectra of products are consistent with proposed polyetherol structure (Fig. 4). The valence and deformation bands of hydroxyl groups are observed in the 3373 and 1247 cm^{-1} region. In the 1040–1068 cm^{-1} region, there is a hydroxyl groups deformation band overlapped with valence one from —C—O—C— ; this indicates clearly the addition of oxirane to the RS-IA system. In the products, there are also the carbonyl bonds in IA and RS, which are demonstrated by the presence of 1729 and 1692 cm^{-1} bands. The perhydro-1,3,5-triazine ring gives the sharp band at 765 cm^{-1} .

We have observed that EO and PO react with RS leading to polyetherols. Both *C*-hydroxymethyl and

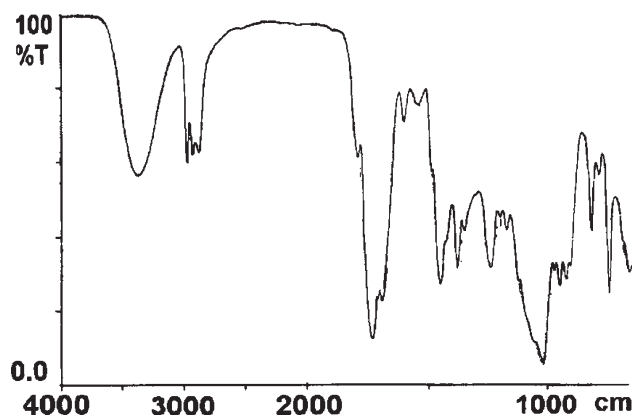


Figure 4 IR spectrum of polyetherol obtained from IA, RS, and PO (IA : RS : PO molar ratio 1 : 1.4 : 6; ratio acetone : CH_2O in RS = 1 : 3.3).

TABLE III
Some Physical Properties of Polyetherols Obtained from IA in RS with Oxiranes, in the Range of Temperature 20–80°C

Oxirane	Molar ratio, IA : RS : oxirane	Temperature (°C)	Refraction index n_{20}^D	Density d (g/cm ³)	Viscosity η (N s/m ²)·×10 ³	Surface tension τ (N/m)·×10 ³	
EO	1 : 1.4 : 6	20	1.4943	1.2858	6727	52.36	
		30	1.4919	1.2788	4229	51.52	
		40	1.4891	1.2757	1724	50.96	
		50	1.4861	1.2679	1051	50.72	
		60	1.4830	1.2611	364.4	50.55	
		70	1.4801	1.2541	205.3	50.40	
		80	1.4779	1.2463	132.9	50.12	
	1 : 1.4 : 9	20	1.4896	1.2623	3611	55.16	
		30	1.4870	1.2552	1493	54.04	
		40	1.4841	1.2471	937.0	52.64	
		50	1.4810	1.2394	311.9	51.24	
		60	1.4778	1.2319	164.5	50.40	
		70	1.4749	1.2246	137.7	49.00	
		80	1.4722	1.2166	58.75	48.16	
PO	1 : 1.4 : 6	20	1.4848	1.2032	76,970	54.04	
		30	1.4820	1.1961	14,165	51.52	
		40	1.4792	1.1889	4995	49.56	
		50	1.4757	1.1809	1669	46.76	
		60	1.4727	1.1736	918.0	44.52	
		70	1.4697	1.1659	292.1	43.96	
		80	1.4662	1.1585	143.0	43.85	
		1 : 1.4 : 9	20	1.4691	1.1411	1805	49.14
			30	1.4657	1.1320	536.7	48.44
	40		1.4631	1.1252	169.2	48.02	
	50		1.4596	1.1173	127.3	46.76	
	60		1.4561	1.1100	68.2	45.78	
	70		1.4527	1.1022	26.1	43.26	
	80		1.4491	1.0903	17.2	41.72	

O-hydroxymethyl groups of RS are involved. The latter release formaldehyde upon addition of oxirane. The formaldehyde is transferred at the end of chain with formation of unstable hemiacetals. This, among others makes the products thermally unstable. During dissolution of IA in RS, formaldehyde reacts totally with IA to form its *N*-hydroxymethyl derivatives. Thus, the resulting solution is composed formally of 1,3,5-tris(hydroxymethyl) isocyanurate (THMI) and RS, which does not bear O-hydroxymethyl groups any longer. The oxirane, when intro-

duced to such solution, reacts with both components to form polyetherols described in this work.

