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Polyhydroxyalkyl derivatives and polyetherols obtained from azacyclic compounds

Part II. REACTIONS WITH FORMALDEHYDE AND ALKYLENE CARBONATES

Summary — In this part of the paper modification of the method to obtain polyetherols from azacyclic compounds and oxiranes involving an initial hydroxyalkylation of formaldehyde was presented. Hydroxymethyl derivatives of azacyclic compounds were obtained. Very often they were better soluble in organic solvents than the initial compounds, even directly in oxiranes. These derivatives underwent further reaction with oxiranes so that polyetherols were obtained. The method of hydroxyalkylation with an application of ethylene and propylene carbonates was also presented. These carbonates constitute environment friendly solvents and reagents of azacyclic compounds.
Keywords: heterocyclic compounds with nitrogen atoms, formaldehyde, oxiranes, alkylene carbonates.

WIELOHYDROKSYALKILOWE POCHODNE I POLIETEROLE OTRZYMYWANE ZE ZWIĄZ-KÓW AZACYKLICZNYCH. Cz. II. REAKCJE Z FORMALDEHYDEM I WĘGLANAMI ALKILE-NOWYMI
Streszczenie — W tej części pracy przedstawiono modyfikację metody otrzymywania polieteroli ze związków azacyklicznych i oksiranów polegającą na wstępnym hydroksyalkilowaniu tych związków formaldehydem. Otrzymane hydroksymetylowe pochodne azacykli, często lepiej rozpuszczalne od związków wyjściowych w rozpuszczalnikach organicznych, a nawet bezpośrednio w oksiranach, poddawano dalszym reakcjom z oksiranami, w celu uzyskania polieteroli. Scharakteryzowano, nabierającą coraz większego znaczenia, metodę hydroksyalkilowania z użyciem węglanów alkilenowych (węglan etylenu i węglan propylenu) stanowiących jednocześnie przyjazne ekologicznie rozpuszczalniki i reagenty związków azacyklicznych.
Słowa kluczowe: związki heterocykliczne z atomami azotu, formaldehyd, oksirany, węglany alkilenowe.

In the first part of the paper the methods of synthesis of polyhydroxyalkyl derivatives of azacycles and polyetherols with azacycles and oxiranes have been reviewed [1]. The method of hydroxyalkylation of melamine, adenine, isocyanuric, barbituric, uric and parabanic acids with oxiranes like ethylene and propylene oxides and epichlorohydrin in medium of different organic solvents was discussed. These compounds are useful substrates to obtain polymers of enhanced thermal stability like polyurethanes, polyesters or polyacrylates. The synthesis conditions, catalysts and solvents used for successful synthesis protocols for the substrates and chosen applications of substrates were encountered.

REACTION WITH FORMALDEHYDE AND OXIRANES

The insolubility of azacycles in organic solvents prompted us to invent another pathway for diols and polyetherols with azacycles. One of the possibilities took advantage of better solubility of hydroxymethyl derivatives of azacycles in organic solvents and in water as it has been widely known for melamine and its derivatives.

Isocyanuric acid

In successive reactions of addition of formaldehyde to isocyanuric acid [formula (I) in Scheme A] all three
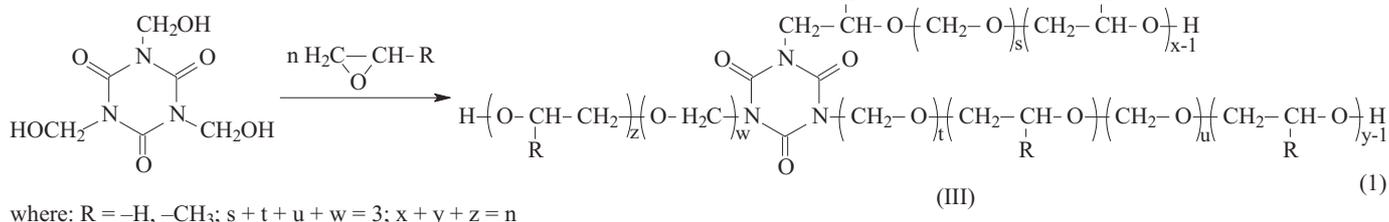
(I)

(II)
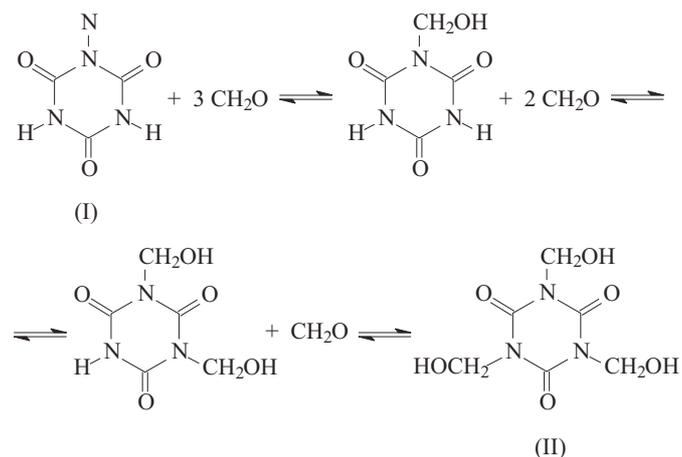
Scheme A. Reaction of isocyanuric acid with formaldehyde

(IV)

Scheme B. Reactions of THMI with oxiranes

hydrogen atoms can be substituted, according to the scheme [2—4].

