

# Oligoetherols based on melamine–formaldehyde–butanone resins

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**Abstract** New oligoetherols with 1,3,5-triazine ring were obtained from melamine–formaldehyde–butanone resins using 12 molar excess propylene oxide (with respect to the amount of introduced melamine). The resins were obtained from melamine solutions in reactive solvent obtained from simple chemical compound—methyl ethyl ketone (butan-2-one) in its reaction with 3 molar excess formaldehyde. Physical and chemical properties of obtained oligoetherols were determined and their structure was confirmed on the basis of proton magnetic resonance, infrared spectral data and MALDI-ToF mass analysis. The amount of by-products was specified on the basis of chromatographic analysis. Initial tests proved that obtained oligoetherols can constitute a potential substrate for obtaining polyurethane foams of increased thermal resistance.

**Keywords** Oligoetherols · Reactive solvent · Melamine · Propylene oxide · Melamine–formaldehyde–butanone resins

## Introduction

The currently known methods of obtaining oligoetherols, which may constitute substrates for creating heat-resistant polyurethane foams, are in majority based on melamine reactions (Mel) isocyanuric acid (or their selected derivatives) with oxiranes or alkylene carbonates [1]. Insertion of azacyclic rings into the polymer structure is difficult due to weak solubility of their compounds in organic solvents.

One of such rings is (present in the melamine structure) 1,3,5-triazine (s-triazine) ring. Its presence results in high heat resistance of melamine and raises the temperature of decomposition to 360 °C. Introducing the 1,3,5-triazine ring into the

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polymer structure is impeded by melamine solubility, as it is weakly soluble only in dimethyl sulfoxide (DMSO) and water. So far, oligoetherols with the 1,3,5-triazine ring have been obtained in direct reactions of melamine and oxiranes (such as ethylene oxide or propylene oxide) conducted mostly in suspension of various solvents or the aforementioned DMSO [2–4].

The disadvantage of these methods was the necessity to distil toxic solvents after the reaction to separate oligoetherol. Moreover, DMSO used as the most popular melamine solvent would undergo thermal decomposition producing oligoetherol with unpleasant scent. Apart from this, using DMSO in industry encountered difficulties in the form of dissolving gaskets in pressurized reactors. The factors explain why effective anhydrous melamine solvents are still sought, as the presence of water causes creation of glycols and polyglycols as by-products undesirable in production of foamed polyurethane materials [5].

Such solvents may be the so-called reactive solvents, i.e. hydroxymethyl derivatives created in reactions of compounds built with active hydrogen atom [e.g. methyl ethyl ketone (MEK)] with formaldehyde [6]. Dissolution of melamine in reactive solvents leads to production of solutions being potential resources for synthesis of a new polycondensation polymer group with characteristics different from melamine to formaldehyde resins.

Research conducted in the Department of Organic Chemistry at the Rzeszow University of Technology led to obtaining solid materials with high water resistance, filled molding compounds and materials as well as heat-resistant foamed materials based on the reactive solvents (RS) obtained from hydroxymethyl derivatives of cyclohexanone [7] and methyl ethyl ketone [8–10]. In the recent years, a new group of oligoetherols was obtained, which was based on melamine solutions in reactive solvents subjected to reactions with oxiranes (ethylene and propylene oxides) in pressurized reactors. The results of the research are presented in this publication. In the synthesis, oxiranes (ethylene and propylene oxides) are used and the reactions are performed in pressurized reactors [11]. The literature does not contain any information on the use of the reactive solvents in the synthesis of oligoetherols with azacyclic rings except for one publication, where instead of melamine, isocyanuric acid was used [12].

This manuscript presents results of research concerning possibilities of obtaining new oligoetherols with 1,3,5-triazine ring based on polypropylene oxide ( $n_{\text{MeI}}:n_{\text{PO}} = 1:12$ ) and melamine solutions in a reactive solvent obtained from methyl ethyl ketone ( $n_{\text{MEK}}:n_{\text{CH}_2\text{O}} = 1:3$ ). Such oligoetherols might be a potential substrate for obtaining polyurethane foams with increased thermal stability.

## Experimental

### Chemical

Ethyl methyl ketone, Chempur, Poland; Formalin, Chempur, Poland; Triethylamine, Fluka, Switzerland; Melamine, Fluka, Switzerland; ( $\pm$ ) Propylene oxide, Fluka, Switzerland.

## Synthesis of reactive solvent

Ethyl methyl ketone (MEK), (64.8 g, 0.9 mol), formaldehyde (81.0 g, 2.7 mol), introduced in the form of formalin (275.2 g), as well as triethylamine (catalyst) in the amount necessary for pH 11, similar to the paper [13] were put into a three-neck flask of capacity 500 cm<sup>3</sup> equipped with a reflux condenser and thermometer. Flask contents were mixed with a mechanical stirrer. After mixing the substrates, the reaction was carried out at 80 °C for 18 h. After the synthesis, the water and the catalyst were removed from the reaction environment by distillation under reduced pressure. To define the yield of the substrates in reaction of MEK and formaldehyde, mass balance of RS was established. Actual molar ratio  $n_{\text{MEK}} : n_{\text{CH}_2\text{O}}$  was calculated according to the formula:

$$n_{\text{MEK}} : n_{\text{CH}_2\text{O}} = \frac{m_{\text{MEK}}}{M_{\text{MEK}}} : \frac{m_{\text{RS}} - m_{\text{MEK}}}{M_{\text{CH}_2\text{O}}} \quad (1)$$

where  $n_{\text{MEK}}$  number of moles of methyl ethyl ketone (mol),  $n_{\text{CH}_2\text{O}}$  number of moles of formaldehyde (mol),  $m_{\text{MEK}}$  mass of methyl ethyl ketone used in reaction (g),  $M_{\text{MEK}}$  molar mass of methyl ethyl ketone (g/mol),  $m_{\text{RS}}$  mass of reactive solvent after distillation (g), and  $M_{\text{CH}_2\text{O}}$  molar mass of formaldehyde (g/mol).

A reactive solvent was obtained for which  $n_{\text{MEK}} : n_{\text{CH}_2\text{O}} = 1:2.7$ , with yield 94 wt%.

