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## New possibilities to synthesize oligoetherols with azacyclic rings

### RAPID COMMUNICATION

**Summary** — A new method of preparation of oligoetherols containing azacyclic rings from isocyanuric acid (IA), uric acid (UA) or melamine (MEL) with an excess of glycidol (GL) and oxiranes without using solvent is presented. The method can be extended on synthesis of oligoetherols with other azacyclic compounds containing amine, amide or imide groups.

**Keywords:** azacyclic compounds, glycidol, oxiranes, synthesis, properties of products.

#### NOWE MOŻLIWOŚCI SYNTEZY OLIGOETEROLI Z PIERŚCIENIAMI AZACYKLICZNYMI

**Streszczenie** — Dotychczasowe sposoby syntezy oligoeteroli z pierścieniami azacyklicznymi polegają najczęściej na reakcjach melaminy (MEL) lub kwasu izocyjanurowego z oksiranami. Wadą tego sposobu syntezy jest brak dobrych rozpuszczalników melaminy i kwasu izocyjanurowego, w których można by prowadzić reakcje z oksiranami, bowiem wspomniane związki heterocykliczne rozpuszczają się tylko w DMSO i DMF ale dość słabo. Po zakończeniu reakcji istnieje konieczność oddestylowania toksycznych i wysokowrzących rozpuszczalników. W pracy zaproponowano nową, bezrozpuszczalnikową metodę otrzymywania oligoeteroli z pierścieniami azacyklicznymi w reakcjach kwasu izocyjanurowego (IA), moczowego (UA) lub melaminy (MEL) z glicydołem (GL), a następnie z oksiranem, takim jak tlenek etylenu (EO) lub tlenek propylenu (PO). Wskazano możliwości rozszerzenia tej metody na syntezę oligoeteroli z zastosowaniem innych związków azacyklicznych z grupami aminowymi, amidowymi lub imidowymi, które do tej pory nie reagowały ze wspomnianymi oksiranami.

**Słowa kluczowe:** związki azacykliczne, glicydoł, oksirany, synteza, właściwości produktów.

Methods used till now in synthesis of oligoetherols with azacyclic rings involved reactions with melamine (MEL) or isocyanuric acid (IA) with oxiranes, such as ethylene oxide (EO) or propylene oxide (PO) [1–4]. Oligoetherols synthesized this way, containing in its structure 1,3,5-triazine ring or perhydro-1,3,5-triazine ring, can be used to produce polyurethane foams with improved thermal stability [5, 6]. This property occurs mainly due to the presence of the rings, which begin to decompose at 360 °C. The main obstacle to employ this method of synthesis was the lack of feasible solvents providing sufficient solubility of MEL and IA in which synthesis with oxiranes could be carried out. The above mentioned compounds are soluble to some extent in dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) [7]. Furthermore, the high boiling and toxic solvent has to be removed from final products by distillation. Distillation usually leads to partial decomposition of DMSO and hence contamination of oligoetherols with products of

the decomposition that have an unpleasant odor. Thus, researchers are still looking for more convenient methods of synthesis of oligoetherols. The best choice would be a method excluding solvents, *i.e.* the protocol based on a straightforward reaction of the azacyclic compound and a hydroxyalkylating agent. It seemed that this could be achieved in a reaction of some azacyclic compounds with glycidol (GL). The reaction of glycidol with mentioned azacycles was not described in literature except that of IA with GL at initial molar ratio 1:3 [8, 9].

The aim of this paper was the study of a possibility to apply the reaction of glycidol with some azacyclic compounds to obtain new precursors of oligoetherols.

### EXPERIMENTAL

#### Materials

The following materials were used in this work: isocyanuric acid (IA, pure, Fluka, Switzerland), uric acid (UA, pure, Avocado, Germany), melamine (MEL, pure,

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Table 1. Results of elemental analysis and some physical properties of reaction products of azacyclic compounds with GL and oxiranes for various molar ratios of reagents