The reaction is reversible and in aqueous solution the successive semi-products are in equilibrium. Some authors suggest that while water is removed, in the presence of a mineral acid, the product undergoes a reaction of condensation with formation of methylene or dimethylene ether bridges. The reaction was utilized for preparation of isocyanuric-formaldehyde [5], isocyanuric-urea-formaldehyde or isocyanuric-melamine-formaldehyde resins [6, 7].

Dissolved in water, 1,3,5-tris(hydroxymethyl) isocyanurate (THMI), given by formula (II) in Scheme A, decomposes to di- and monohydroxymethyl derivatives or to the acid itself [3]. Their proportions depend on concentration. This is the reason why THMI solutions in water become cloudy and retain acidic character of isocyanuric acid. It has been found that introduction of water (to reach 5 wt. % of THMI solution) enabled to obtain the semisolid resin well soluble in oxiranes and reacting with them at 80—120 °C in the presence of ternary amines as catalysts to form polyetherols with a perhydro-1,3,5-triazine ring [formula (III)] [7]:

from ethylene oxide (EO) or propylene oxide (PO) is metastable and upon heating or in solution it undergoes elimination and usually moves to the end of the hydroxyalkyl chain:

(2)
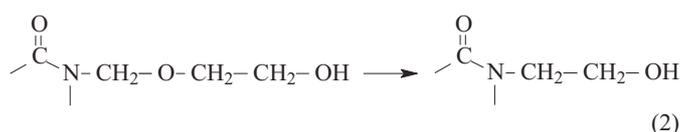
Prolonged heating of such a product, *i.e.* the product of addition with molar ratio THMI:EO = 1:3, yields 1,3,5-tris(2-hydroksyethyl) isocyanurate {formula (IX), R = H in [1]}. As the excess of oxirane increases, the amount of formaldehyde capable to eliminate successively decreases and the 6-fold molar excess of oxirane is reduced to zero. Permanent blocking of the formaldehyde molecule occurs when 1 mole of hydroxymethyl groups reacts with at least two moles of oxiranes. The products of hydroxyalkylation of isocyanuric acid or its derivatives are used in manufacturing of polyethers, polyester resins, polyurethanes, plasticizers, adhesives and coatings that are distinguished from their classical counterparts with improved thermal stability.

(III)

(1)

where: R = –H, –CH₃; s + t + u + w = 3; x + y + z = n

Under these conditions, oxiranes react with the equilibrium mixture of hydroxymethyl derivatives of isocyanuric acid that are formed from THMI dissolved in water. They add both to the acidic imide groups and to hydroxymethyl groups [9] (Scheme B).

The chemically blocked formaldehyde at the nitrogen atom of the ring by one hydroxyalkyl group originating

Barbituric acid

Reactions of barbituric acid [BA, formula (V) in Scheme C] with formaldehyde are a suitable way of its modification and allow to obtain multifunctional polyetherols with a pyrimidine ring. This is not possible to achieve in a straightforward reaction of barbituric acid

with oxiranes due to tautomerization of barbituric acid to the trienol form. Thus this pathway is currently the best way to synthesize hydroxyalkyl derivatives of barbituric acid. Depending on the initial molar ratio $BA:CH_2O$, hydroxymethyl derivatives of barbituric acid of variable level of substitution of hydrogens on a nitrogen atom or C_5 can be obtained [10]. At the molar ratio $BA:CH_2O$ = $1:\geq 4$ all the hydrogen atoms can be replaced with hydroxymethyl groups; both in imide and methylene rings. For the ratio $BA:CH_2O$ = 1:2 the structure of the product depends on the temperature of reaction; at the ambient temperature the major reactive center is the methylene group of barbituric acid, while at temperature above 90 °C the imide groups react predominantly:
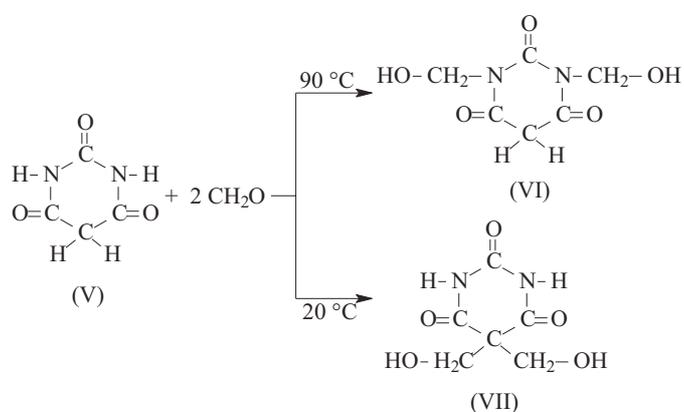
*Scheme C. Reactions of barbituric acid with formaldehyde*

Between 40—60 °C formaldehyde reacts with both groups. The reactivity of barbituric acid is then typical of kinetic versus thermodynamic control. This has been further confirmed by observation that 5,5-bis(hydroxymethyl)barbituric acid [formula (VII)] rearranges into 1,3-bis(hydroxymethyl) barbiturate [formula (VI)] upon prolonged heating [10]. Total blocking of acidic groups (imide and methylene) occurs upon addition of 4 equivalents of formaldehyde to barbituric acid. The product obtained at initial molar ratio $BA:CH_2O$ = 1:6 is also soluble in ethylene and propylene oxide already at the ambient temperature, so it can be used for obtaining linear polyetherols with a pyrimidine ring [11—14]. It should also be mentioned that these polyetherols in the reaction with isocyanate and water form polyurethane foams of enhanced thermal stability, probably due to the presence of a pyrimidine ring incorporated into their structure. Thermal stability of these foams is slightly lower than those obtained from polyetherols synthesized from hydroxymethyl derivatives of isocyanuric acid.