## Melamine solubility in reactive solvent

The amount of melamine introduced into the reactive solvent (3-HMMEK) stemmed from previous studies [6, 13] and this was the maximal amount that did not cause gelation of the solution. 20.0, 36.7 and 46.1 g of melamine was introduced into 100 g of 3-HMMEK at the proportion of water (dosed during dissolving) 0, 10 and 20 wt%, respectively. Melamine–formaldehyde–butanone resins were obtained.

## Obtaining of oligoetherols

3-HMMEK, melamine (in the amount that stemmed from solution tests) and water (in the amount, respectively, 0, 10 or 20 wt%) were introduced into a beaker of capacity 100 ml. The mixture was heated up to 90–100 °C, stirring with a glass rod until melamine has fully dissolved. Obtained melamine–formaldehyde–butanone resins was cooled down and put into a pressurized water reactor, where catalyst was also introduced (triethylamine (TEA)), as well as stirring element and an adequate amount of propylene oxide (PO). The reactor was closed with a stopper, provided with a heating–cooling jacket and placed on a magnetic stirrer. The mixture was heated up to 50–70 °C and kept in this condition until the oxirane has fully reacted. The reaction was considered as terminated when no loss of mass of post-reaction mixture was observed. Reaction products were orange or burgundy-brown resins.

The amount of PO necessary to obtain oligoetherols was calculated according to the formula:

$$n_{\text{Mel}} : n_{\text{PO}} = \frac{m_{\text{Mel}}}{M_{\text{Mel}}} : \frac{m_{\text{PO}}}{M_{\text{PO}}} = 1 : 12 \quad (2)$$

where  $n_{\text{Mel}}$  number of moles of melamine (mol),  $n_{\text{PO}}$  number of moles of propylene oxide (mol),  $m_{\text{Mel}}$  mass of melamine used in reaction (g),  $M_{\text{Mel}}$  molar mass of melamine (g/mol),  $M_{\text{PO}}$  mass of propylene oxide used in reaction (g), and  $M_{\text{PO}}$  mass of propylene oxide (g/mol).

### Physical and chemical properties

Physical properties of oligoetherols were evaluated in the temperature scope 20–80 °C. Density was determined using a pycnometer, viscosity with Höppler viscometer, surface tension by the detaching ring method and refractive index with the refractometric method (Abbe refractometer). The content of formaldehyde in oligoetherols permanently and removably bound was determined, respectively, with the use of sulphite and iodometric methods [14]. The hydroxyl number was determined according to the acylation method with acetic anhydride in the presence of pyridine [14].

### Spectral analysis

$^1\text{H-NMR}$  spectra were carried out with the use of  $^1\text{H-NMR}$  spectrometer of operating frequency 500 MHz AVANCE<sup>II</sup> from BRUKER Biospin Company.  $d_6$ -DMSO was used as the solvent and hexamethyldisiloxane (HMDSO) as the external standard. Recording was done in  $\delta$  ppm. IR spectrum was carried out with the use of IR Paragon 1000 FT spectrometer from PERKIN ELMER Company by ATR technique.

Laser desorption/ionization (LDI) time-of-flight (ToF) mass spectrometry experiments were performed using a Bruker Autoflex Speed reflection time-of-flight mass spectrometer, equipped with a SmartBeam II laser (352 nm) in 80–1500  $m/z$  range. The laser impulse energy was approximately 60–120  $\mu\text{J}$ , the laser repetition rate was 1000 Hz and the deflection value was set on  $m/z = 60$ . The first accelerating voltage was held at 19 kV and the second ion-source voltage was held at 16.7 kV. The reflector voltages used were 21 kV (first) and 9.55 kV (second). The data were recorded and analyzed using the software provided with the Autoflex instrument (FlexAnalysis version 3.3). Mass calibration typically cubic calibration based on five to seven points was performed using internal standards (gold ions and clusters from  $\text{Au}^+$  to  $\text{Au}_{10}^+$  depending on  $m/z$  range). Sample solutions (ca. 5 mg/ml in  $\text{CH}_3\text{OH}$ ) were placed on AuNPET [15] (0.5  $\mu\text{L}$ ) with 0.5  $\mu\text{L}$  standard DHB solution. Sum of ca. 7000 scans was collected for each sample.

### Gas chromatography

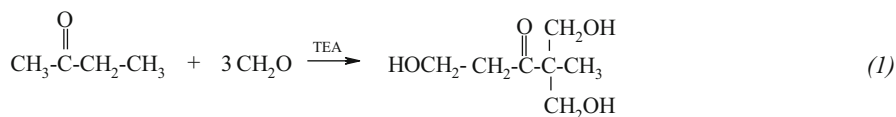
Chromatographic analysis of oligoetherols was carried out with the use of internal standard (cyclohexanone). This method aimed to determine the presence of glycols

in obtained products. Measurements were taken at the following recording conditions: initial temperature: 35 °C, heating rate: 20 °C/min, final temperature: 220 °C, time of heating at 220 °C: 6 min, dispenser temperature: 250 °C, and detector temperature: 300 °C. While preparing chromatograms of methanol solutions, as first appeared peak of cyclohexanone, and then expected by-products, that is glycols; propylene (PG), dipropylene (DPG) as well as tripropylene (TPG).

## Results and discussion

Oligoetherols with 1,3,5-triazine ring were obtained from melamine–formaldehyde–butanone resin (Mel-F-MEK) and propylene oxide in the presence of alkaline catalyst. Mel-F-MEK resins were obtained from melamine solutions in a reactive solvent with the use of water (in the amount 0, 10 or 20 wt%) introduced during dissolving. All the reagents were placed in a pressurized reactor, and reactions were carried out at 50–70 °C (Table 1). The lower temperature range was restricted by too low speed of reaction, whereas the upper by the possibility of evaporation of low-boiling oxirane from the reaction environment. Oligoetherols were obtained as a result of reaction of 1 mol of melamine (in the form of solution in a reactive solvent) with 12 molar excess propylene oxide.

The product of reaction of 1 mol of methyl ethyl ketone (MEK) with 3 mol of formaldehyde was used as the reactive solvent (3-HMMEK) (see reaction below):



While choosing the reactive solvent as a substrate for obtaining oligoetherols, the following assumptions were made: the reactive solvent shall be obtained at the lowest possible molar relation MEK to formaldehyde, and the amount of dissolved melamine should be the highest possible, at the lowest possible share of water [10].