Number of reaction	Reagents	Molar ratio of reagents	Elemental analysis, wt. %						Refractive index $n_D^{20}$	Density <sup>a)</sup> $g/cm^3$	Viscosity <sup>a)</sup> $\cdot 10^3$ $N \cdot s/m$	Surface tension <sup>a)</sup> $\cdot 10^3$ , $N/m$	Functionality of product <sup>b)</sup>	HN, mg KOH/g	
			calculated			found								found	calc.
			C	H	N	C	H	N							
1	IA:GL	1:4	42.35	6.35	9.88	42.12	6.25	6.22	— <sup>c)</sup>	— <sup>c)</sup>	— <sup>c)</sup>	7	924	905	
2	IA:GL	1:6	43.98	6.81	7.33	43.89	6.54	7.56	1.3465	631 100	— <sup>c)</sup>	9	854	881	
3	IA:GL	1:9	45.28	7.17	5.28	44.82	6.80	5.16	1.3406	52 100	— <sup>c)</sup>	12	867	846	
4	MEL:GL	1:8	45.13	7.52	11.70	45.32	7.79	11.82	— <sup>c)</sup>	— <sup>c)</sup>	— <sup>c)</sup>	14	1073	1093	
5	MEL:GL	1:18	46.91	7.82	5.76	47.16	7.67	5.93	— <sup>c)</sup>	— <sup>c)</sup>	— <sup>c)</sup>	24	1063	923	
6	UA:GL	1:6	45.10	6.54	9.15	45.05	6.72	8.82	— <sup>c)</sup>	— <sup>c)</sup>	— <sup>c)</sup>	10	890	916	
7	UA:GL	1:8	45.79	6.84	7.37	45.73	7.17	7.46	1.3170 <sup>70</sup>	41 633 <sup>70</sup>	55.72 <sup>70</sup>	12	867	885	
8	UA:GL	1:12	46.59	7.20	5.30	46.25	7.11	5.08	1.3513 <sup>60</sup>	62 116 <sup>60</sup>	58.10 <sup>60</sup>	16	826	850	
9	UA:GL	1:16	47.04	7.40	4.14	46.85	7.22	3.97	1.3089 <sup>60</sup>	42 865 <sup>60</sup>	55.72 <sup>60</sup>	20	810	830	
10	IA:GL:PO	1:6:6	50.81	8.14	4.56	50.70	8.32	4.71	1.4888	32 350	46.76	9	537	548	
11	IA:GL:EO	1:6:6	47.31	7.53	5.02	47.51	7.24	5.04	1.4981	17 220	52.64	9	585	603	
12	MEL:GL:EO	1:8:16	49.79	8.30	5.91	49.60	8.43	5.44	1.4946	34 256	46.20	14	538	552	
13	MEL:GL:PO	1:8:12	53.47	8.91	5.94	53.72	8.85	5.92	1.4910	32 463 <sup>30</sup>	42.14	14	570	555	
14	UA:GL:EO	1:6:7	48.26	7.39	6.09	48.51	7.03	6.21	1.5185	33 956 <sup>30</sup>	58.94	10	616	610	
15	UA:GL:PO	1:6:8	52.41	8.18	5.20	52.11	8.51	5.40	1.4949	55 158	44.38	10	510	521	

<sup>a)</sup> The measurements were performed at 20 °C unless stated otherwise (in upper index).

<sup>b)</sup> Functionality was calculated according to the chemical formula of the obtained compound [formulas (III), (IV) and (V)].

<sup>c)</sup> Products are semisolid resins, for which determinations cannot be performed at room temperature with the methods used here (see Experimental).

Merck, Germany), glycidol (GL, pure, Sigma-Aldrich, Germany), triethylamine (TEA, pure, Avocado, Germany), ethylene oxide, propylene oxide (EO and PO, respectively, pure, Fluka, Switzerland).

## Syntheses

0.1 mol of acid (IA or UA) or MEL and a proper amount of GL were placed in a pressure reactor of 250 cm<sup>3</sup> capacity. The reactor was closed, the content was mixed, heated up to 140, 160 or 100 °C for reactions of GL with IA, UA and MEL, respectively, and maintained in these conditions until the reaction completed (1–3 h, time determined by the epoxide number). Yellow resin-like products were obtained. Then 2 cm<sup>3</sup> of TEA as a catalyst and the next proper amount of PO or EO were introduced. Molar ratios of reagents used in the performed reactions are specified in Table 1. The mixture was heated up to 80–100 °C and maintained at that temperature under stirring until the reaction completed (several hours). After the reaction the catalyst was removed under reduced pressure ( $p = 20–27$  hPa at  $t = 120$  °C).