Obtained bifunctional 1,3-bis(hydroxymethyl) barbiturate can be further converted in the reaction with typical isocyanates to obtain linear polyurethanes of enhanced thermal stability [14]. Even better strategy leading to linear polyurethanes with a pyrimidine ring is

using hydroxyalkyl derivatives of 5,5-diethylbarbituric acid {formula (XV) in [1]} as a substrate. The latter can be obtained from 5,5-diethylbarbituric acid and oxiranes in dimethylformamide (DMF) or dioxane, thus the use of formaldehyde is unnecessary. Nevertheless, hydroxymethyl derivatives of this imide of variable level of substitution are known and described in [15].

Uric acid

Successful results of synthesis of polyetherols from THMI and oxiranes [9] prompted us to perform studies on polyetherols with a purine ring using hydroxymethyl derivatives of uric acid (UA) [16]. As already mentioned the attempts to synthesize polyetherols from UA and oxiranes failed due to insolubility of UA in organic solvents. Synthesis of *N*-hydroxymethyl derivatives of uric acid (HMUA) was first described by Hanada and Misu in a patent [17]. They carried out reactions of this acid with formalin at constant pH = 3—4 at 5—40 °C for 60 days. They managed to introduce between 1 and 4 *N*-hydroxymethyl groups into the molecule of UA. Details on this reaction are described in [18]. At the molar ratio $UA:CH_2O$ = 1:<6 the acid reacts with formaldehyde yielding water insoluble HMUA. At the molar ratio 1:>6 the product of the reaction fully dissolves in the reaction medium yielding clear solutions remaining homogeneous even after cooling down to the room temperature. The whole amount of formaldehyde introduced to the system is found reacted, even though UA is tetrafunctional. The excess of formaldehyde reacts with *N*-hydroxymethyl groups yielding hemiacetal groups:
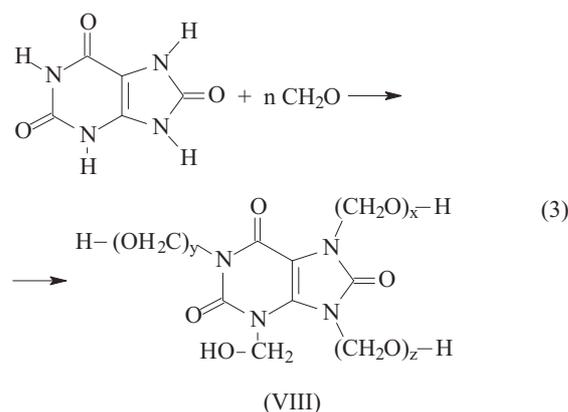
with x + y + z = n - 1

HMUA are thermally reasonably stable products, since their decomposition starts at 260 °C, whereas hydroxymethyl derivatives of melamine or isocyanuric acid start to decompose as early as at 80—90 °C [9].

The products of addition for molar ratio $UA:CH_2O$ = 1:>6 are well soluble in cold water [19]. When a small amount of water (5 wt. %) is introduced to the product of addition for $UA:CH_2O$ = $1:\geq 7$, liquid products are obtained that when slightly heated (up to 65—70 °C) dis-

solve in oxiranes, ethylene oxide or propylene oxide. In the presence of triethylamine catalyst oxiranes react with the derivative to polyetherols containing thermostable purine rings presented by formula (IX) [16].

(IX)
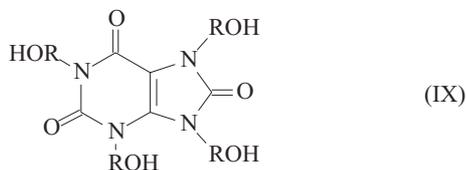
where: R — oxyalkylene groups

The advantage of the method is that the reaction does not require any solvents. The analysis of the reaction of HMUA with oxiranes [19—21] revealed that three initial moles of ethylene oxide (per a mole of HMUA), or two moles of propylene oxide, are not enough to block *N*-hydroxymethyl groups, or such a blocking is only temporary. The third propylene oxide mole or fourth ethylene oxide mole blocks permanently a part or the whole mole of *N*-hydroxymethyl groups, respectively. After the reaction there is as much as 12 equivalents of ethylene oxide or 14 equivalents of propylene oxide per one molecule of HMUA [19]. Resulting polyetherols [22] were used for obtaining polyurethane foams of enhanced thermal stability [23].

Adenine

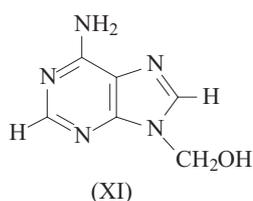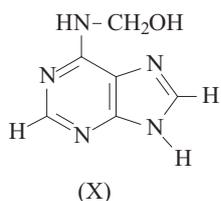Unfortunately, the described method of hydroxyalkylation cannot be used for synthesis of polyetherols from adenine. Adenine dissolves in formalin at 95 °C within several minutes, but then a white solid precipitates from the solution [24]. The solid is an equimolar mixture of

(X) (XI)

monohydroxymethyl derivatives of adenine presented by formulas (X) and (XI) that is insoluble in an organic solvent nor in water and does not react with formaldehyde excess nor with oxiranes.