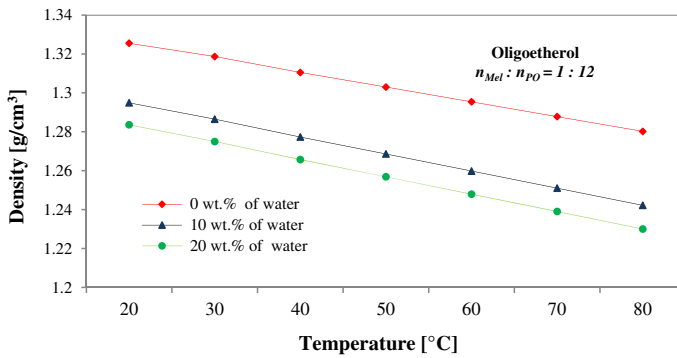
Given physical properties of obtained oligoetherols were determined, that is, density, viscosity, surface tension and refractive index (Table 2) and the influence of temperature on given properties of oligoetherols (anhydrous and obtained with the participation of water) was evaluated (Figs. 1, 2, 3, 4). A linear decrease of viscosity, surface tension, and refractive index as well as non-linear dependence on viscosity in the function of temperature were observed. The highest values of examined properties were observed for anhydrous oligoetherol and the lowest in case of oligoetherol obtained at 20 % of water introduced during dissolving of melamine. Sample physical values fall within the scope typical for polyols used for obtaining polyurethane foams. Surface tension is a decisive factor for the proper foaming process (that is, size of the pores and their uniformity) and viscosity influences foam stabilization.

**Table 1** Optimal conditions of synthesis and mass balance of reaction of obtaining oligoetherols

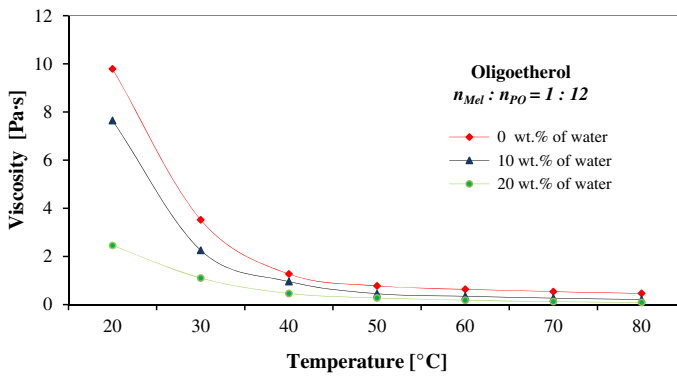
| Oligoetherol<br>$n_{\text{MeI}}/n_{\text{TP}}$ | Share of water introduced<br>during dissolving (wt%) | Reaction<br>time (h) | Reaction<br>temperature (°C) | Amount of substrates (g/100 g RS) |          |        | Oligoetherol characteristics |                                 |
|--|--|----------------------|------------------------------|-----------------------------------|----------|--------|------------------------------|---------------------------------|
|  |  |                      |                              | RS                                | Melamine | TEA PO |                              |                                 |
| 1:12   | 0  | 74.0                 | 50–70                        | 100                               | 20.0     | 2.4    | 110.8                        | Bright orange, thick resin      |
|  | 10   | 85.3                 | 50–70                        | 100                               | 36.7     | 2.4    | 257.5                        | Dark orange, thick resin        |
|  | 20   | 98.9                 | 50–70                        | 100                               | 46.7     | 2.4    | 370.8                        | Maroon-brown resin, thick resin |

**Table 2** Physical and chemical properties of oligoetherol

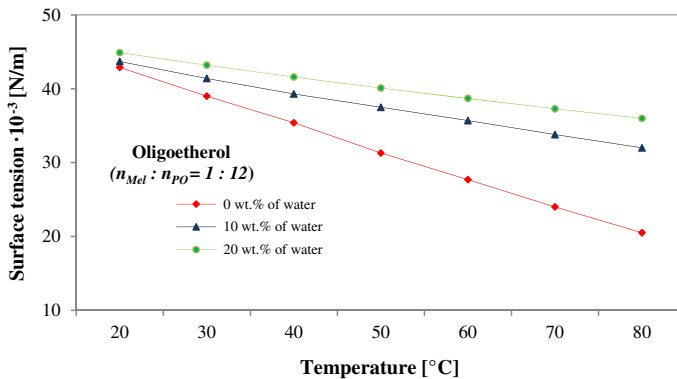
| Oligoetherol<br>$n_{MeI}/n_{TP}$ | Share of water introduced<br>during dissolving (wt%) | Properties of oligoetherol      |                     |  |                     |          | Chemical |  |
|----------------------------------|--|---------------------------------|---------------------|--|---------------------|----------|----------|--|
|                                  |  | Physical                        |                     |  |                     |          | Method   | Hydroxyl number<br>$L_{OH}$ (mg KOH/g) |
|                                  |  | Density<br>(g/cm <sup>3</sup> ) | Viscosity<br>(Pa s) | Surface tension<br>$\cdot 10^{-3}$ (N/m) | Refractive<br>index | Sulphite |          |  |
| 1:12                             | 0  | 1.3255                          | 9.789               | 42.9                                     | 1.4781              | 0.025    | 0.245    | 204.20                                 |
|                                  | 10   | 1.2949                          | 7.648               | 43.7                                     | 1.4768              | 0.195    | 0.000    | 300.41                                 |
|                                  | 20   | 1.2836                          | 2.456               | 44.9                                     | 1.4750, 1.4753      | 0.015    | 0.185    | 375.38                                 |



**Fig. 1** Density of oligoetherols (anhydrous and obtained with the participation of water) as a function of temperature



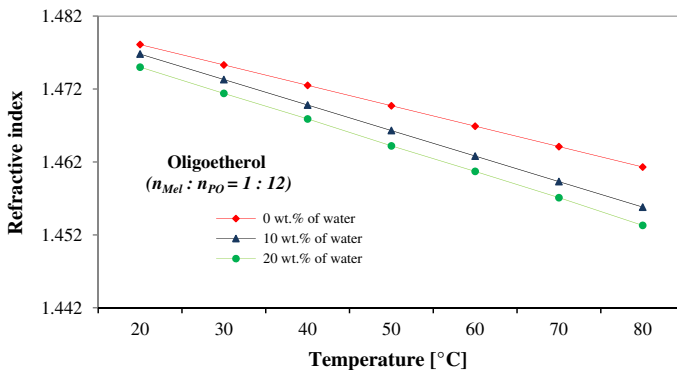
**Fig. 2** Viscosity of oligoetherols (anhydrous and obtained with the participation of water) as a function of temperature