## Methods of testing

The course of reaction between the azacyclic compound, GL and alkylene oxide was followed by measuring the content of unreacted epoxide groups with hydrochloric acid-dioxane method [10].

The hydroxyl number (HN) of oligoetherols was determined with Glinka and Majewska method [11].

Elemental analysis for C, H, N, was done with EA 1108, Carlo-Erba analyzer.

The <sup>1</sup>H NMR spectra of products were recorded at 500 MHz Bruker UltraShield in DMSO-d<sub>6</sub> with hexamethyldisiloxane as internal standard.

IR spectra were registered on PARAGON 1000 FT-IR Perkin Elmer spectrometer in KBr pellets or ATR technique.

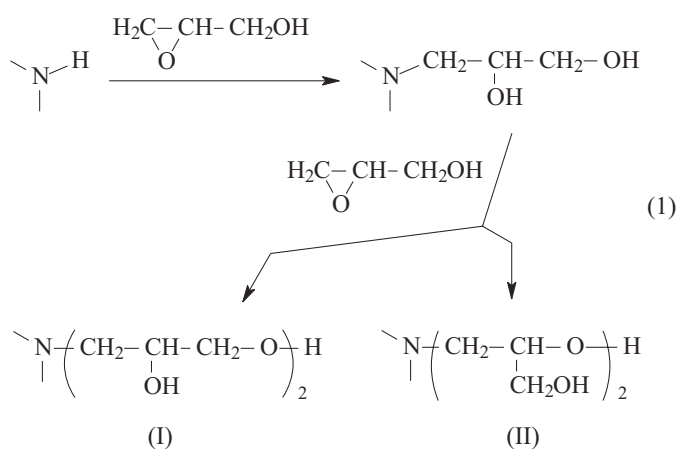
MALDI-TOF analysis of products was obtained on Voyager-Elite Perceptive Biosystems (US) mass spectrometer working in linear mode with delayed ion extraction, equipped with nitrogen laser working at 337 nm. As matrix solution of 2,5-dihydroxybenzoic acid in tetrahydrofuran were used. The samples were diluted with methanol to concentration of 1 mg/cm<sup>3</sup>, followed by addition of 10 mg/cm<sup>3</sup> solution of NaI in

acetone. Therefore in some cases the molecular ion masses were increased by the mass of  $\text{Na}^+$  and  $\text{CH}_3\text{OH}$ .

Refraction index, density, viscosity, and surface tension of oligoetherols were determined with Abbe refractometer, picnometer, Höppler viscosimeter (type BHZ, Prüfgeratewerk, Germany) and by the detaching ring method, respectively.

## RESULTS AND DISCUSSION

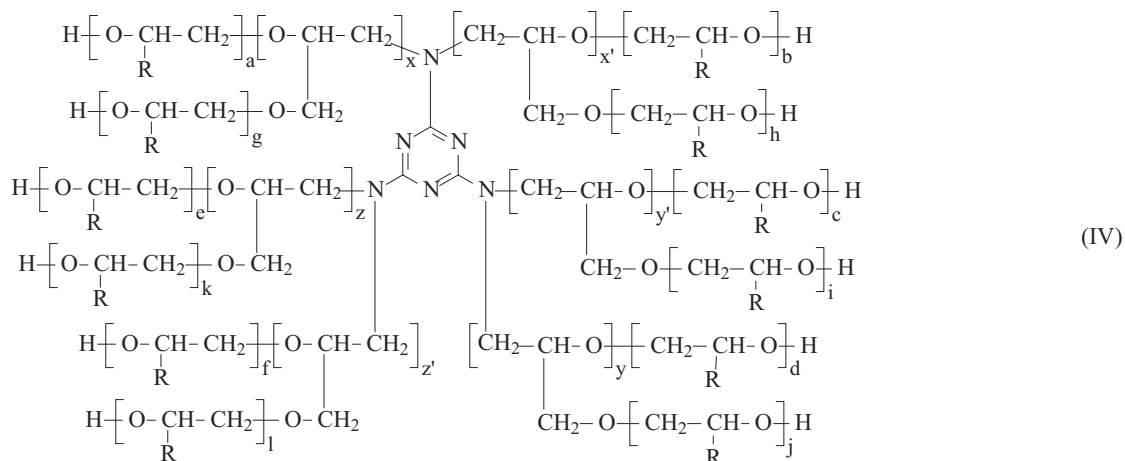
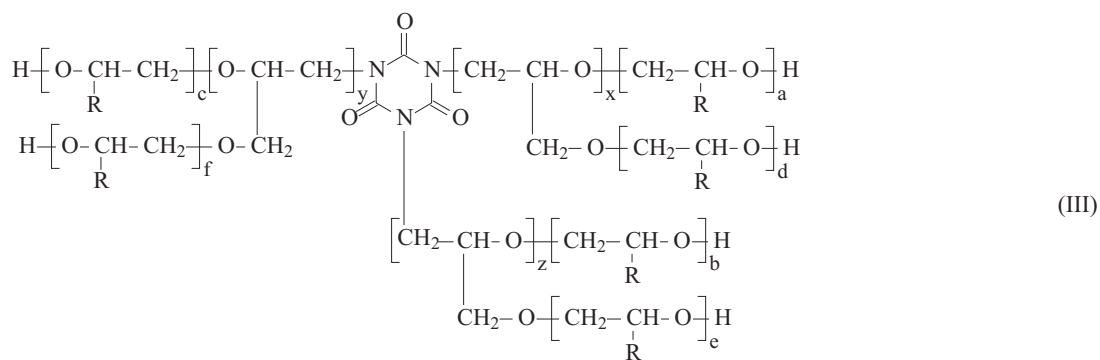
Acids IA, UA or MEL react with GL after heating the reaction mixture to 100–160 °C. There are two possible conversion routes of the product of addition of epoxide to azacycle as shown below:

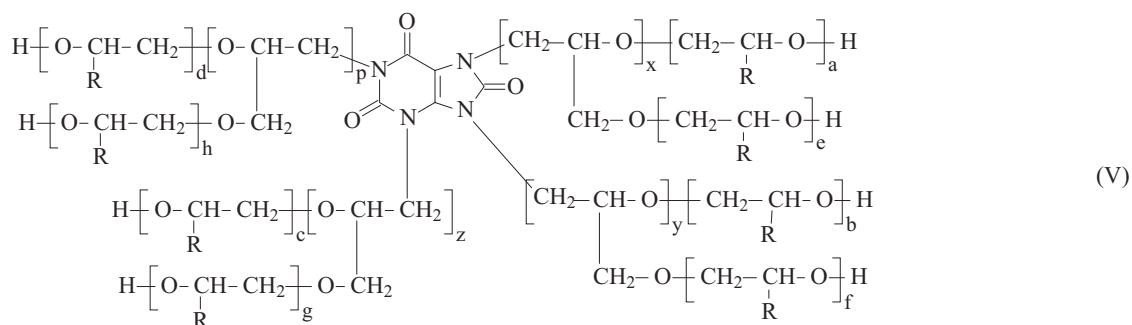


The exothermic reaction requires cooling and occurs without a catalyst. The reactions were conducted at initial molar ratio of reagents:  $\text{GL}:\text{MEL} \geq 8:1$ , and in other cases  $\text{GL}:\text{acid} \geq 4:1$ , in order to avoid precipitation of unreacted azacyclic compound in the product. Due to formation of secondary alcoholate upon epoxide ring opening the formation of product described by formula (II) seems to be more probable than that described by formula (I). On the other hand formation of product (II) is limited by low excess of glycidol (Table 1, reactions 1, 2, 6–8, 10–15). The obtained products are not homogeneous compounds but they are mixtures of hydroxyalkyl derivatives of specific azacycles.

Formulas (III)–(V) show products of reactions of IA or MEL or UA respectively with GL and ethylene or propylene oxides ( $\text{R} = \text{H}$  or  $-\text{CH}_3$ , respectively), where  $a$ – $l$  and  $x$ ,  $x'$ ,  $y$ ,  $y'$  and  $z$ ,  $z'$  denote numbers of oxyalkylene units in a chain of oligoetherols.