Parabanic acid

Reactions of parabanic acid with formaldehyde were studied in the 1960s by Oda and Baba [25] and later, in the 1980s by Cassidy *et al.* [26]. In a reaction of one mole of formaldehyde with one mole of parabanic acid Oda and Baba obtained *N*-hydroxymethyl hydroparabanate [formula (XII)] that crystallizes with one water molecule and

(XII) (XIII)

(XIV)
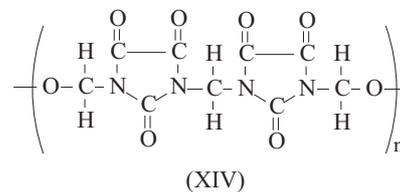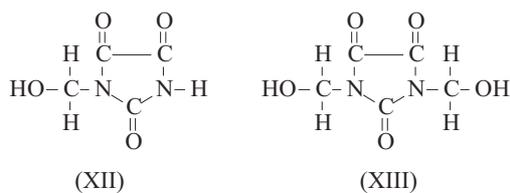
melts at 142 °C. Cassidy failed to obtain the same compound, but with two moles of formaldehyde 1,3-bis(hydroxymethyl) parabanate [formula (XIII)] it can be obtained.

Its synthesis was carried out in diluted formalin (containing *ca*. 9 wt. % of formaldehyde) at the room temperature for 12 days. The presence of triethylamine as a catalyst reduced the reaction time to mere 30 min [27]. With regular formalin, the time for a precipitate to appear is very short, about 8 min at room temperature and no catalyst is required. It has been shown that the reaction with formaldehyde takes place at nitrogen in the ketonic form [27], and not as Cassidy suggested at oxygen in the enolic form of parabanic acid [26]. A prolonged reaction time at the molar ratio of parabanic acid to formaldehyde equal to 1:2.2 with diluted formalin (9 wt. %) leads to products with some hydroxymethyl groups partly condensed. The products can be isolated by extraction with methanol. The attempts to polymerize 1,3-bis(hydroxymethyl) parabanate have shown that upon 7—16 h heating at 50—60 °C a polymer [formula (XIV)], insoluble in organic solvents is formed.

Melamine

In reactions of melamine with formaldehyde, hydroxymethyl derivatives of melamine are formed that are used for manufacturing melamine-formaldehyde resins [28]. Depending on the starting molar ratio of melamine to formaldehyde (1:*z*), derivatives of melamine, given by general formula (XV) in Table 1, containing various amounts of hydroxymethyl groups per molecule are obtained [27—29].

Specific conditions under which the successive hydroxymethyl derivatives of melamine are conveniently obtained are the subject of patents [32—37]. For $2 \leq z \leq 4$, two structural isomers exist differing in the distribution of substitution degrees of nitrogen atoms. At a given ratio of melamine to formaldehyde equal to, say, 1:*z* one obtains not just the *z*-hydroxymethyl derivative, but a distribution of products of various substitution degree of the global ratio 1:*z* [38]. Isolation of individual derivatives is difficult and can be done by liquid chromatography.

T a b l e 1. Different melamine derivatives obtained in the reaction of melamine and formaldehyde

| General formula	Meaning of symbols R_x	Name of the melamine derivative	Abbreviation
	$R_1 = R_3 = -CH_2OH$, $R_2 = R_4 = R_5 = R_6 = -H$	N,N'-bis(hydroxymethyl)melamine	BHMM
	$R_1 = R_2 = -CH_2OH$, $R_3 = R_4 = R_5 = R_6 = -H$	N,N-bis(hydroxymethyl)melamine	
	$R_1 = R_3 = R_5 = -CH_2OH$, $R_2 = R_4 = R_6 = -H$	N,N',N''-tris(hydroxymethyl)melamine	THMM
	$R_1 = R_2 = R_3 = -CH_2OH$, $R_4 = R_5 = R_6 = -H$	N,N,N'-tris(hydroxymethyl)melamine	
	$R_1 = R_2 = R_3 = R_5 = CH_2OH$, $R_4 = R_6 = -H$	N,N,N',N''-tetrakis(hydroxymethyl)melamine	TeHMM
	$R_1 = R_2 = R_3 = R_4 = CH_2OH$, $R_5 = R_6 = -H$	N,N,N',N'-tetrakis(hydroxymethyl)melamine	
(XV)	$R_1 = R_2 = R_3 = R_4 = R_5 = -CH_2OH$, $R_6 = -H$	N,N,N',N',N''-pentakis(hydroxymethyl)melamine	PHMM
	$R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = -CH_2OH$	N,N,N',N',N'',N''-heksakis(hydroxymethyl)melamine	HHMM
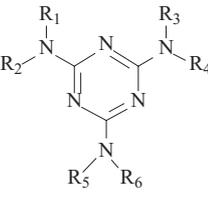
Tomita isolated these compounds and recorded their ^{1}H NMR spectra [39]. Somewhat easier to prepare are (methoxymethyl)melamines [29, 34, 40]. The hydroxymethyl groups directly linked to nitrogen atoms are unstable. They easily condense in acidic media [28]. Those condensation processes were studied many times by many researchers (*e.g.* [41—53]) since the reactions are widely used in manufacturing of widely known melamine-formaldehyde resins. Therefore, these problems are not to be discussed here. Since, as it is well known, the solubility of melamine can be substantially improved by reacting it with formaldehyde to form (hydroxymethyl)melamines that are well soluble in hot water and in dimethyl sulfoxide (DMSO). (Hydroxymetyl)melamines do have reactive protons that can react with oxiranes to polyetherols. Until recently, however, very little was known on such reactions. The only exception was a patent [54] where reactions of ethylene oxide with N,N-bis(hydroxymethyl)melamine and HHMM were described. The reactions were carried out in the presence of transition metal alcoholates. The authors of the former patent [54] claimed that amino groups in hydroxymethyl derivatives, such as BHMM, did not react with oxiranes at all. This conclusion was challenged in [55]. It was also found that the addition of (hydroxymethyl)melamines to ethylene or propylene oxide in DMSO or DMF is accompanied by condensation of hydroxymethyl groups occasionally leading to crosslinked products. The amount of this product depended on the initial molar ratio of reagents and on the conditions applied. By using BHMM it was shown [54] how the ratios of reagents and conditions could be altered to avoid formation of crosslinked products. The rationale of the condensation was the catalytic effect of the products of addition of oxirane, the highest