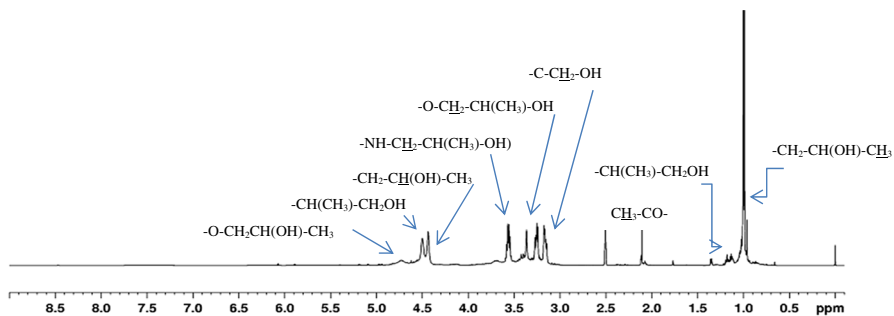
**Fig. 3** Surface tension of oligoetherols (anhydrous and obtained with the participation of water) as a function of temperature







**Fig. 4** Refractive index of oligoetherols (anhydrous and obtained with the participation of water) as a function of temperature

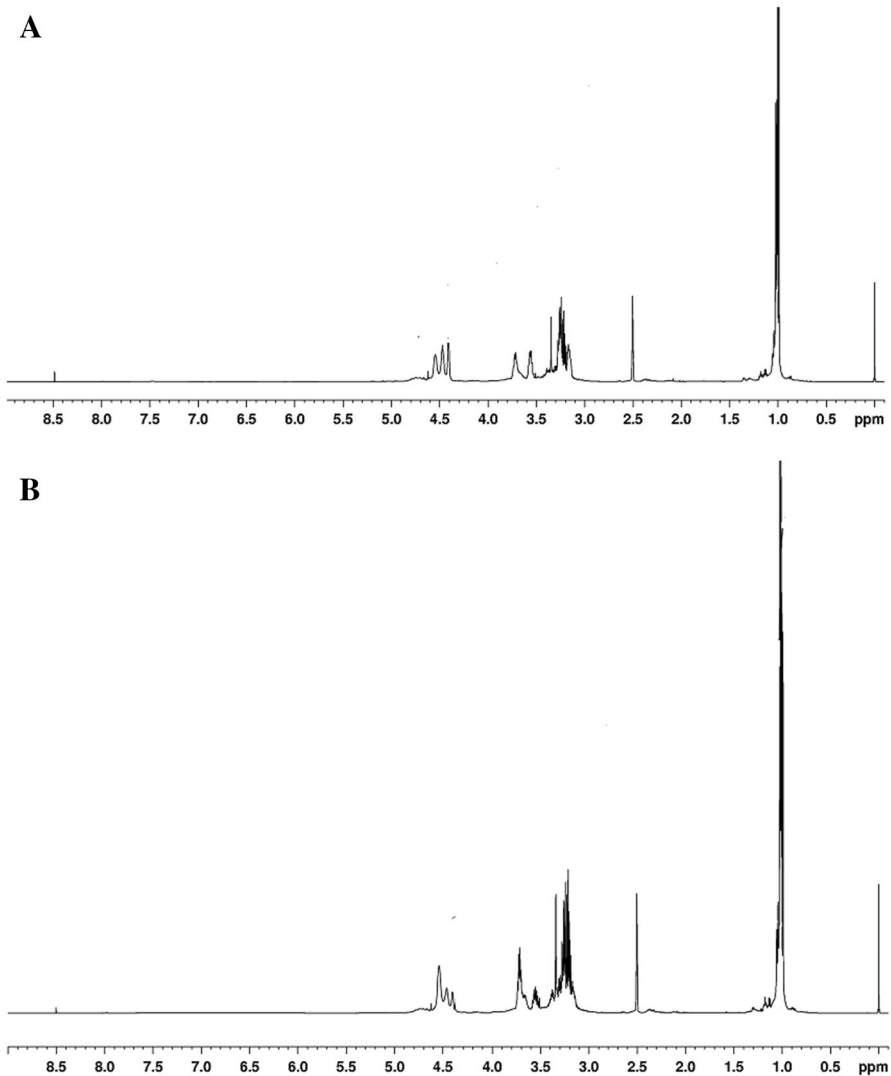


**Fig. 5** Spectrum of  $^1\text{H}$ -NMR anhydrous oligoetherol in DMSO

amount of reactive hydroxyl groups. Share of these reactions decreases with the increase of share of water introduced during dissolving melamine.

Structure of oligoetherols was confirmed on the basis of spectrum analysis of  $^1\text{H}$ -NMR and IR.