The physical properties of polyetherols were studied, namely: refraction index, density, viscosity and surface tension (Table III). All these properties change typically in function of temperature. Traditional polyols used as substrates for polyurethane foams have the viscosity within 0.5–100 N s/m² and surface tension within 0.03–0.05 N/m.²⁶ Some polyetherols obtained by reaction of melamine, bis(hydroxymethyl)melamine, or 1,3,5-tris(hydroxymethyl)

TABLE IV
Some Physical Properties of Polyetherols Obtained from Melamine, Bis(hydroxymethyl)melamine (BHMM), or 1,3,5-Tris(hydroxymethyl) Isocyanurate (THMI) with Oxiranes in Temperature 20°C

Heterocyclic compound (HC)	Oxirane	Molar ratio, HC : oxirane	Refraction index n_{20}^D	Density d (g/cm ³)	Viscosity η (N s/m ²) × 10 ³	Surface tension τ (N/m) × 10 ³	References
Melamine	EO	1 : 9	1.5260	1.205	110,000	31.1	27
		1 : 12	1.5165	1.199	32,100	30.7	
	PO	1 : 9	1.4990	1.1024	95,000	38.25	12
		1 : 12	1.4921	1.0878	35,000	38.58	
BHMM	EO	1 : 9	1.5123	1.199	8370	36.2	28
		1 : 12	1.5105	1.201	10,100	36.6	
	PO	1 : 12	1.4852	1.082	3400	30.0	
THMI	EO	1 : 6	1.493	1.293	6850	51.4	14
		1 : 9	1.487	1.249	2700	50.4	
		1 : 12	1.485	1.231	1760	49.5	

TABLE V
The Influence of Composition on Foaming Process

Oxirane	Molar ratio, IA : oxyalkylene groups in product	Comp. no	Composition ^a (g/100 g of polyetherol)		Foaming process ^b			Characteristics of foams after obtaining directly
			Isocyanate	Catalyst	Time of creaming (s)	Time of expanding (s)	Time of drying (s)	
EO	1 : 6	1	112	1,0	93	180	1	Large shrinkage
		2	112	2,0	80	55	15	Not crosslinked
		3	140	2,5	29	8	1	Rigid
		4	132	2,5	50	53		Not crosslinked
	1 : 9	5	96	0,5	22	77	1	Small shrinkage
		6	120	1,5	15	22	1	Large porosity/rigid
		7	112	1,5	23	10	1	Rigid
PO	1 : 6	8	80	1,5	16	42	1	Small shrinkage/rigid
		9	100	1,5	19	24	1	Rigid
	1 : 9	10	88	1,5	20	27	1	Small shrinkage
		11	108	2,0	17	20	1	Rigid
		12	120	2,0	16	32	1	Rigid

^a Amount of surfactant (Silicon 5340), 1 g per 100 g of polyetherol; amount of water 2 g per 100 g of polyetherols.

^b Time of creaming: the time elapsed from the moment of mixing to the start of volume expansion; time of expanding: the time from the start of expansion to the moment of reaching the sample final volume; time of drying: the time from reaching by the sample its final volume to the moment of losing its surface adhesion to powdered substances.

isocyanurate with EO or PO (Table IV), used for thermally resistant polyurethane foams, have similar parameters. Therefore, it was important to estimate the physical parameters of polyetherols obtained here to classify them as suitable candidates for synthesis of polyurethane foams.

Preliminary studies on foaming with diisocyanates and water have shown that homogeneous systems are easily formed. The foaming on laboratory scale was aimed at optimization of the process, considering the amount of isocyanate, the kind of catalyst, and the length of polyether chain (Table V). It was found that the best foams were obtained when 100–120 g of 4,4'-diphenyl isocyanate was used per 100 g of polyetherol obtained from PO and EO if the molar ratio of IA to EO was 1 : 9 or using 140 g of 4,4'-diphenylmethane diisocyanate in case polyetherols obtained

from IA to EO 1 : 6 system. When the amount of isocyanate was lower or higher, the foams were not hardened completely and revealed the polymerization shrinkage. The influence of water content in foaming was studied within 1–3 wt % region. It was found that the best foams were formed when 2 wt % of water was used. At larger amount of water, the foams had irregular pores; at lower amount, the foams had high apparent density. TEA was used as typical catalyst for the reaction of isocyanates with alcohols; the optimized amount of catalyst was 1.5–2.5 wt % in 100 g of polyetherol (Table V). Creaming and expanding times of studied compositions are short. It has been observed that creaming times of composition with PO are shorter (15–20 s) in comparison with those of EO (up to 1.5 min). Drying time of the foams was within 1 s. It can be concluded that short creaming, expanding,