for ethylene oxide and the lowest for propylene oxide based products. It has been shown [57—59] that the condensation accompanying addition is caused by formation of alcoholate anions $>N\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O^-$, which serve as condensation catalyst [58] (eqs. 4, 5).

In reality, the last stage is more complicated, since hydroxyl anions take over the role of $>N\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O^-$ anion and act as the catalyst of condensation:

$$-CH_2-OH + OH^- \rightleftharpoons -CH_2-O^- + H_2O \quad \textit{etc.} \qquad (6)$$
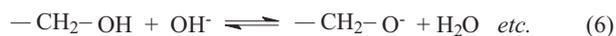
The condensation is a coupled reaction to the addition of (hydroxymethyl)melamines to oxiranes. Formaldehyde fades away continuously during the addition of (hydroxymethyl)melamines to ethylene or propylene oxide. Permanent blocking of formaldehyde is accomplished when at least two oxirane molecules react with the hydroxymethyl group, similarly as in the reactions of THMI with oxiranes. Suitable for polyetherol synthesis are the melamine derivatives containing 4 and more hydroxymethyl groups per molecule. Otherwise, crosslinked products and products containing unreacted amino groups are formed. Following the findings, optimal conditions of the synthesis of *s*-triazine polyetherols were proposed comprising reactions of PHMM with oxiranes at 45—75 °C for 25—47 h [60]. A disadvantage of the method of synthesis of polyetherols from (hydroxymethyl)melamines was the necessity of separation the highly boiling solvent. To overcome the problem, melamine derivatives well soluble in oxiranes were sought for. Also water was tested as reaction medium, but with no satisfactory results [61, 62]. Attention was focused on the products with hydroxymethyl groups blocked with methanol. The latter converted into polyols by ethylene glycol yielded substances soluble in oxiranes. This method of preparing *s*-triazine polyetherols was described in [63]. The idea is illustrated in Scheme D for the fragment of hydroxymethyl derivative of melamine (PHMM was used).

The methoxylation was carried out at a substantial excess of methanol (20 moles CH_3OH per mole of PHMM). The only secondary amino group did not enter the reac-

$$-N\text{-}CH_2-O\text{-}CH_2-CH_2-O^- + HO\text{-}CH_2-N- \rightleftharpoons$$

$$\rightleftharpoons -N\text{-}CH_2-O\text{-}CH_2-CH_2-OH + {}^-O\text{-}CH_2-N- \qquad (4)$$

$$-N\text{-}CH_2-O^- + HO\text{-}CH_2-N- \longrightarrow$$

$$\longrightarrow -N\text{-}CH_2-O\text{-}CH_2-N- + OH^- \qquad (5)$$

$$-N\begin{array}{c}CH_2OH\\CH_2OH\end{array}\xrightarrow[65-75\ °C]{CH_3OH}-N\begin{array}{c}CH_2-O-CH_3\\CH_2-O-CH_3\end{array}\xrightarrow[-CH_3OH]{HO(CH_2)_2OH}$$

$$\longrightarrow -N\begin{array}{c}CH_2-O-CH_2-CH_2OH\\CH_2-O-CH_2-CH_2OH\end{array}\xrightarrow[35-100\ °C,\ 4-12\ h]{\overset{R}{\underset{O}{\triangle}}}$$