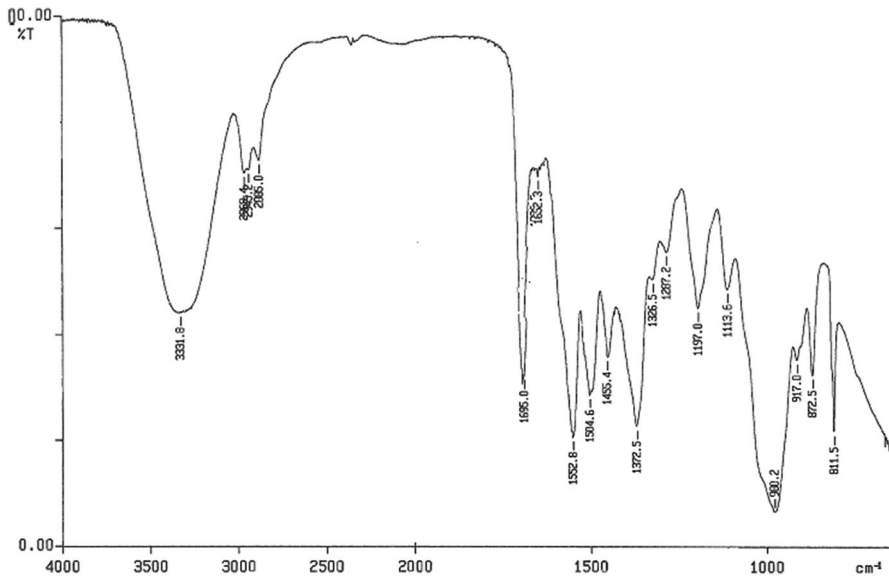
In  $^1\text{H}$ -NMR spectrum of anhydrous oligoetherol (Fig. 5), the presence of  $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_3$  protons signals can be observed, which indicates a regular opening of propylene oxide ring (in the scope 0.9–1.1 ppm). Product of abnormal ring opening is formed in trace levels (small signal of protons of  $-\text{CH}(\text{CH}_3)-\text{CH}_2\text{OH}$  group at 1.1–1.2 ppm). Signal of methyl protons from starting ketone  $\text{CH}_3-\text{CO}-$  arises at chemical shift  $\sim 2.1$  ppm. The presence of methylene protons can be observed in the scope 3.1–3.6 ppm (respectively,  $-\text{C}-\underline{\text{C}}\text{H}_2-\text{OH}$ ,  $-\text{O}-\underline{\text{C}}\text{H}_2-\text{CH}(\text{CH}_3)-\text{OH}$ ,  $-\text{NH}-\underline{\text{C}}\text{H}_2-\text{CH}(\text{CH}_3)-\text{OH}$ ), and methine protons at chemical shift, respectively, 4.4 ppm  $-\text{CH}_2-\underline{\text{C}}\text{H}(\text{OH})-\text{CH}_3$  and 4.5 ppm  $-\underline{\text{C}}\text{H}(\text{CH}_3)-\text{CH}_2\text{OH}$ . The presence of hydroxyl group  $-\text{O}-\text{CH}_2\text{CH}(\text{OH})-\text{CH}_3$  can be observed at 4.6 ppm. Having added  $\text{D}_2\text{O}$  to the sample, the signal goes low. Lack of signal of primary amino group  $-\text{NH}_2$  (at 5.9 ppm) proves its complete reaction with reactive solvent or/and propylene oxide.



**Fig. 6** Spectrum of  $^1\text{H}$ -NMR (in DMSO) oligoetherols obtained at 10 % (a) and 20 % share of water (b) introduced while dissolving melamine

In  $^1\text{H}$ -NMR spectra of oligoetherols obtained at 10 and 20 % of water introduced during dissolving melamine (Fig. 6) no significant changes in signals compared to the spectrum of anhydrous oligoetherol (Fig. 5) can be observed, apart from emergence of signal from water (at 3.2 ppm).

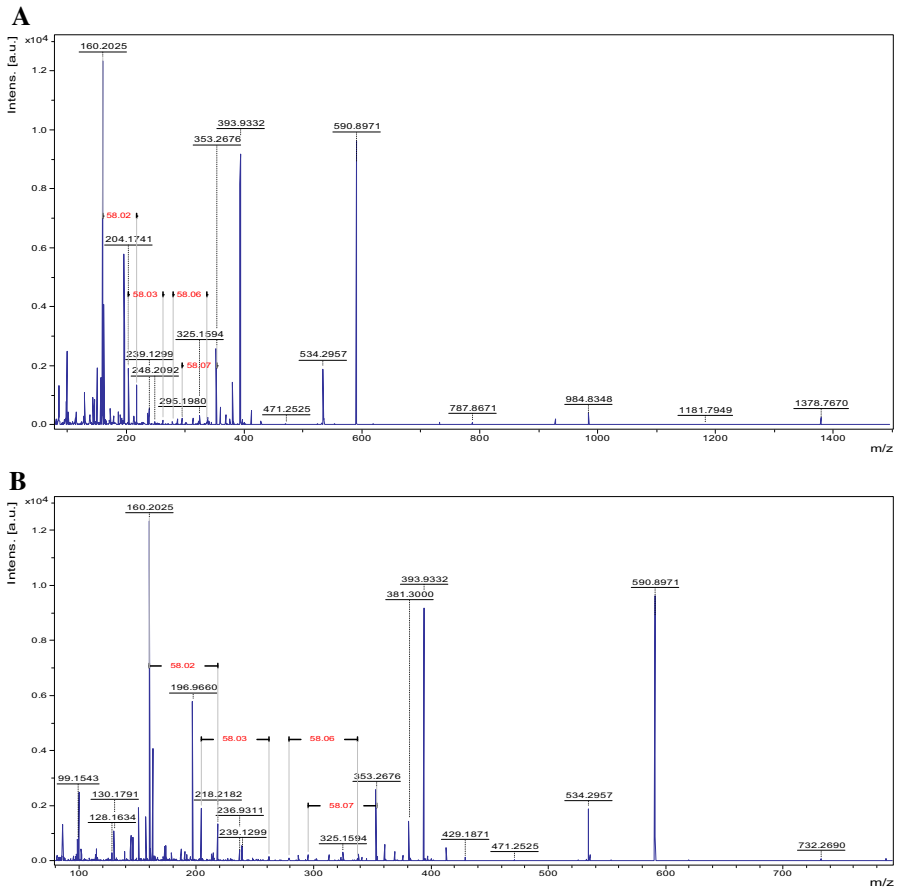
In IR spectrum of anhydrous oligoetherol (Fig. 7) one can observe the presence of strong and broad spectra of vibrations of associated hydroxyl groups ( $\nu_{\text{O-H}}$ ,



**Fig. 7** IR spectrum of anhydrous oligoetherol

$3323\text{ cm}^{-1}$ ) and conjugated deforming vibrations of this group ( $\delta_{\text{O-H}}$ ,  $1373\text{ cm}^{-1}$ ), vibrations of methyl and methylene groups ( $\nu_{\text{CH}_2\text{-CH}_3}$ ,  $2968\text{--}2875\text{ cm}^{-1}$ ) and strong vibrations of carbonyl group from starting ketone ( $\nu_{\text{C=O}}$ ,  $1699\text{ cm}^{-1}$ ). Moreover, there are vibration bands of ether groups ( $\nu_{\text{C-O-C}}$ ,  $1133\text{ cm}^{-1}$ ) as well as strong band of skeletal vibration of s-triazine ring ( $815\text{ cm}^{-1}$ ) confirming melamine integration into oligoetherol structure. In IR spectra of oligoetherols obtained with the use of water (introduced during dissolving of melamine), no significant differences in comparison with the spectrum of anhydrous oligoetherol were observed, with the exception of increased intensity of vibration bands from hydroxyl groups, which indicates that the number of these groups increases with the amount of water used to dissolve melamine.