TABLE VI
Some Properties of Polyurethane Foams with Perhydro-1,3,5-triazine Ring

Hetero cyclic compound (HC)	Oxirane	Molar ratio, HC : oxyalkylene groups in product	Comp. no as in Table IV	Density (kg/m ³)	Absorb. of water (wt %) after			Linear postshrinkage (%)
					5 min	3 h	24 h	
IA	EO	1 : 6	3	56.6	3.52	7.42	9.90	Without change
		1 : 9	6	97.2	10.61	14.66	19.83	Without change
			7	54.3	3.05	5.25	5.99	+1.6
	PO	1 : 6	9	50.6	9.74	12.02	18.05	Without change
		1 : 9	12	47.7	2.79	5.15	5.78	Without change
			20	35.8	3.04	4.75	5.21	+5.2
THMI	EO	1 : 6	–	44.3	–	3.0	4.0	0.2
		1 : 9	–	41.5	–	4.5	5.7	0.3
		1 : 12	–	49.7	–	6.9	7.9	0.3

THMI, 1,3,5-tris(hydroxymethyl) isocyanurate; the results from Ref. 29.

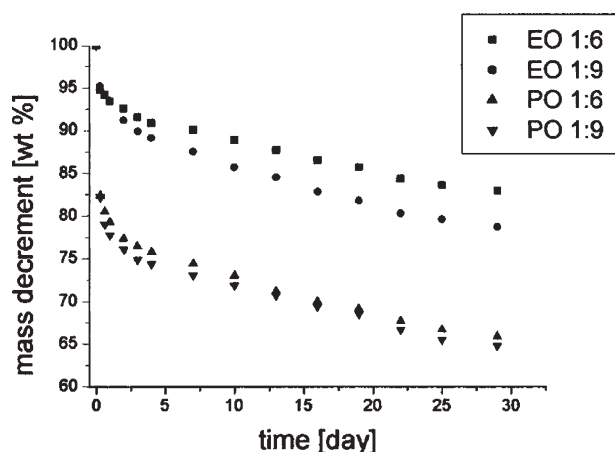


Figure 5 Thermal stability of polyurethane foams as mass loss at 175°C.

and drying time predestinate the obtained polyurethane composites for fabrication by spraying.

The apparent density of polyurethane foams of stable dimension was within 47–57 kg/m³; the water uptake was 9–18 wt %, indicating that obtained foams have closed pores (Table VI). All the obtained foams are flammable.

The properties of obtained polyurethane foams were compared with those obtained previously²⁹ in straight reactions between THMI with oxiranes. The foams obtained here have no linear postshrinkage, but have two to three times higher water uptake because of the presence of more open pores in their structure.

The studies on thermal stability of obtained polyurethane foams were performed at 150, 175, and 200°C, by measuring mass loss and compression strength before and after thermal exposure. Continuous mass loss of foams was observed during thermal exposure. The largest mass loss occurred within first 24 h of experiment (Figs. 5 and 6). The best thermal stability showed the foams obtained from polyetherols containing six oxyethylene units per molecule of IA. For these foams, the mass loss at 150°C was merely 8%, whereas after exposure to 200°C it reached 30%. The least thermal stability had the foams obtained from polyetherols obtained from PO; for those the mass loss at 200°C reached even 48%.

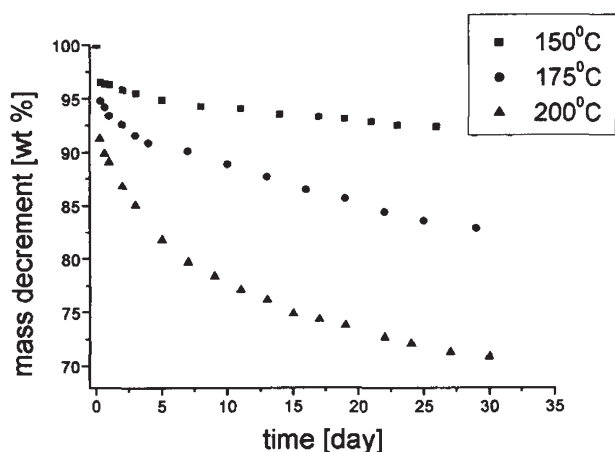


Figure 6 Mass loss of polyurethane foams of the highest thermal stability.