Table 2 shows the composition of the obtained product in reaction of IA with GL at molar ratio 1:4 confirmed by MALDI-TOF mass spectrum. The product contains derivatives with different degree of substitution of IA with GL. The signals from dehydration products are also present in the MALDI-TOF spectra. However, their intensity is small and any olefin proton resonances in the  $^1\text{H}$  NMR spectra are not observed. Comparison of calculated for oligoetherols, given by formulas (III)–(V), and determined for products values of hydroxyl number and results of elemental analysis confirms the agreement of





products chemical structures with the proposed formulas. The  $^1\text{H NMR}$  spectra of the reaction products showed the disappearance of imide proton resonance (at 10–12 ppm) of IA and UA and amine proton resonance (at 6.0 ppm) of MEL with simultaneous growth of hydroxyl proton signal in 4.1–4.9 ppm region and methylene and methine resonances in the 3.3–3.8 ppm region. The exemplary  $^1\text{H NMR}$  spectrum for product of reaction of IA and GL is shown in Figure 1. For products of reaction with lower molar ratio of glycidol:azacycle compound the resonances from unsubstituted NH group protons were observed at 7–8 ppm, which disappeared upon deuteration with  $\text{D}_2\text{O}$ . In the IR spectra of obtained products the bands in the region of 3300–3400  $\text{cm}^{-1}$  as well as at ca. 1100  $\text{cm}^{-1}$  were attributed to hydroxyl groups while the band as 1050  $\text{cm}^{-1}$  were assigned to valence vibration of the ether bond. The exemplary spectrum for the product obtained in reaction of IA and GL with molar ratio 1:6 is presented in Figure 2.

**Table 2. Interpretation of MALDI-TOF spectrum of reaction product obtained from 1 mole of IA and 4 moles of GL**

Signal position m/z	Relative intensity of the signal, %	The molecular ion structure	Calculated molecular weight
184.9	100	IA + GL – $\text{H}_2\text{O}$	185
209.0	39	(IA + GL – $\text{H}_2\text{O}$ ) + $\text{Na}^+$	208
240.1	40	(IA + GL – $\text{H}_2\text{O}$ ) + $\text{CH}_3\text{OH}$ + $\text{Na}^+$	240
316.2	28	(IA + 3 GL – 2 $\text{H}_2\text{O}$ ) + $\text{H}^+$	316
334.1	46	(IA + 3 GL – 2 $\text{H}_2\text{O}$ ) + $\text{H}^+$	334
352.1	16	(IA + 3 GL) + $\text{H}^+$	352
376.1	12	(IA + 3 GL) + $\text{Na}^+$	374
408.1	19	(IA + 4 GL – $\text{H}_2\text{O}$ ) + $\text{H}^+$	408
425.1	15	IA + 4 GL	425
450.1	10	IA + 4 GL + $\text{Na}^+$	448
499.1	17	IA + 5 GL	499
500.1	9	(IA + 5 GL) + $\text{H}^+$	500
506.2	5	(IA + 5 GL – $\text{H}_2\text{O}$ ) + $\text{Na}^+$	504
524.1	10	(IA + 5 GL) + $\text{Na}^+$	522
573.1	13	IA + 6 GL	573
574.1	7	(IA + 6 GL) + $\text{H}^+$	574

596.2	6	(IA + 6 GL) + $\text{Na}^+$	596
610.1	8	(IA + 6 GL – $\text{H}_2\text{O}$ ) + $\text{CH}_3\text{OH}$ + $\text{Na}^+$	610
647.1	9	IA + 7 GL	647
670.1	6	(IA + 7 GL) + $\text{Na}^+$	670
744.2	5	IA + 8 GL + $\text{Na}^+$	744
832.2	3	(IA + 9 GL – $\text{H}_2\text{O}$ ) + $\text{CH}_3\text{OH}$ + $\text{Na}^+$	832
875.2	3	(IA + 10 GL – $\text{H}_2\text{O}$ ) + $\text{Na}^+$	874
892.1	5	(IA + 10GL) + $\text{Na}^+$	892
943.2	3	IA + 11 GL	943
980.4	4	(IA + 11 GL – $\text{H}_2\text{O}$ ) + $\text{CH}_3\text{OH}$ + $\text{Na}^+$	980
1017.4	3	IA + 12 GL	1017

GL – oxyalkylene unit from glycidol.