The structure of oligoetherols is confirmed by MALDI-ToF mass spectra. Example spectrum of anhydrous oligoetherol is shown in Fig. 8. Basing on the spectrum analysis, it may be concluded that (irrespective of the amount of water introduced while dissolving melamine) mixtures of products of various degree of propylene oxide connection are obtained as oligoetherols (Table 3). On spectra, one can observe molecular peaks of  $m/z$  values corresponding to molecular weights of reaction products of following hydroxy groups with propylene oxide. MALDI-ToF analysis suggests that oligoetherols of various degrees of oxypropylene groups introduction arise, as in the spectrum, apart from peaks from raw materials (occurring at  $m/z$  values  $<160$ ),  $\text{Au}^+$  ions (AuNPET plate



**Fig. 8** MALDI-ToF spectrum of anhydrous oligoetherol (a–d)

[15]) as well as by-products—glycols (PG, DPG and TPG), one can observe molecular peaks different from each other by  $m/z$  units = 58 (in Table 3, e.g. sn. 51 and 53). MALDI-ToF mass analysis of anhydrous oligoetherol confirmed the presence of 12 mol of propylene oxide in the obtained product (Table 3).

On the basis of  $^1\text{H-NMR}$  and IR spectra as well as MALDI-ToF mass analysis, the structure of obtained oligoetherols was confirmed.

Obtained oligoetherols were subjected to chromatographic analysis (GC) to evaluate share of by-products created in the reaction of propylene oxide (PO) and water introduced to melamine–formaldehyde–butanone resins during dissolving of melamine or propylene oxide and condensing water (reaction 4). By-products are mainly glycols: propylene (PG), dipropylene (DPG) and tripropylene (TPG). DPG and TPG glycols are created as a result of consequent reaction of PG with, respectively, 1 and 2 mol of PO (reactions 5 and 6).

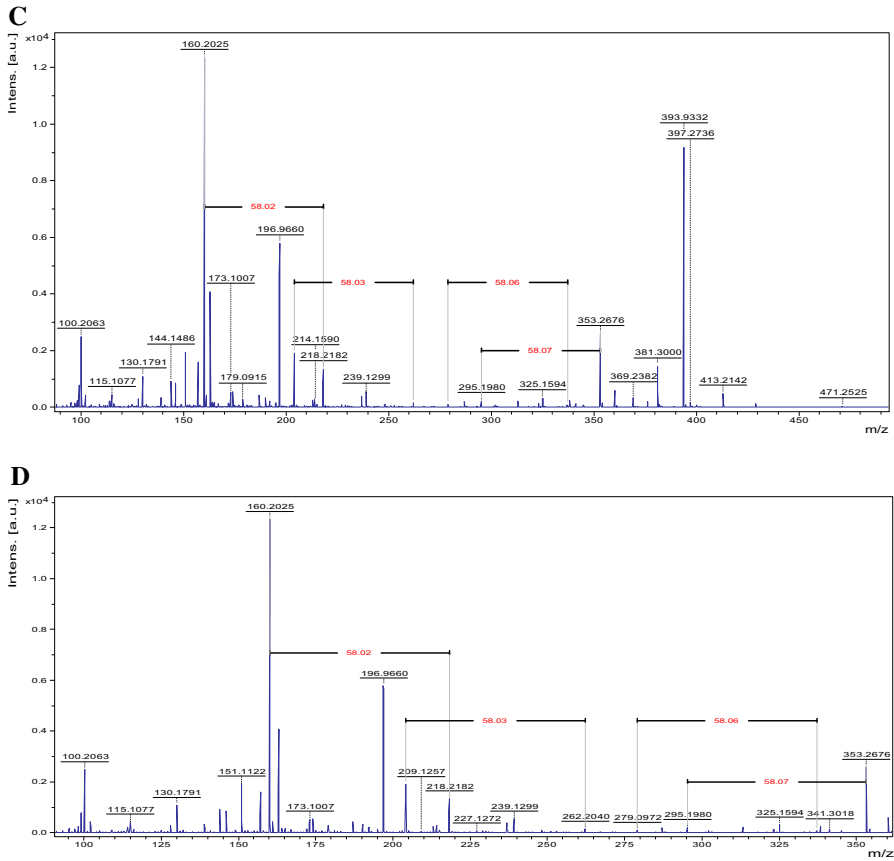
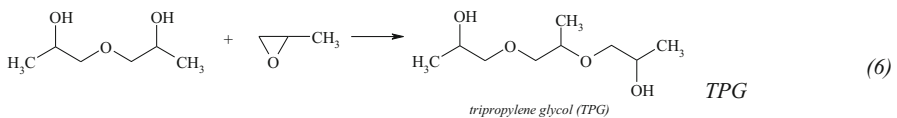
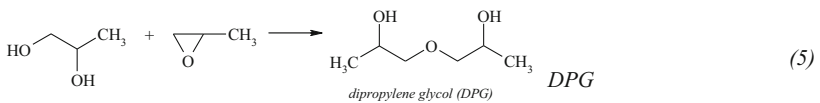
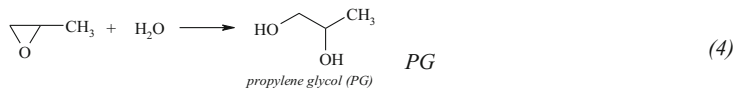


Fig. 8 continued



Share of by-products in oligoetherols is different, depending on the amount of water introduced during dissolving of melamine (Table 4). The lowest amount of