The studies of compressive strength of the foams indicated that compressive strength of all foams increased after thermal exposure (Table VII). The foams obtained from polyetherols synthesized from PO had lower compressive strength than those obtained from EO. The foams obtained from the polyetherol containing nine oxyethylene units per molecule of IA have the best compressive strength. It should be mentioned here that classic foams degrade at about 90°C,²⁶ whereas the foams obtained here can be long exposed to 200°C maintaining their mechanical properties. In summary, it can be concluded that the foams obtained from polyetherols synthesized with the use of RS of IA have similar properties to classic, rigid foams but demonstrate higher thermal resistance and better mechanical properties after thermal exposure.

For comparison purposes, the thermal and mechanical properties of polyurethane foams of enhanced thermal stability obtained here as well as those synthesized from polyetherols obtained in reactions of melamine or its derivatives in organic solvents³⁰ and in reactions of hydroxymethyl derivatives of IA with oxiranes are collected in Table VIII.²⁹ Some properties can be compared in straightforward fashion, because the physical properties were measured at the same time intervals (1, 5, or 14

TABLE VII
Thermal Stability and Compression Strength of Foams with Perhydro-1,3,5-triazine Ring

Oxi-rane	Molar ratio, IA : oxirane in product	Comp. no as in Table IV	Mass loss (wt %) after exposition for 1 month in temperature			Compression strength (MPa)			
			150°C	175°C	200°C	Before exposition	After exposition in temperature		
							150°C	175°C	200°C
EO	1 : 6	3	8.0	18.0	30.0	0.185	0.253	0.291	0.325
	1 : 9	7	10.5	22.5	37.5	0.245	0.137	0.484	0.545
PO	1 : 6	9	25.0	35.0	45.0	0.098	0.157	0.168	0.222
	1 : 9	12	22.5	35.0	48.0	0.162	0.228	0.173	0.303

TABLE VIII
Comparison of Thermostability and Compression Strength of Foams Obtained from Polyetherols Based on Melamine (Mel), Pentakis(hydroxymethyl)melamine (PHMM), Pentakis(methoxymethyl)melamine (PMMM), Bis(methoxymethyl)melamine, and IA in RS

Hetero cyclic compound (HA)	Hydroxyalkylation agent	Molar ratio, HA : oxirane	Mass loss (wt %) after exposition						Compression strength (MPa)						Ref.		
			for 1 day in temperature (°C)		for 5 days in temperature (°C)		for 14 days in temperature (°C)		Before exposition		After exposition for 1 day in temperature (°C)		After exposition for 14 days in temperature (°C)				
			150	175	200	175	200	150	175	200	150	175	200	150		175	
Mel	PO	1 : 9	-	-	16.7	-	-	24.8	-	-	-	0.215	0.227	0.303	0.280	0.313	30
PHMM	EO	1 : 6	-	26.2	-	30.4	-	24.8	-	-	-	0.353	0.359	0.387	0.365	0.422	30
PMMM	EG, PO	1 : 5 : 7	-	5.7	17.2	11.4	23.8	-	-	-	-	0.378	0.361	0.389	0.645	0.545	30
THMI	EO	1 : 6	2.0	4.8	5.2	-	-	-	4.1	4.8	-	0.215	0.227	0.303	0.280	0.313	29
		1 : 9	2.6	6.0	14.2	-	-	-	6.5	15.5	-	0.353	0.359	0.387	0.365	0.422	29
		1 : 12	2.0	5.3	15.2	-	-	-	7.1	18.2	-	0.378	0.361	0.389	0.645	0.545	29
IA in RS	EO	1 : 6	3.7	6.6	10.9	9.5	18.2	24.0	6.5	12.5	24.0	-	-	-	-	-	This work
		1 : 9	3.7	6.6	14.2	10.5	23.8	31.2	8.2	16.0	31.2	-	-	-	-	-	

EG, ethylene glycol.

days), whereas the mechanical properties were measured at various times. However, based on those determinations, it can be concluded that the foams obtained here reveal slightly higher mass losses than those obtained from polyetherols synthesized by straightforward reaction of THMI with oxiranes. On the other hand, the foams described here have considerably higher compression strength after thermal exposure (compare Table VII with Table VIII). Moreover, they possess remarkably higher thermal resistance in comparison with foams obtained from polyetherols based on melamine or its derivatives.