The products cannot be used as polyol substrates for polyurethane foams because the viscous products were immiscible with isocyanates. Large excess of GL (up to 18 moles per a mole of azacycle) does not cause significant decrease in viscosity (see Table 1). However, these viscous products are readily miscible at elevated temperature (above 60 °C) with EO or PO and in fact can be used as solvents and react in presence of catalyst (TEA) to give oligoetherols of lower viscosity, which are miscible with isocyanates. Then in the presented process of the reaction between azacycles with EO or PO the high-boiling sol-

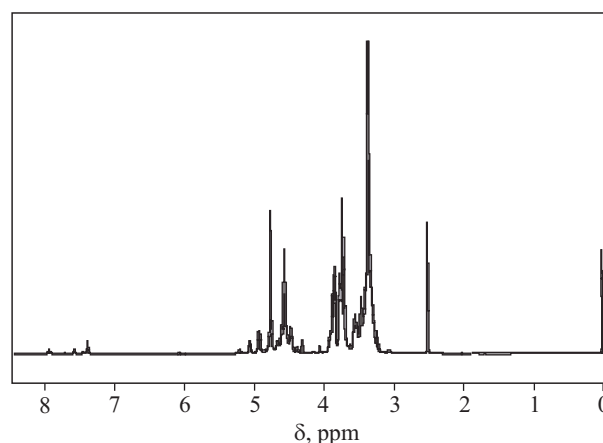


Fig. 1. An example of  $^1\text{H NMR}$  spectrum of reaction product obtained at molar ratio of IA:GL equal to 1:6

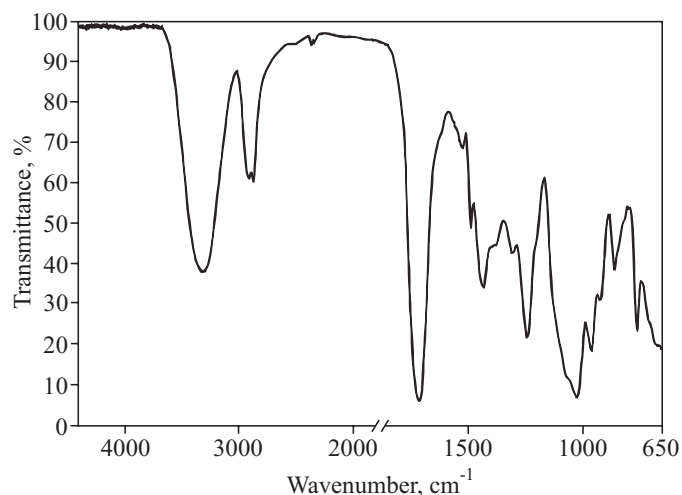


Fig. 2. An example of IR spectrum of reaction product obtained at molar ratio of IA:GL equal to 1:6

vents could be avoided. Straightforward reaction of an azacycle with GL allowed obtaining hydroxyalkyl derivatives and oligoetherols of enhanced functionality in comparison with those based upon reaction of azacycles with oxiranes. Consecutive introduction of GL into azacycle leads to increase of functionality of the semiproduct by one unit in comparison to substrate. The increase of functionality of oligoetherol has some advantages, especially concerning better crosslinking and formation of rigid foams. Main properties of semiproducts obtained from azacycles and GL and those synthesized from azacycles and oxiranes are collected in Table 1. The values of viscosity, surface tension and miscibility of semiproducts with isocyanates suggest that obtained polyols can be successfully used as substrates for formation of thermostable polyurethane foams. Using the method described in this article, the synthesis of oligoetherols with a purine ring could be performed. Otherwise they are not obtainable *i.e.* they are not formed upon reaction of UA with oxiranes due to insolubility of UA in organic solvents and EO or PO. Moreover, the purine ring decomposes at 400 °C, while the 1,3,5-triazine ring decomposes already at 360 °C, thus the polyurethane foams with purine ring

are expected to have higher thermal resistance than those obtained from triazines. Generally the azacycles, which were not accessible substrates for reaction with oxiranes due to the insolubility of the former in common organic solvents, now become readily functionalized. Similar positive results on oligoetherol synthesis were obtained not only for UA, but also with guanine and melamine. Preliminary results indeed demonstrated that polyurethane foams obtained from the mentioned oligoetherols have enhanced thermal stability. The results of their thermal properties investigations will be reported elsewhere.

## CONCLUSION

The resinous liquids are obtained upon hydroxyalkylation of IA, UA or MEL with excess of GL. These liquids are soluble in oxiranes like EO or PO and react further to give oligoetherols containing azacyclic rings. The proposed method of synthesis enables the use of solvents in contrary to the reaction of azacycles with oxiranes. This method has general application to such azacycles, which otherwise do not react with oxiranes. The obtained oligoetherols are suitable substrates for obtaining thermally resistant polyurethane foams.

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