**Table 3** MALDI-ToF mass analysis of anhydrous oligoetherol

| Sn. | Signal position $m/z$ | Relative signal intensity (%) | Molar structure of ions  | Calculated molar mass of ions (g/mol) |
|-----|-----------------------|-------------------------------|--|---------------------------------------|
| 1   | 81.2035               | 1.4                           | [RR (MEK + 3CH <sub>2</sub> O) + 2H] <sup>2+</sup>             | 82.0524                               |
| 2   | 102.1993              | 3.5                           | [RR (MEK + CH <sub>2</sub> O) + H] <sup>+</sup>                | 103.0759                              |
| 3   | 115.1077              | 2.9                           | [RR (MEK + CH <sub>2</sub> O) + Mel + 2H] <sup>2+</sup>        | 115.0746                              |
| 4   | 125.1405              | 0.2                           | [RR (MEK + CH <sub>2</sub> O) + Na] <sup>+</sup>               | 125.0578                              |
| 5   | 130.1791              | 8.9                           | [RR (MEK + 2CH <sub>2</sub> O) + Mel + 2H] <sup>2+</sup>       | 130.0799                              |
| 6   | 132.1777              | 0.8                           | [RR (MEK + 2CH <sub>2</sub> O) + H] <sup>+</sup>               | 133.0865                              |
| 7   | 140.9423              | 0.4                           | [RR (MEK + CH <sub>2</sub> O) + K] <sup>+</sup>                | 141.0318                              |
| 8   | 144.1486              | 7.4                           | [RR (MEK + CH <sub>2</sub> O) + Mel + OP + 2H] <sup>2+</sup>   | 144.0955                              |
| 9   | 146.1603              | 6.9                           | [RR (MEK + 3CH <sub>2</sub> O) + Mel + 2H] <sup>2+</sup>       | 145.0851                              |
| 10  | 155.1139              | 0.5                           | [DHB + H] <sup>+</sup>   | 155.0344                              |
| 11  | 155.1139              | 0.5                           | [RR (MEK + 2CH <sub>2</sub> O) + Na] <sup>+</sup>              | 155.0684                              |
| 12  | 157.1316              | 12.8                          | [GDP + Na] <sup>+</sup>  | 157.0841                              |
| 13  | 160.2025              | 100.0                         | [RR (MEK + 2CH <sub>2</sub> O) + Mel + OP + 2H] <sup>2+</sup>  | 159.1008                              |
| 14  | 163.1010              | 33.7                          | [RR (MEK + 3CH <sub>2</sub> O) + H] <sup>+</sup>               | 163.0970                              |
| 15  | 172.1624              | 1.2                           | [RR (MEK + 2CH <sub>2</sub> O) + K] <sup>+</sup>               | 171.0424                              |
| 16  | 173.1007              | 4.0                           | [GDP + K] <sup>+</sup>   | 173.0580                              |
| 17  | 173.1007              | 4.0                           | [RR (MEK + CH <sub>2</sub> O) + Mel + 2OP + 2H] <sup>2+</sup>  | 173.1164                              |
| 18  | 174.1773              | 3.9                           | [RR (MEK + 3CH <sub>2</sub> O) + Mel + OP + 2H] <sup>2+</sup>  | 174.1060                              |
| 19  | 177.1142              | 0.5                           | [DHB + Na] <sup>+</sup>  | 177.0164                              |
| 20  | 187.1278              | 3.3                           | [RR (MEK + 2CH <sub>2</sub> O) + Mel + 2OP + 2H] <sup>2+</sup> | 188.1217                              |
| 21  | 192.1839              | 1.7                           | [DHB + K] <sup>+</sup>   | 192.9903                              |
| 22  | 193.0885              | 0.4                           | [GTP + H] <sup>+</sup>   | 193.1440                              |
| 23  | 196.9660              | 46.8                          | [Au] <sup>+</sup>  | 196.9666                              |
| 24  | 204.1741              | 16.0                          | [RR (MEK + 3CH <sub>2</sub> O) + Mel + 2OP + 2H] <sup>2+</sup> | 203.1270                              |
| 25  | 204.1741              | 16.0                          | [2RR (MEK + CH <sub>2</sub> O) + H] <sup>+</sup>               | 205.1440                              |
| 26  | 215.1459              | 0.5                           | [GTP + Na] <sup>+</sup>  | 215.1259                              |
| 27  | 218.2182              | 10.9                          | [RR (MEK + 2CH <sub>2</sub> O) + Mel + 3OP + 2H] <sup>2+</sup> | 217.1427                              |
| 28  | 229.1094              | 0.4                           | [RR (MEK + CH <sub>2</sub> O) + Mel + H] <sup>+</sup>          | 229.1413                              |
| 29  | 230.1410              | 0.3                           | [RR (MEK + CH <sub>2</sub> O) + Mel + 4OP + 2H] <sup>2+</sup>  | 231.1583                              |
| 30  | 251.1279              | 0.3                           | [RR (MEK + CH <sub>2</sub> O) + Mel + Na] <sup>+</sup>         | 251.1232                              |
| 31  | 262.2040              | 1.1                           | [RR (MEK + 3CH <sub>2</sub> O) + Mel + 4OP + 2H] <sup>2+</sup> | 261.1688                              |
| 32  | 287.1500              | 1.5                           | [RR (MEK + CH <sub>2</sub> O) + Mel + OP + H] <sup>+</sup>     | 287.1832                              |
| 33  | 325.1594              | 2.6                           | [RR (MEK + CH <sub>2</sub> O) + Mel + OP + K] <sup>+</sup>     | 325.1390                              |
| 34  | 325.1594              | 2.6                           | [2RR (MEK + 3CH <sub>2</sub> O) + H] <sup>+</sup>              | 325.1862                              |
| 35  | 338.3454              | 2.0                           | [RR (MEK + 2CH <sub>2</sub> O) + Mel + OP + Na] <sup>+</sup>   | 339.1757                              |
| 36  | 345.1872              | 0.7                           | [RR (MEK + CH <sub>2</sub> O) + Mel + 2OP + H] <sup>+</sup>    | 345.2250                              |
| 37  | 360.3269              | 4.9                           | [RR (MEK + 3CH <sub>2</sub> O) + Au] <sup>+</sup>              | 359.0558                              |
| 38  | 369.2382              | 2.5                           | [RR (MEK + 3CH <sub>2</sub> O) + Mel + OP + Na] <sup>+</sup>   | 369.1862                              |
| 39  | 376.3012              | 1.5                           | [RR (MEK + 2CH <sub>2</sub> O) + Mel + 2OP + H] <sup>+</sup>   | 375.2356                              |
| 40  | 376.3012              | 1.5                           | [RR (MEK + CH <sub>2</sub> O) + Mel + 9OP + 2H] <sup>2+</sup>  | 376.2629                              |