CONCLUSIONS

1. In reactions of acetone with excess of formaldehyde, the RS is obtained. It can be successfully applied for dissolving of IA. Dissolving is accompanied by formation of hydroxymethyl derivatives of IA.
2. The solutions of IA in RS react with oxiranes in the presence of triethylamine as catalysts resulting in formation of polyetherols with perhydro-1,3,5-triazine ring. In this way, the difficulties related to a lack of good solubility of IA and hence limited reactivity toward oxiranes can be avoided.
3. Obtained polyetherols are useful substrates for formation of polyurethane foams, which have a set of properties similar to traditional, rigid polyurethane foams. However, they have improved thermal resistance because of the presence of perhydro-1,3,5-triazine ring in their structure.

References

1. Wirpsza, Z.; Brzeziński, J. Aminoplaste; WNT: Warsaw, 1970 (in Polish).
2. Wirpsza, Z. Polimery 1996, 41, 456.
3. Kucharski, M.; Głowacz-Czerwonka, D. J Appl Polym Sci 2002, 84, 2650.
4. Głowacz-Czerwonka, D.; Kucharski, M. J Appl Polym Sci 2005, 95, 1319.
5. Głowacz-Czerwonka, D.; Kucharski, M. J Appl Polym Sci 2005, 96, 77.
6. Głowacz-Czerwonka, D.; Kucharski, M. J Appl Polym Sci 2006, 99, 1083.
7. Głowacz-Czerwonka, D.; Kucharski, M. e-Polymers, International Polymer Seminar Gliwice 2006, P_007, 1.
8. Głowacz-Czerwonka, D.; Kucharski, M. J Appl Polym Sci 2006, 100, 1496.
9. Wirpsza, Z.; Kucharski, M.; Lubczak, J. J Appl Polym Sci 1998, 67, 1039.
10. Głowacz-Czerwonka, D.; Kucharski, M. J Appl Polym Sci 2006, 100, 1496.
11. Lubczak, J.; Lubczak, R.; Zarzyka-Niemiec, I. J Appl Polym Sci 2003, 90, 3390.

12. Kucharski, M.; Lubczak, J. *Acta Polym* 1991, 42, 186.
13. Frisch, K.; Tummers, D.; Nijenhuis, A. U.S. Pat. 4,198,505 (1980).
14. Kucharski, M.; Lubczak, J.; Rokaszewski, E. *Chem Stos* 1983, 27, 65.
15. Lubczak, J. *J Appl Polym Sci* 1997, 65, 2589.
16. Brojer, Z.; Hertz, Z.; Penczek, P. *Epoxy Resins*; WNT: Warsaw, 1972 (in Polish).
17. Kastierina, T.; Kalinina, E. *Chemical Analysis of Polymers*; WNT: Warsaw, 1965 (in Polish).
18. Broniewski, T.; Kapko, J.; Płaczek, W.; Thomalla, J. *The Methods of Investigation and Estimation of Plastics*; WNT: Warsaw, 2000 (in Polish).
19. Dryński, T. *Laboratory Practice from Physics*; PWN: Warsaw, 1967 (in Polish).
20. Cellular Plastics and Rubbers. Determination of apparent (bulk) Density, Polish (European) Standards, PN-EN ISO 845 – 2000, Ed. Polish Committee for Standardization.
21. Cellular Plastics, rigid. Determination of Water Absorption, Polish (European) Standards, PN-EN ISO 2896 – 1987, Ed. Polish Committee for Standardization.
22. Cellular Plastics, rigid. Test for dimensional Stability, Polish (European) Standards, PN-EN ISO 2796 – 1986, Ed. Polish Committee for Standardization.
23. Standard Test Method for Rate of Burning and/or Extent and Time of Burning of Plastics in a Horizontal Position, ASTM D635-06, Ed. Am. Soc. Testing Materials, 2006.
24. Cellular Plastics. Compression Test for rigid Materials, Polish (European) Standards, PN-EN ISO 844 – 1978, Ed. Polish Committee for Standardization.
25. Węglowska, E.; Lubczak, J. *J Appl Polym Sci* 2005, 98, 2130.
26. Wirpsza, Z. *Polyurethane*; WNT: Warsaw, 1991.
27. Kucharski, M.; Lubczak, J. *Chem Stos* 1985, 29, 277.
28. Lubczak, J. *Polimery* 1987, 32, 314.
29. Kucharski, M.; Lubczak, J. *Polimery* 1985, 30, 354.
30. Lubczak, J.; Chmiel, E. *Polimery* 1990, 35, 194.