product soluble in oxiranes

$$\longrightarrow -N\begin{array}{c}CH_2-O-CH_2-CH_2-O-(CH_2-\overset{R}{CH}-O)_x-H\\CH_2-O-CH_2-CH_2-O-(CH_2-\underset{R}{CH}-O)_y-H\end{array}$$
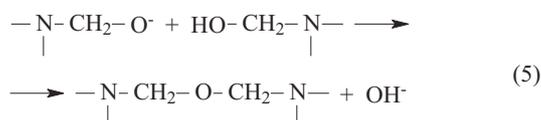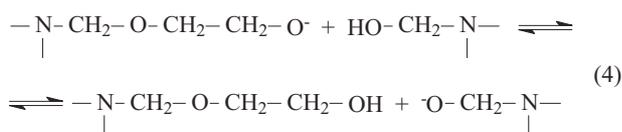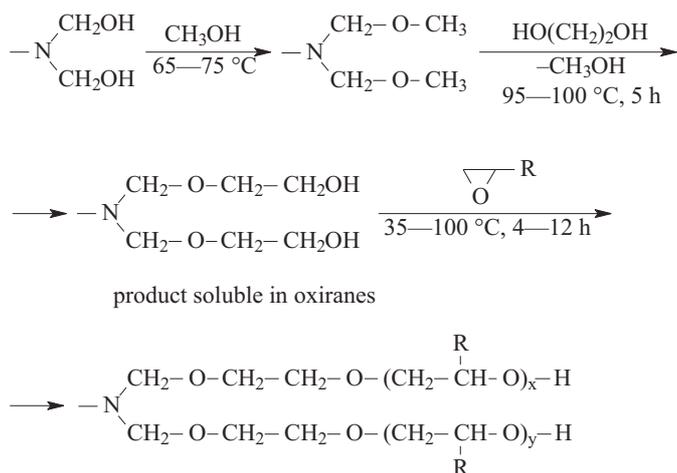
Scheme D. The method of preparation of s-triazine polyetherols from (hydroxymethyl)melamine

tion. Transesterification stage was carried out to 75 % conversion degree (at *ca*. 80 % conversion the system starts to gel). The final reaction mixture contained, besides the transesterification product, also unreacted pentakis(methoxymethyl)melamine and ethylene glycol. It was dissolved in ethylene and propylene oxides and reacted with these oxiranes in the homogeneous phase. Both hydroxyalkyl and amino groups became oxyalkylated and the final product had the following general formula (XVI) [63]:

(Scheme E, right column)

HO-CH₂-HN, triazine ring, NH-CH₂-OH, NH₂

$$\xrightarrow[excess]{CH_3OH}\ 65-75\ °C,\ 1.5\ h$$

CH₃-O-CH₂-HN, triazine ring, NH-CH₂-O-CH₃, NH₂

(XVII)

$$\xrightarrow[18-40\ h]{n\ \triangle R\ \ 70-90\ °C}$$

(XVIII)
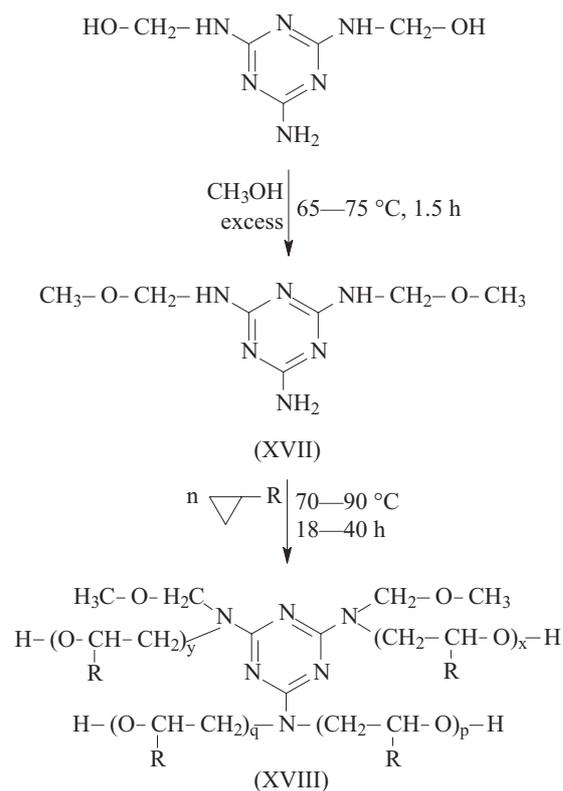
where: x + y + p + q = n

Scheme E. Method of preparation of polyetherol from BHMM

(XVI)
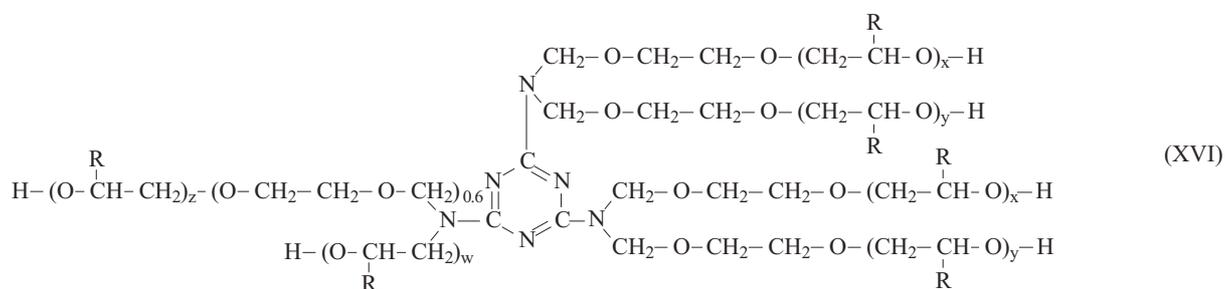
where: R = –H, –CH₃ or –CH₂Cl, 2x + 2y + z + w = n ≤ 7

This alternative synthetic route had two disadvantages. It comprised many stages and unreacted compounds contaminated the product. The latter had no serious effect upon the thermal stability of polyurethane foams that was much higher than that of classical foams [63]. The first disadvantage was partly neutralized by replacing PHMM with disubstituted compound, *i.e.*, BHMM. It was possible to eliminate the transesterification stage, where reactions were carried out according to Scheme E, since bis(methoxymethyl)melamine (XVII) dissolved in oxiranes at elevated temperature [59, 64]

In the reaction of BHMM with excess of methanol the conversion of hydroxymethyl groups was not complete. In fact, a mole of product contained *ca*. 0.5 mole of unblocked hydroxymethyl groups [59] and at 70 °C it was a liquid resin soluble in oxirane.