**Table 3** continued

| Sn. | Signal position $m/z$ | Relative signal intensity (%) | Molar structure of ions  | Calculated molar mass of ions (g/mol) |
|-----|-----------------------|-------------------------------|--|---------------------------------------|
| 41  | 376.3012              | 1.5                           | [RR (MEK + 3CH <sub>2</sub> O) + Mel + 8OP + 2H] <sup>2+</sup> | 377.2526                              |
| 42  | 389.2664              | 0.3                           | [GTP + Au] <sup>+</sup>  | 389.1027                              |
| 43  | 393.9332              | 78.4                          | [2 Au] <sup>+</sup>  | 393.9332                              |
| 44  | 397.2736              | 1.2                           | [RR(MEK + 2CH <sub>2</sub> O) + Mel + 2OP + Na] <sup>+</sup>   | 397.2176                              |
| 45  | 413.2142              | 3.9                           | [RR (MEK + 2CH <sub>2</sub> O + Mel + 2OP + K) <sup>+</sup>    | 413.1915                              |
| 46  | 471.2525              | 0.2                           | [RR(MEK + 2CH <sub>2</sub> O) + Mel + 3OP + K] <sup>+</sup>    | 471.2334                              |
| 47  | 590.8971              | 71.4                          | [3 Au] <sup>+</sup>  | 590.8998                              |
| 48  | 732.2690              | 0.5                           | [RR (MEK + CH <sub>2</sub> O) + Mel + 8OP + K] <sup>+</sup>    | 731.4321                              |
| 49  | 732.2690              | 0.5                           | [RR (MEK + 3CH <sub>2</sub> O) + Mel + 7OP + K] <sup>+</sup>   | 733.4113                              |
| 50  | 787.8671              | 0.7                           | [4 Au] <sup>+</sup>  | 787.8664                              |
| 51  | 928.2211              | 1.4                           | [RR(MEK + 3CH <sub>2</sub> O) + Mel + 11OP + H] <sup>+</sup>   | 927.6229                              |
| 52  | 984.8348              | 2.6                           | [5 Au] <sup>+</sup>  | 984.8330                              |
| 53  | 984.8348              | 2.6                           | [RR (MEK + 3CH <sub>2</sub> O) + Mel + 12OP + H] <sup>+</sup>  | 985.6647                              |
| 54  | 1181.7949             | 0.1                           | [6 Au] <sup>+</sup>  | 1181.7996                             |
| 55  | 1378.7670             | 1.4                           | [7 Au] <sup>+</sup>  | 1378.7662                             |

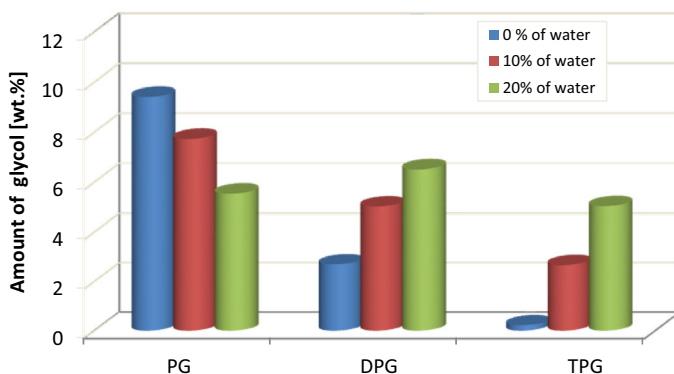
*DHB* 2,5-dihydroxybenzoic acid (matrix), *n* OP designates *n* oxypropylene groups in product structure, *Mel* melamine, *RS* reactive solvent, *DPG* dipropylene glycol, *TPG* tripropylene glycol,  $-H_2O$  means that the product is subject to dehydration in reaction conditions

**Table 4** Content of propylene glycols in oligoetherols (determined using GC method)

| Oligoetherol $n_{Mel}:n_{TP}$ | Share of water introduced during dissolving (wt%) | Amount of by-products (wt%) in oligoetherol |       |       |
|-------------------------------|---|---|-------|-------|
|                               |   | PG  | DPG   | TPG   |
| 1:12                          | 0   | 9.405                                       | 2.685 | 0.218 |
|                               | 10  | 7.725                                       | 5.019 | 2.658 |
|                               | 20  | 5.534                                       | 6.504 | 5.032 |

glycols was observed in anhydrous oligoetherol, and the highest in the product obtained at 20 % share of water. Share of propylene glycol is the highest in anhydrous oligoetherol and decreases with increase of share of water (introduced while dissolving), which suggests that in case of anhydrous oligoetherol, the share of condensation reaction is the highest (Fig. 9). Higher share of water increases the probability of occurrence of consequent reactions of obtained propylene glycol with propylene oxide, which leads to increased share of dipropylene glycol (DPG) and tripropylene glycol (TPG) (Fig. 9).





**Fig. 9** Content of by-products in oligoetherols depending on the type of glycol

## Conclusion

Oligoetherols containing 1,3,5-triazine ring (being potential substrates for obtaining heat-resistant polyurethane foams) were obtained from melamine–formaldehyde–butanone resins using 12-molar excess propylene oxide (in relation to the amount of introduced water). Oligoetherols at 0, 10 and 20 % of water (introduced during dissolving of melamine) were obtained. The greater the amount of water used for dissolving, the greater is the amount of introduced melamine. Physical and chemical properties of obtained oligoetherols were examined. Lack of free formaldehyde in obtained products confirms its full blocking in reaction with oxirane. Oligoetherols structure was confirmed on the basis of  $^1\text{H-NMR}$  spectra, IR spectra as well as MALDI-ToF mass analysis. The amount of by-products was determined on the basis of chromatographic analysis. An increase in the amount of by-products was observed while increasing the amount of water introduced into melamine during its dissolution in a reactive solvent.

On the basis of the obtained results, one may presume that oligoetherols with 1,3,5-triazine ring based on melamine–formaldehyde–butanone resins might constitute a potential polyol factor for obtaining polyurethane foams of increased thermal resistance, which will be the subject of a separate publication.

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