REACTIONS WITH ALKYLENE CARBONATES

As it was mentioned the hydroxyalkyl derivatives of azacycles can be obtained in a straightforward reaction between alkylene carbonates, like ethylene carbonate or propylene carbonate with azacycle. Azacycles are poorly soluble in DMSO and/or water, therefore syntheses with oxiranes were performed in DMSO. In the presence of water the side reactions of oxiranes with this solvent resulted in formation of glycols or polyglycols. After completion of the reaction, DMSO had to be removed under reduced pressure. Nevertheless heating of the post-reaction mixture led to partial decomposition of DMSO and the product thus purified had characteristic odor. Moreover, oxiranes themselves are low-boiling, toxic and flammable compounds, and form an explosive mixture

with air. All these features render them hazardous chemicals [65]. The use of hydroxymethyl derivatives of azacycles instead of unsubstituted azacycles enabled to perform the reaction with oxiranes thanks to better solubility of the derivatives in organic solvents, sometimes in neat oxiranes. The disadvantage of this method was release of formaldehyde blocked with one oxirane, and migration of formaldehyde to the end of the etherol chain [16]. Therefore larger excess of ethylene oxide or propylene oxide used to obtain polyetherols from hydroxymethyl derivatives was necessary, instead of straightforward reaction of azacycles with oxiranes.

Thus, another method for synthesis of polyetherols without solvent, between azacycle and hydroxyalkylating agent was finally achieved by the use of alkylene carbonates, which give the same products as oxiranes. Alkylene carbonates are not hazardous chemicals, because they are non-flammable, non-toxic, polar [66] enough to dissolve azacycles. Thus, they can be the solvents and reagents at the same time, they do not have to be removed from the post-reaction mixture, because they completely react with azacycles. First suggestions on the use of alkylene carbonates for synthesis of polyetherols with azacycles are dated at 1993 [67], where it was mentioned that alkylene carbonates are useful reagents for melamine to obtain polyetherols.

Isocyanuric acid

No data was found in literature on the reaction of isocyanuric acid with alkylene carbonates. The only exception was patents description published in 1990 [68], where a reaction of isocyanuric acid (IA) with up to 4-fold molar excess of ethylene carbonate (EC) was described. The product was 1,3,5-tris(2-hydroxyethyl) isocyanurate {formula (IX), R = H in [1]}. In order to obtain polyetherols the reaction of IA with EC requires an excess of the hydroxyalkylating agent. As it was proven in [69] the resin-like products, free of *N*-(2-hydroxyethyl) derivatives of IA are formed when the initial molar ratio IA:oxirane is 1:>5. The reactions were performed at 155—160 °C within 3 h in the presence of potassium carbonate as a catalyst. While examining the mechanism of the reaction, it was found that reaction rate limiting factor is decomposition of ethylene dicarbonate dianion (which is formed during the reaction) to ethylene glycol dianion and carbon dioxide. The proposed mechanism explained formation of a small amount of ethylene glycol during synthesis of polyetherols from IA and EC [70, 71].

The synthesis of polyetherols from IA and propylene carbonate (PC) should not be conducted in the presence of potassium carbonate, because the product is always contaminated with solid potassium isocyanurate, which is formed during the synthesis of polyetherols. The best catalyst is here 1,4-diazabicyclo-[2.2.2]octane (DABCO) or tetrabutylammonium hydroxide, at temperature 175—180 °C [72].

Barbituric acid

Barbituric acid does not undergo hydroxyalkylation with ethylene or propylene carbonate. Instead it tautomerizes to enol forms, which are insoluble in the reaction mixture [73]. 5-Ethylbarbituric acid in EC also enolizes to poorly soluble tautomers [73], but 5,5-diethylbarbituric acid in the presence of DABCO relatively easy reacts with EC to give 1,3-bis(2-hydroxyethyl)-5,5-diethylbarbiturate {formula (XV), R = H, x = 1 in [1]} [74]. At a larger excess of EC linear oligoetherols {formula (XV), x >1 in [1]} are formed. *N*,*N*'-bis(hydroxyalkyl) derivatives of 5,5-diethylbarbituric acid can be also obtained without a solvent in the straightforward reaction of the acid with alkylene carbonates. The obtained products are new diol components, suitable for synthesis of polyurethanes containing a thermally resistant pyrimidine ring [74].

Uric acid

Studies on the reaction of uric acid (UA) with alkylene carbonates showed that at an excess of carbonates like EC or PC slow dissolving of UA occurs with formation of polyetherols with a purine ring included. It has been expected that reactions performed at a small excess of alkylene carbonates could result in formation of lower hydroxyalkyl derivatives of UA, better soluble than UA itself. This could give a chance to use UA in organic syntheses and polymer chemistry. It has been shown that at lower molar ratio UA:EC = 1:<5 the unreacted UA in the solid form remains apart from the resin-like product, the latter being difficult to separate lower hydroxyalkyl derivatives of UA and products of its consecutive reaction with alkylene carbonates [75, 76]. The process of synthesis of polyetherols from purine with EC is usually conducted at 180 °C and with DABCO catalyst, while those from UA and PC in the presence of tetrabutylamonium hydroxide and KOH at *ca*. 185 °C [75]. Obtained polyetherols reveal higher thermal stability than those obtained from hydroxymethyl derivatives of UA and oxiranes, in which unstable oxymethylene groups are present; these can result in diminishing of thermal stability of the products. Similarly, the thermal stability of polyurethane foams obtained from polyetherols and diisocyanates is higher in comparison with those obtained from polyetherols and hydroxymethyl derivatives of UA [77].

Adenine

Polyetherols with a purine ring can also be obtained in reactions of adenine with alkylene carbonates [78]. At the molar ratio of adenine to ethylene carbonate equal 1:1, the same product is obtained as in the reaction between 1 mole of adenine and 1 mole of ethylene oxide. Another mole of ethylene carbonate introduced to the system reacts with amino group, again similarly as in the case of

ethylene oxide. The amino group, however, remains monofunctional, probably the reason is the steric effect. Apparently, large cyclic molecules cannot approach sufficiently close to already substituted amino group in the vicinity of a purine ring. Therefore, subsequent molecules of oxirane react with hydroxyl groups of the previously linked molecules. In reactions of adenine with EC one may obtain bifunctional polyetherols containing unreacted secondary amino groups {formula (XIX), x = 0 in [1]} [78].

Parabanic acid

Parabanic acid subjected to hydroxyalkylation with alkylene carbonates behaves different than other azacycles of similar structure. During the reaction opening of the parabanic acid ring takes place and linear oligomeric products, given by formula (XIX), are formed [79, 80]:

$$
\text{HO} \left[\text{CH}_2-\text{CH-O} \right]_x \overset{\overset{O}{\|}}{\text{C}} - \overset{\overset{O}{\|}}{\text{C}} - \text{N} \left[\text{CH}_2-\text{CH-O} \right]_w \text{H}
$$

$$
\text{H} \left[\text{O-CH-CH}_2 \right]_z \text{N} \left[\text{CH}_2-\text{CH-O} \right]_y \text{H}
$$

(XIX)

where: R = –H, –CH$_3$

thors did not analyze products of the reaction of melamine with an excess of carbonate. The studies of the author's research group showed that at the initial molar ratio of melamine to alkylene carbonates 1:<12 in the presence of potassium carbonate or hydroxide as catalysts, the resin products are contaminated with lower hydroxyalkyl derivatives and melamine, which indicates that the catalysts are ineffective. Instead of them DABCO was proven to be a good catalyst [85, 86]. Quite pure products are in this case obtained already at melamine to EC molar ratio 1:6. Reactions were performed at 160—165 °C for EC and at 175—180 °C for PC [86]. In these conditions not only oxyethylene and oxypropylene groups but also the carbonate groups are incorporated into polyetherols. The structure of obtained oligoetherols can be represented by the formula (XX).

The methods of synthesis of polyetherols from melamine provides the opportunity of synthesis of thermally stable polyurethane foams from a cheap substrate, *i.e.*, melamine [87].

CONCLUSIONS

Formaldehyde is a useful hydroxyalkylation agent for azacycles. In some cases, it is the only way to obtain soluble derivatives of azacycles. The latter are soluble in organic solvents and in oxiranes and can be converted into

$$
\text{H} - (\text{O-CH-CH}_2)_p \quad \text{N} \quad \text{N} - (\text{CH}_2-\text{CH-O})_x \left[\text{CH}_2-\text{CH-O-} \overset{\overset{O}{\|}}{\text{C}} \text{-O-CH}_2-\text{CH-O} \right]_l (\text{CH}_2-\text{CH-O})_y - \text{H}
$$

(XX)

where: x + y + z + v + w + p + q = n - 1

Such structures were found in products obtained from parabanic acid and excess of oxiranes at temperature above 70 °C in the presence of 4 g triethylamine/mole of parabanic acid [81]. At lower initial ratio of parabanic acid to alkylene carbonate the products may have imide groups, primary, secondary and tertiary amide groups and oxalamidoester groups. Products of hydroxyalkylation obtained from them have good thermal stability [82]. This is probably due to not only the presence of trioxoimidazolidine rings, but also due to the presence of the groups formed from them. These products can be successfully used as polyetherols for obtaining polyurethane foams of enhanced thermal stability [83].

Melamine

There were no reports on a reaction of melamine with alkylene carbonates until 1995 except patent [84]. The au-

polyetherols with azacycles. In this way polyetherols with purine and pyrimidine rings can be obtained, which cannot be achieved in direct reactions of uric and barbituric acids with oxiranes like ethylene and propylene oxides.

Recently alkylene carbonates were applied as hydroxyalkyl agents. When alkylene carbonates are used, it is possible to avoid a traditional reagent like ethylene oxide and propylene oxide which have low boiling temperatures (14 and 34 °C, respectively), are flammable and explosive. Instead high boiling, non-flammable and nontoxic carbonates can be used, additionally pressure reactors can be avoided and reaction can be performed under reflux.

Preliminary studies conducted by the author's research group showed that alkylene carbonates can be successfully used as hydroxyalkylating agents for such poorly soluble azacyclic substrates like melamine isocya-

nurate, melam or melem. Especially the latter has very high thermal stability and decomposes above 660 °C, which renders it a perfect candidate for obtaining a polymeric material of very high thermal stability.

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